APPENDIX K

Fingerprinting Justification Memo

TECHNICAL MEMORANDUM

Oakland Bay Sediment Investigation
Potential for Fingerprinting Analysis using Sediment Data

April 2009

Prepared for

Washington Department of Ecology
Toxics Cleanup Program
Southwest Regional Office

TECHNICAL MEMORANDUM

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April 23, 2009

Prepared for

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Acronyms

C	carbon number
CDD	chlorinated dibenzo-p-dioxin compounds
CDF	chlorinated dibenzofuran compounds.
cm	centimeters
ft	foot
HpCDD	heptachlorodibenzo-p-dioxin
HpCDF	heptachlorodibenzofuran
HxCDD	hexachlorodibenzo-p-dioxin
HxCDF	hexachlorodibenzofuran
MDL	method detection limit
mg/kg	milligrams per kilogram
NWTPH-HCID	Northwest Total Petroleum Hydrocarbon (TPH) method for Hydrocarbon Identification
OCDD	octachlorodibenzo-p-dioxin
OCDF	octachlorodibenzofuran
PAH	polycyclic aromatic hydrocarbons
PCDD/PCDF	dioxin/furan
PeCDD	pentachlorodibenzo-p-dioxin
PeCDF	pentachlorodibenzofuran
PQL	practical quantitation limit
RL	reporting limit
TCDD	tetrachlorodibenzo-p-dioxin
TCDF	tetrachlorodibenzofuran
TPH	total petroleum hydrocarbons

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Potential for Fingerprinting Analysis using Oakland Bay Sediment Data

1. Introduction

A screening-level "fingerprinting" evaluation of total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), and dioxin/furan (PCDD/PCDF) sediment data has been conducted to provide a preliminary indication of the usefulness of the analytical data collected during the Oakland Bay Sediment Investigation to differentiate between sources of contaminants. The anticipated goal of fingerprinting is linking contaminants found in sediment to either general or specific sources by comparing the sediment data with known source data. Three lines of forensic evidence have been qualitatively investigated: TPH, PAHs, and PCDD/PCDF. Results of the evaluation of the potential utility of fingerprinting studies for each contaminant type are discussed in the following sections.

2. Fingerprinting Usability

Generally accepted guidelines for reporting data recommend that concentrations between the method detection limit and what would effectively be three times the practical quantitation limit should be reported as detected but not quantified due to the potential for misuse of low-level data of relatively high quantitative uncertainty (Taylor 1987). For this investigation, concentrations of all analytes reported between the method detection limits (MDL) and practical quantitation limits (PQL [also known as reporting limits]) have all been annotated with a "J" qualifier (estimated concentration) indicating the high level of uncertainty in the quantitative value. Statistical evaluations of data whose uncertainties are "high" can lead to erroneous conclusions; especially if the sample populations being compared are limited in size or highly censored (high percentages of non-detect data). In developing this preliminary indication of the usefulness of the analytical data to differentiate between sources of contaminants, only un-annotated data measured at concentrations three times or more above the practical quantitation limit are used to estimate the viability of the data for further analysis.

3. Oakland Bay Sampling

Previous studies in Oakland Bay provided evidence that sediment in some areas had been impacted by the presence of wood waste (Ecology 2000). Station names and sample designations in these areas are differentiated to facilitate data interpretation; the same sampling protocols were followed at all stations.

Sediment and wood waste sample locations were identified in the Oakland Bay Sediment Characterization Study Sampling and Analysis Plan (E & E 2008). Surface sediment samples were collected using grab samplers. Surface sediment samples were collected

from the 0-10 centimeter (cm) interval. Subsurface sediment samples were collected using a corer. Core samples were collected over multiple depth ranges. (E & E 2008)

Core samples submitted for testing at the same time as the surface samples included sediment taken from the 1- 2 foot (ft) below surface interval at a subset of the stations.

4. Analytes Considered for Fingerprinting

The following subsections discuss the fingerprinting potential of Oakland Bay Sediment Investigation TPH, PAH, and dioxin/furan sediment data. Each analyte group is defined followed by a brief discussion of the analytical protocols used. Data summaries are presented and the utility of the data for fingerprinting is discussed.

4.1 Petroleum Hydrocarbons (TPH)

4.1.1 Nature of Petroleum Hydrocarbons

Petroleum products are often complex mixtures of hydrocarbons. Sources of petroleum products in the environment are numerous, including: diesel and motor oil from ships, motor vehicles, municipal/industrial outfalls, and runoff from combined sewer overflows and storm drains. The "genetic" composition of crude oil is altered during refining which may yield different petroleum products with distinct gas chromatographic patterns. These mixtures of petroleum hydrocarbons "weather" upon release into the environment. Weathering processes include: evaporation, dissolution into water, sorption onto sediments, photo-oxidation, and biological degradation; which alter the fingerprint of the refined petroleum source material. Mixtures of different petroleum products released into the environment at different times, together with naturally occurring hydrocarbons, may confound the identification of the type of petroleum in an environmental sample. Gas chromatogram patterns of peaks and their relative intensities may be evaluated to identify similarities and differences between environmental samples containing petroleum. (Murphy and Morrison 2002)

4.1.2 Petroleum Hydrocarbon Analysis

Petroleum hydrocarbons were analyzed using the Total Petroleum Hydrocarbon (TPH) method NWTPH-HCID for Hydrocarbon Identification. NWTPH-HCID is a qualitative and semi-quantitative screening tool used to confirm the presence and type of petroleum product in a sediment sample. Results are qualitatively reported as gasoline, diesel, or heavy oils. The method is most useful for elimination of the need for more detailed petroleum analyses where NWTPH-HCID results indicate TPH concentrations are below regulatory limits. The method, dry-weight reporting limits for sediment are 20 milligrams per kilogram (mg/kg) for gasoline, 50 mg/kg for #2 diesel, and 100 mg/kg for motor oil. Reporting limits are often elevated for sediment samples due to the water content (per cent moisture) in the samples. Pattern matching with known reference

product chromatograms is used to identify the type of hydrocarbon. Laboratory analysts categorize the TPH based on chromatogram identification.

In addition to the uncertainties associated with low level gasoline, diesel and motor oil concentrations, TPH fingerprinting is further limited by an inherent limitation in the method: based on their operating parameters, different chromatographic instruments yield unequal spectra. Chromatograms from one gas chromatograph may not be directly comparable with spectra from other gas chromatographs or even the same gas chromatograph operating at earlier or later times. Significant effort would be required to convert spectral data using relative retention times and peak heights or areas normalized to known standards in order to reasonably compare sample results.

4.1.3 Summary of Oakland Bay Petroleum Hydrocarbon Analysis Results

Sediment sampling was described above. Figures 1 and 2 illustrate the locations of the samples analyzed for TPH.

As can be seen in Tables 1, 2, and 3 petroleum hydrocarbons were rarely detected; and when detected, had concentrations close to detection limits. These “low” concentrations are associated with high uncertainty in quantitative accuracy (Taylor 1987).

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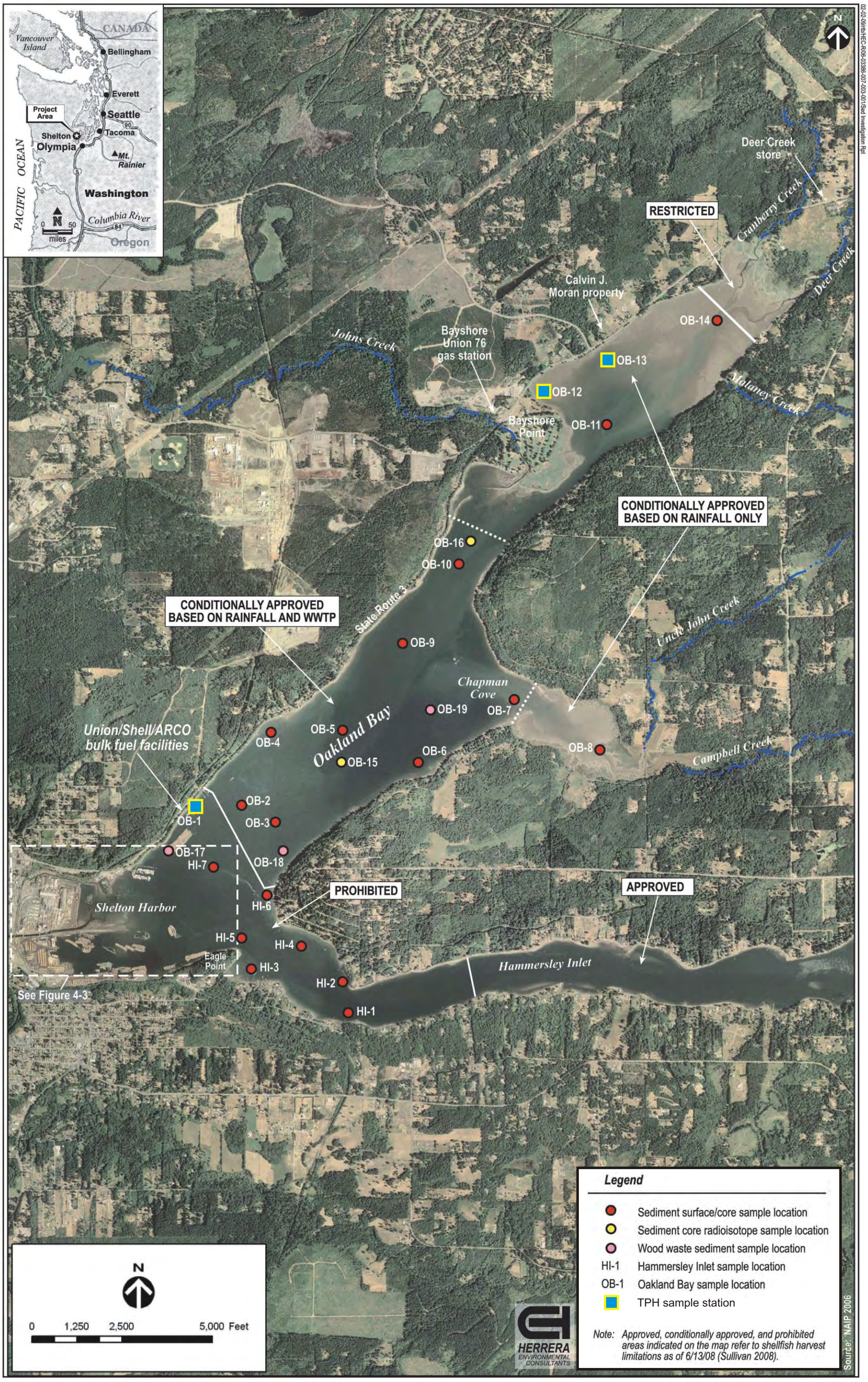


Figure 1 Oakland Bay and Hammersley Inlet Stations with Total Petroleum Hydrocarbon (TPH) Data

Figure 2 Shelton Harbor Stations with Total Petroleum Hydrocarbon (TPH) Data

Table 1. Summary of Gasoline Data from Oakland Bay Sediment Investigation

Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
0-10 cm	11	0	0	11	0	0%
1- 2 ft	2	0	0	2	0	0%
All	13	0	0	13	0	0%

Table 2. Summary of #2 Diesel Data from Oakland Bay Sediment Investigation

Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
0-10 cm	11	0	0	11	0	0%
1 – 2 ft	2	0	0	2	0	0%
All	13	0	0	13	0	0%

Table 3. Summary of Motor Oil Data from Oakland Bay Sediment Investigation

Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
0-10 cm	11	1	0	10	0	0%
1 – 2 ft	2	0	1	1	0	0%
All	13	1	1	11	0	0%

4.1.4 Utility of Petroleum Hydrocarbon Data for Fingerprinting

As shown in Tables 1, 2, and 3; there are no samples with petroleum concentrations above the recommended range of less certain quantitative data (greater than 3 times the PQL); with 0% of the gasoline, 0 % of the #2 diesel and 0% of the motor oil data meeting the minimum requirement for additional evaluation.

Based on the inherent limitations in TPH analyses and the highly censored nature of these data, conducting a detailed fingerprinting analysis of the petroleum hydrocarbon data would not be practicable.

Only general statements regarding petroleum hydrocarbon presence and absence can be made based on the data gathered during these studies.

4.2 Polycyclic Aromatic Hydrocarbons (PAH)

4.2.1 Nature of Polycyclic Aromatic Hydrocarbons

PAHs occur both naturally and from anthropogenic sources. PAHs are known to have characteristic distributions in differing materials. For example, petroleum and wood combustions sources are known to have different PAH patterns, Creosote and coal tar creosote are often used as preservatives on piling for docks, dolphins, and piers; these complex mixtures degrade in the environment and release PAH compounds in characteristic patterns. However, as with TPH, PAHs also weather in the environment. (Murphy and Morrison 2002)

4.2.2 Polycyclic Aromatic Hydrocarbons Analysis

Sediment samples were analyzed for 17 distinct PAHs using USEPA SW-846 method 8270 (EPA 1986). Analytes include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, 2-methylnaphthalene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene. (E & E 2008)

4.2.3 Summary of Oakland Bay Polycyclic Aromatic Hydrocarbons Analysis Results

Sediment sampling was described above. Figures 3 and 4 illustrate the locations of the samples analyzed for PAH.

As can be seen in Tables 4, 5, and 6; PAHs were only sporadically detected; and when detected often had concentrations close to detection limits. These “low” concentrations are associated with high uncertainty in quantitative accuracy (Taylor 1987). Almost all of the annotated data were “flagged” because the concentrations measured were above the MDL but below the PQL.

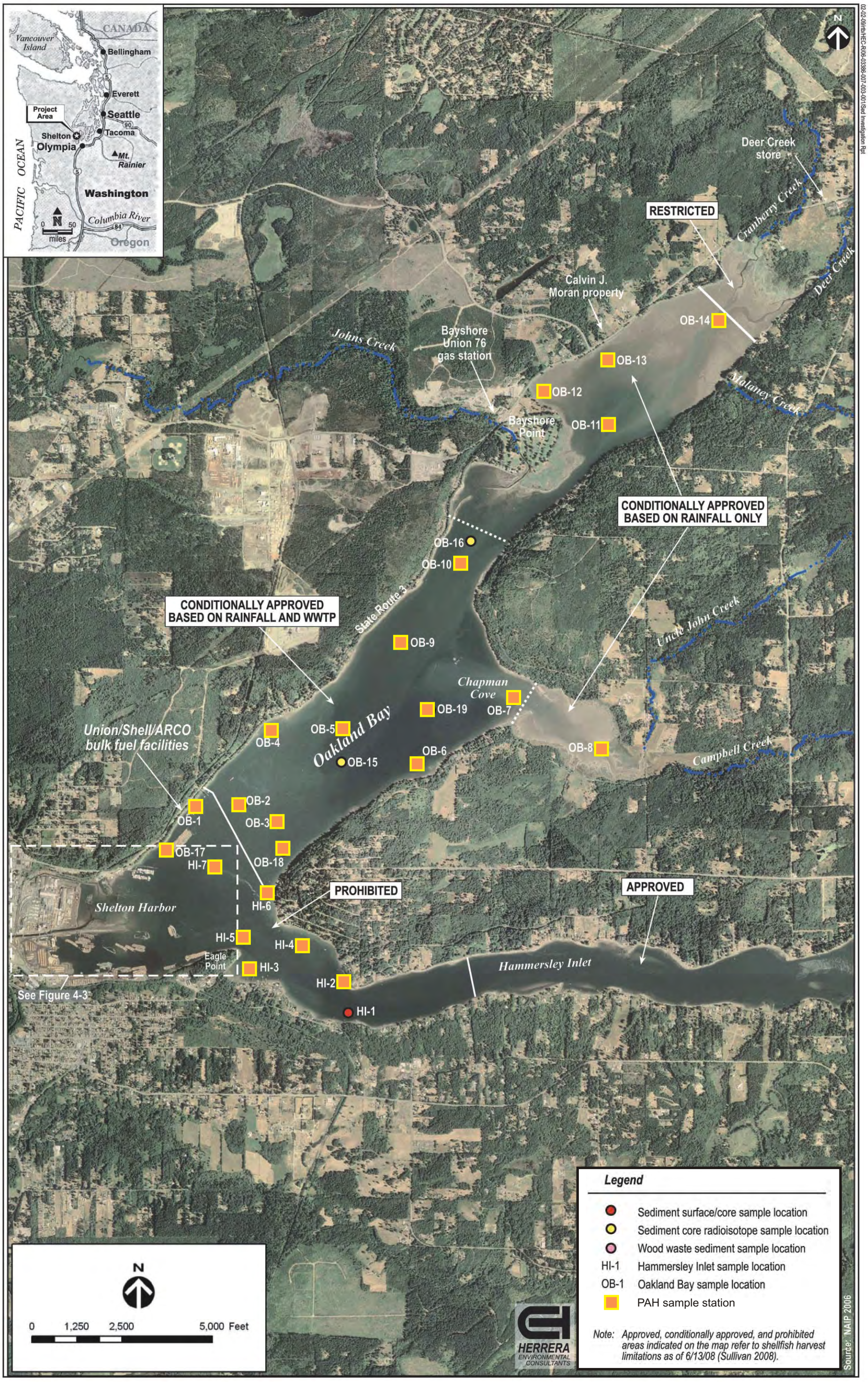


Figure 3 Oakland Bay and Hammersley Inlet Stations with Polycyclic Aromatic Hydrocarbons (PAH) Data

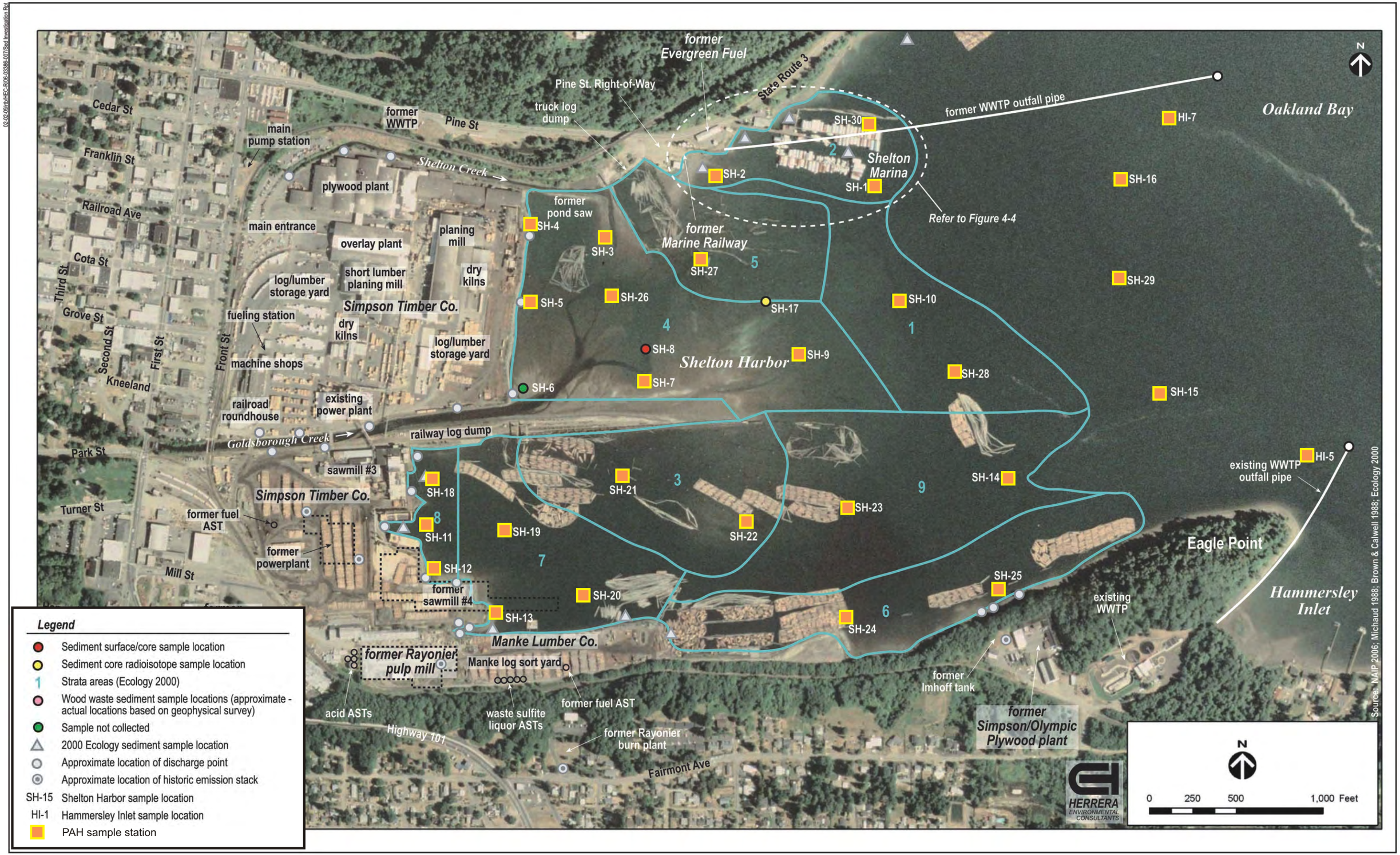


Figure 4 Shelton Harbor Stations with Polycyclic Aromatic Hydrocarbons (PAH) Data

Table 4. Summary of Individual PAH Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
naphthalene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	3	2	9	0	0%
	SH (WS)	0-10 cm	13	0	1	12	0	0%
	SH (SC)	1-2 ft	14	3	2	9	1	7%
	SH (WC)	1-2 ft	11	2	0	9	1	9%
	All	All	78	8	5	65	2	3%
2-methyl naphthalene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	0	0	14	0	0%
	SH (WS)	0-10 cm	13	0	0	13	0	0%
	SH (SC)	1-2 ft	14	0	0	14	0	0%
	SH (WC)	1-2 ft	11	0	0	11	0	0%
	All	All	78	0	0	78	0	0%
acenaphthylene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	2	2	10	0	0%
	SH (WS)	0-10 cm	13	1	0	12	0	0%
	SH (SC)	1-2 ft	14	1	1	12	1	7%
	SH (WC)	1-2 ft	11	0	0	11	0	0%
	All	All	78	4	3	71	1	1%

Table 4 continued. Summary of Individual PAH Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
acenaphthene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	0	2	12	0	0%
	SH (WS)	0-10 cm	13	0	1	12	0	0%
	SH (SC)	1-2 ft	14	1	1	12	1	7%
	SH (WC)	1-2 ft	11	1	0	10	1	9%
	All	All	78	2	4	72	2	3%
fluorene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	1	3	10	0	0%
	SH (WS)	0-10 cm	13	0	1	12	0	0%
	SH (SC)	1-2 ft	14	1	1	12	1	7%
	SH (WC)	1-2 ft	11	1	0	10	1	9%
	All	All	78	3	5	70	2	3%
phenanthrene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	2	0	12	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	9	0	5	4	29%
	SH (WS)	0-10 cm	13	7	2	4	1	8%
	SH (SC)	1-2 ft	14	8	3	3	3	21%
	SH (WC)	1-2 ft	11	5	2	4	4	36%
	All	All	78	31	7	40	12	15%

Table 4 continued. Summary of Individual PAH Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
anthracene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	3	2	9	2	14%
	SH (WS)	0-10 cm	13	3	0	10	1	8%
	SH (SC)	1-2 ft	14	2	0	12	1	7%
	SH (WC)	1-2 ft	11	3	0	8	2	18%
	All	All	78	11	2	65	6	8%
fluoranthene	HI (SS)	0-10 cm	6	0	1	5	0	0%
	OB (SS)	0-10 cm	14	2	2	10	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	1	2	0	0%
	SH (SS)	0-10 cm	14	11	1	2	8	57%
	SH (WS)	0-10 cm	13	10	2	1	6	46%
	SH (SC)	1-2 ft	14	12	0	2	6	43%
	SH (WC)	1-2 ft	11	7	0	4	4	36%
	All	All	78	42	7	29	24	31%
pyrene	HI (SS)	0-10 cm	6	0	1	5	0	0%
	OB (SS)	0-10 cm	14	2	2	10	1	7%
	OB (WS)	0-10 cm	3	1	0	2	0	0%
	OB (WC)	1-2 ft	3	0	1	2	0	0%
	SH (SS)	0-10 cm	14	11	1	2	8	57%
	SH (WS)	0-10 cm	13	11	1	1	6	46%
	SH (SC)	1-2 ft	14	13	0	1	7	50%
	SH (WC)	1-2 ft	11	7	0	4	4	36%
	All	All	78	45	6	27	26	33%

Table 4 continued. Summary of Individual PAH Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
benzo(a)anthracene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	1	1	12	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	9	1	4	5	36%
	SH (WS)	0-10 cm	13	6	2	5	1	8%
	SH (SC)	1-2 ft	14	7	2	5	2	14%
	SH (WC)	1-2 ft	11	5	2	4	3	27%
	All	All	78	28	8	42	11	14%
chrysene	HI (SS)	0-10 cm	6	0	1	5	0	0%
	OB (SS)	0-10 cm	14	2	3	9	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	11	1	2	7	50%
	SH (WS)	0-10 cm	13	9	2	2	4	31%
	SH (SC)	1-2 ft	14	9	1	4	5	36%
	SH (WC)	1-2 ft	11	6	1	4	3	27%
	All	All	78	37	9	32	19	24%
benzo(b)fluoranthene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	1	13	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	10	1	3	5	36%
	SH (WS)	0-10 cm	13	8	0	5	2	15%
	SH (SC)	1-2 ft	14	7	0	7	2	14%
	SH (WC)	1-2 ft	11	5	2	4	3	27%
	All	All	78	30	4	44	12	15%

Table 4 continued. Summary of Individual PAH Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
benzo(k)fluoranthene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	1	13	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	9	2	3	5	36%
	SH (WS)	0-10 cm	13	7	0	6	4	31%
	SH (SC)	1-2 ft	14	7	0	7	2	14%
	SH (WC)	1-2 ft	11	5	2	4	3	27%
	All	All	78	28	5	45	14	18%
benzo(a)pyrene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	1	13	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	1	0	2	0	0%
	SH (SS)	0-10 cm	14	9	1	4	6	43%
	SH (WS)	0-10 cm	13	7	1	5	2	15%
	SH (SC)	1-2 ft	14	7	2	5	2	14%
	SH (WC)	1-2 ft	11	6	1	4	2	18%
	All	All	78	30	6	42	12	15%
indeno(1,2,3-cd)pyrene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	1	13	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	5	2	7	1	7%
	SH (WS)	0-10 cm	13	3	0	10	1	8%
	SH (SC)	1-2 ft	14	2	2	10	1	7%
	SH (WC)	1-2 ft	11	0	1	10	0	0%
	All	All	78	10	6	62	3	4%

Table 4 continued. Summary of Individual PAH Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth range	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
dibenzo(a,h)anthracene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	0	0	3	0	0%
	SH (SS)	0-10 cm	14	0	2	12	0	0%
	SH (WS)	0-10 cm	13	0	1	12	0	0%
	SH (SC)	1-2 ft	14	0	0	14	0	0%
	SH (WC)	1-2 ft	11	0	0	11	0	0%
	All	All	78	0	3	75	0	0%
benzo(g,h,i)perylene	HI (SS)	0-10 cm	6	0	0	6	0	0%
	OB (SS)	0-10 cm	14	0	0	14	0	0%
	OB (WS)	0-10 cm	3	0	0	3	0	0%
	OB (WC)	1-2 ft	3	1	0	2	0	0%
	SH (SS)	0-10 cm	14	8	2	4	2	14%
	SH (WS)	0-10 cm	13	3	0	10	1	8%
	SH (SC)	1-2 ft	14	4	3	7	2	14%
	SH (WC)	1-2 ft	11	2	2	7	1	9%
	All	All	78	18	7	53	6	8%

HI (SS) – Hammersley Inlet surface sediment
OB (SS) – Oakland Bay surface sediment
OB (WS) – Oakland Bay wood waste area surface sediment
OB (WC) – Oakland Bay wood waste area subsurface sediment
SH (SS) – Shelton Harbor surface sediment
SH (WS) – Shelton Harbor wood waste area surface sediment
SH (SC) – Shelton Harbor subsurface sediment
SH (WC) – Shelton Harbor wood waste area subsurface sediment

Table 5. Summary of All PAH Analytes Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	Depth Range	# of analytes	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
All PAHs	HI	0-10 cm	102	0	3	99	0	0%
	OB	0-10 cm	289	10	12	267	1	0.3%
	OB	1-2 ft	51	2	2	47	0	0%
	SH	0-10 cm	459	176	39	244	82	18%
	SH	1-2 ft	425	139	31	255	69	16%
	All	All	1326	327	87	912	152	11%

HI – Hammersley Inlet
OB – Oakland Bay
SH – Shelton Harbor

Table 6. Summary of All PAH Data by Station from Oakland Bay Sediment Investigation

# of individual PAHs	# of stations with un-annotated positive results > 3 x PQL	% of stations with un-annotated positive results > 3 x PQL	Cumulative % of stations with un-annotated positive results > 3 x PQL
0	50	64%	64%
1	4	5%	69%
2	2	3%	72%
3	7	9%	81%
4	2	3%	83%
5	1	1%	85%
6	2	3%	87%
7	1	1%	88%
8	2	3%	91%
9	3	4%	95%
10	0	0%	95%
11	2	3%	97%
12	0	0%	97%
13	1	1%	99%
14	0	0%	99%
15	1	1%	100%
16	0	0%	100%
17	0	0%	100%
total	78	100%	100%

4.2.4 Utility of Polycyclic Aromatic Hydrocarbons Data for Fingerprinting

Based on the data presented in Tables 4, 5, and 6, PAH data from Oakland Bay and Hammersley Inlet are highly censored (large number of non-detect data) with only a single un-annotated positive result more than three times the PQL. In Shelton Harbor, 82% of the surface sediment and 84% of the subsurface sediment PAH data were determined to be of relatively high quantitative uncertainty (Taylor 1987).

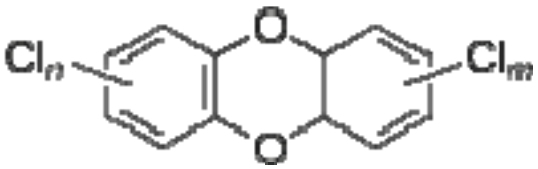
Assuming, for discussion purposes only, that a minimum of five individual PAHs must be present in a sample at concentrations above three times the PQL, then approximately one-sixth of the stations would have sufficient data at one or more depth intervals to fingerprint the PAHs using relative ratios of the individual PAH concentration. Even if the data set is restricted to only Shelton Harbor, more than three-quarters of the stations fail to meet the minimum requirement of 5 individual PAHs with un-annotated concentrations more than 3 times the PQL.

Fingerprinting PAHs in Oakland Bay, Hammersley Inlet, or Shelton Harbor would not provide reliable results.

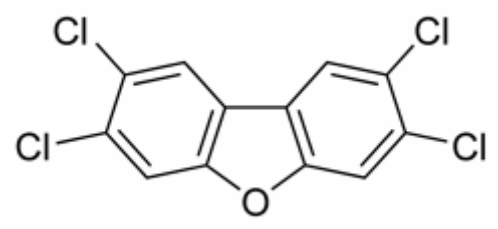
4.3 Dioxin/Furan (PCDD/PCDF)

4.3.1 Nature of Dioxin/Furan (PCDD/PCDF)

Briefly, dioxins and furans are families of related compounds with from 1 to 8 chlorine atoms located at various positions around a base carbon ring structure. Each unique compound is referred to as a congener. Congeners with the same number of chlorine atoms are referred to as homologues. There are 75 different dioxin congeners and 135 different furan congeners. Congeners vary significantly in their toxicity. The following figure illustrates the general structure of dioxin where *n* and *m* represent the number of chlorine atoms and may vary from 0 to 4.



The structure of the congener 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is illustrated below.



It is generally accepted that dioxins and furans do not occur naturally and are not deliberately manufactured. Small quantities of these compounds are inadvertent by-products resulting from a number of chemical processes. For example, pentachlorophenol used in wood preserving often contains dioxin/furan as impurities. Chlorination of wastewater effluent from treatment plants may produce dioxin/furan. Two important sources of dioxin/furan are waste incineration, especially when plastics are burned, and effluent from pulp and paper mills that use chlorine bleaching.

Different processes produce dioxin/furan in differing congener relative ratios. These patterns may be used to indicate the type(s) of sources that may have generated the dioxin/furan. As with the TPH and PAH compounds noted above, dioxin/furan also "weather" in the environment. The use of homologue data for fingerprinting is limited since the concentration of each homologue is based on the sum of several congeners having the same number of chlorine atoms.

4.3.2 Dioxin/Furan Analysis

Sediment samples were analyzed for 17 dioxin/furan congeners and 8 dioxin/furan homologues using USEPA method 1613 (EPA 1994). Target analytes are listed below:

2,3,7,8-TCDD
Total TCDD
1,2,3,7,8-PeCDD
Total PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
Total HxCDD
1,2,3,4,6,7,8-HpCDD
Total HpCDD
OCDD
2,3,7,8-TCDF
Total TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
Total PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
Total HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
Total HpCDF
OCDF

Key:

CDD = chlorinated dibenzo-p-dioxin compounds
CDF = chlorinated dibenzofuran compounds.
HxCDD = hexachlorodibenzo-p-dioxin
HxCDF = hexachlorodibenzofuran
HpCDD = heptachlorodibenzo-p-dioxin

HpCDF = heptachlorodibenzofuran
OCDD = octachlorodibenzo-p-dioxin
OCDF = octachlorodibenzofuran
PeCDD = pentachlorodibenzo-p-dioxin
PeCDF = pentachlorodibenzofuran
TCDD = tetrachlorodibenzo-p-dioxin
TCDF = tetrachlorodibenzofuran

4.3.3 Summary of Oakland Bay Dioxin/Furan Analysis Results

Sediment sampling was described above. Some analyte concentration data were annotated "B" during data validation, indicating that the analyte was detected in the blank associated with the sample. Generally, these blank concentrations were significantly below the measured concentration. Data annotated "B" were considered un-annotated if the measured concentration was 10 times the PQL. Dioxins/furans were only analyzed in surface sediment samples. Figures 5 and 6 illustrate the locations of the samples analyzed for dioxin/furan.

As can be seen in Tables 7, 8, and 9; one or more dioxin/furan congeners were detected in 100% of the samples.

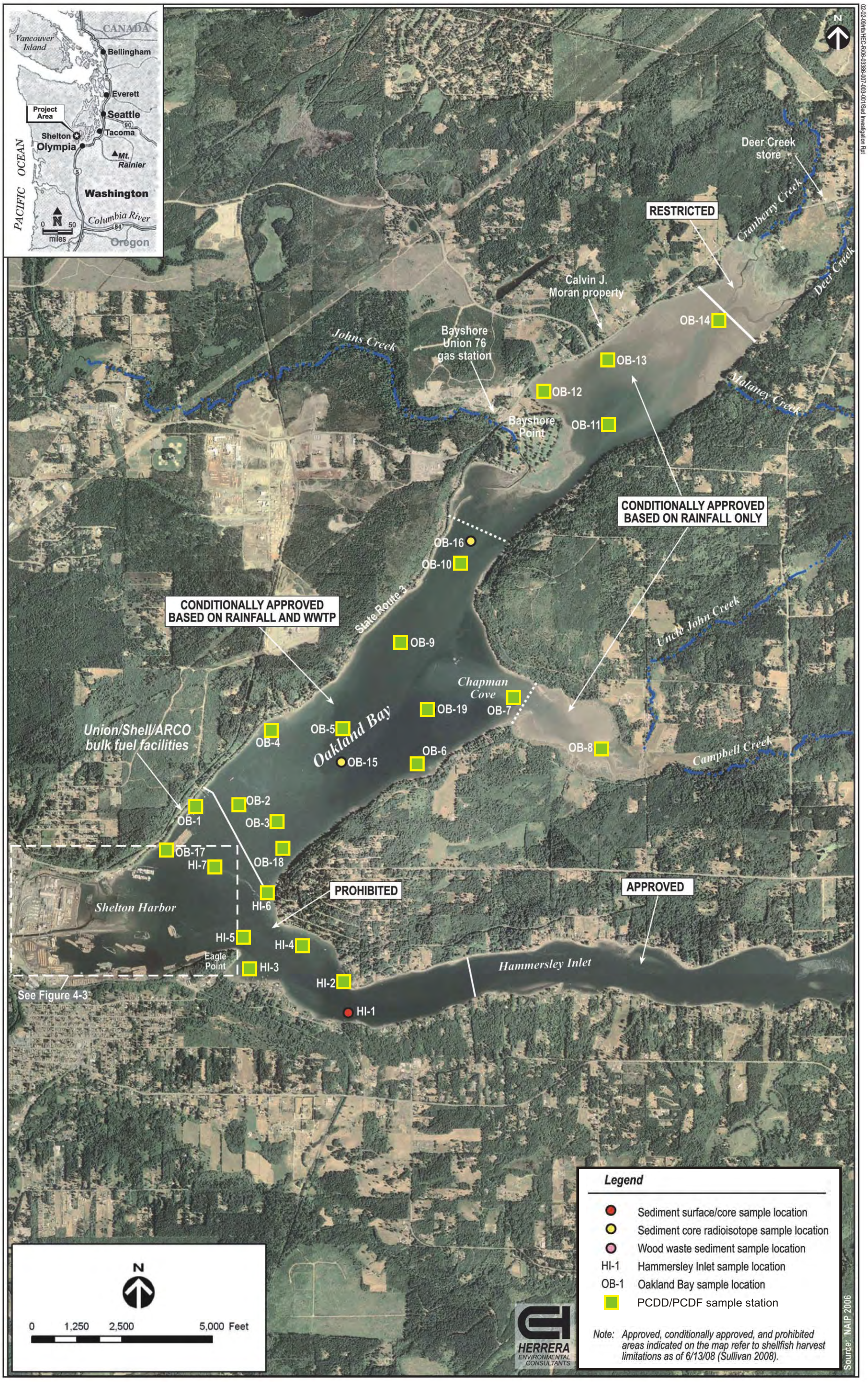


Figure 5 Oakland Bay and Hammersley Inlet Stations with Dioxin/Furan (PCDD/PCDF) Data

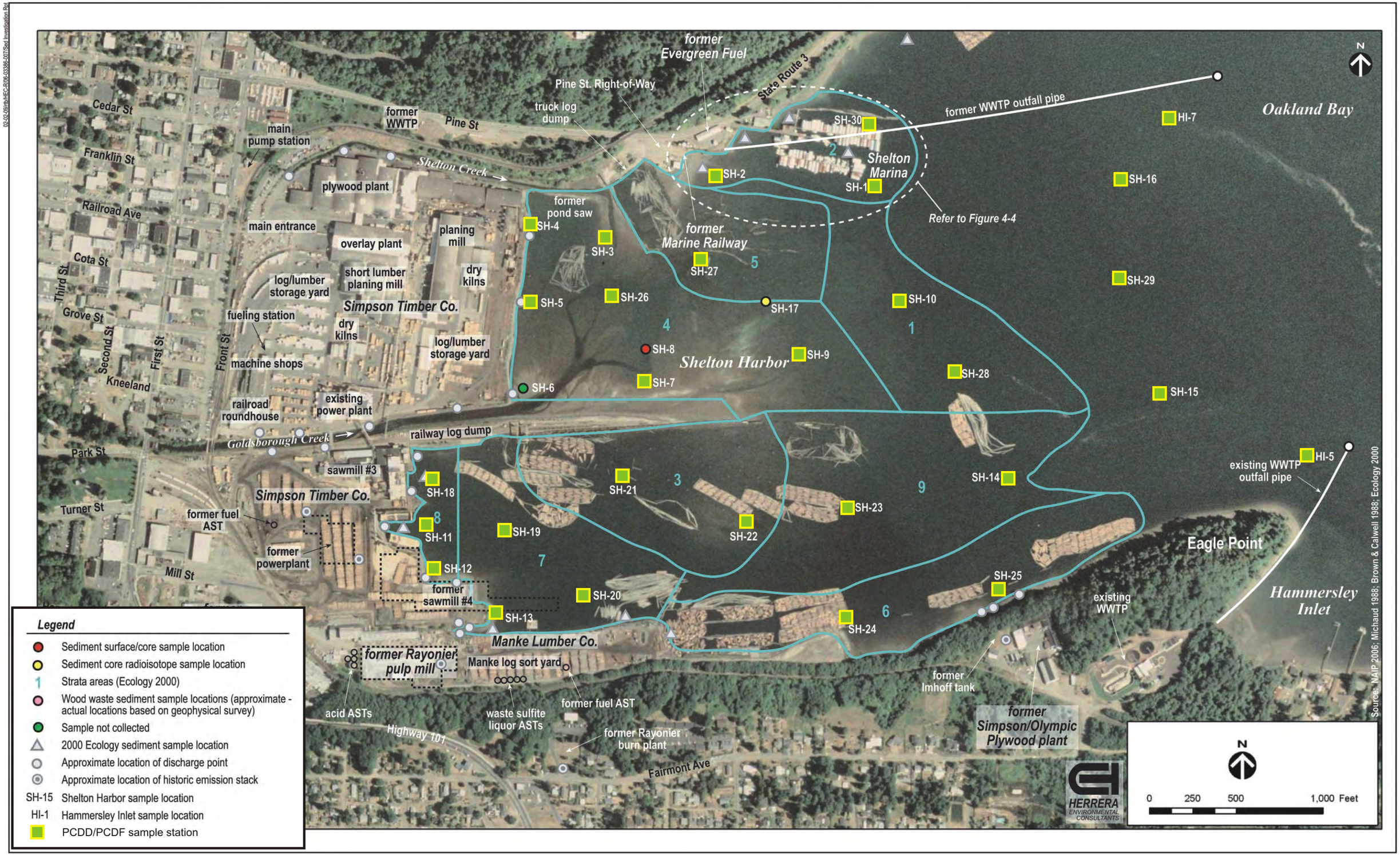


Figure 6 Shelton Harbor Stations with Dioxin/Furan (PCDD/PCDF) Data

Table 7. Summary of Individual Dioxin/Furan Congener Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
1,2,3,4,6,7,8-HpCDD	HI (SS)	6	6	0	0	6	100%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	14	100%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	50	100%
1,2,3,4,6,7,8-HpCDF	HI (SS)	6	6	0	0	6	100%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	14	100%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	50	100%
1,2,3,4,7,8,9-HpCDF	HI (SS)	6	6	0	0	4	67%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	12	86%
	SH (WS)	13	13	0	0	11	85%
	All	50	49	0	0	44	83%
1,2,3,4,7,8,-HxCDD	HI (SS)	6	6	0	0	2	33%
	OB (SS)	14	14	0	0	13	93%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	12	2	0	12	86%
	SH (WS)	13	13	0	0	10	77%
	All	50	48	2	0	40	75%

Table 7 continued. Summary of Individual Dioxin/Furan Congener Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
1,2,3,4,7,8-HxCDF	HI (SS)	6	6	0	0	5	83%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	12	86%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	47	89%
1,2,3,6,7,8-HxCDD	HI (SS)	6	6	0	0	6	100%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	13	93%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	49	92%
1,2,3,6,7,8,-HxCDF	HI (SS)	6	6	0	0	2	33%
	OB (SS)	14	14	0	0	13	93%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	13	1	0	11	79%
	SH (WS)	13	13	0	0	9	69%
	All	50	49	1	0	38	72%
1,2,3,7,8,9-HxCDD	HI (SS)	6	6	0	0	6	100%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	13	93%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	49	92%

Table 7 continued. Summary of Individual Dioxin/Furan Congener Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
1,2,3,7,8,9-HxCDF	HI (SS)	6	0	6	0	0	0%
	OB (SS)	14	11	3	0	0	0%
	OB (WS)	3	2	1	0	0	0%
	SH (SS)	14	9	5	0	3	21%
	SH (WS)	13	9	4	0	0	0%
	All	50	31	19	0	3	6%
1,2,3,7,8-PeCDD	HI (SS)	6	3	3	0	2	33%
	OB (SS)	14	14	0	0	13	93%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	12	2	0	11	79%
	SH (WS)	13	11	2	0	9	69%
	All	50	43	7	0	38	72%
1,2,3,7,8-PeCDF	HI (SS)	6	2	4	0	1	17%
	OB (SS)	14	13	1	0	12	86%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	12	2	0	10	71%
	SH (WS)	13	9	4	0	9	69%
	All	50	39	11	0	35	66%
2,3,4,6,7,8-HxCDF	HI (SS)	6	5	1	0	2	33%
	OB (SS)	14	14	0	0	13	93%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	12	2	0	11	79%
	SH (WS)	13	12	1	0	9	69%
	All	50	46	4	0	38	72%

Table 7 continued. Summary of Individual Dioxin/Furan Congener Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
2,3,4,7,8-PeCDF	HI (SS)	6	1	5	0	1	17%
	OB (SS)	14	11	3	0	10	71%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	11	3	0	11	79%
	SH (WS)	13	11	2	0	9	69%
	All	50	37	13	0	34	64%
2,3,7,8-TCDD	HI (SS)	6	2	4	0	1	17%
	OB (SS)	14	14	0	0	12	86%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	12	2	0	11	79%
	SH (WS)	13	11	1	1	8	62%
	All	50	42	7	1	35	66%
2,3,7,8-TCDF	HI (SS)	6	5	1	0	2	33%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	11	3	0	10	71%
	SH (WS)	13	8	5	0	7	54%
	All	50	41	9	0	36	72%
OCDD	HI (SS)	6	6	0	0	6	100%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	14	100%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	50	100%

Table 7 continued. Summary of Individual Dioxin/Furan Congener Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	# of samples	# of un-annotated positive results	# of annotated positive results	# of non-detect samples	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
OCDF	HI (SS)	6	6	0	0	6	100%
	OB (SS)	14	14	0	0	14	100%
	OB (WS)	3	3	0	0	3	100%
	SH (SS)	14	14	0	0	14	100%
	SH (WS)	13	13	0	0	13	100%
	All	50	50	0	0	50	100%

HI (SS) – Hammersley Inlet surface sediment
OB (SS) – Oakland Bay surface sediment
OB (WS) – Oakland Bay wood waste area surface sediment
SH (SS) – Shelton Harbor surface sediment
SH (WS) – Shelton Harbor wood waste area surface sediment

Table 8. Summary of All Dioxin/Furan Congener Data from Oakland Bay Sediment Investigation

Analyte	Area (sample matrix)	# of analytes	# of un-annotated positive results	# of annotated positive results	# of non-detect analytes	# of un-annotated positive results > 3 x PQL	% of un-annotated data > 3 x PQL
All dioxin/furan congeners	HI	102	78	24	0	58	57%
	OB	289	281	8	0	260	90%
	SH	459	417	41	1	368	80%
	All	850	776	73	1	686	81%

HI (SS) – Hammersley Inlet surface sample
OB (SS) – Oakland Bay surface sample
SH (SS) – Shelton Harbor surface sample

Table 9. Summary of All Dioxin/Furan Congener Data by Station from Oakland Bay Sediment Investigation

# of congeners	# of stations with un-annotated positive results > 3 x PQL	% of stations with un-annotated positive results > 3 x PQL	Cumulative % of stations with un-annotated positive results > 3 x PQL
0	0	0%	0%
1	0	0%	0%
2	0	0%	0%
3	0	0%	0%
4	1	2%	2%
5	0	0%	2%
6	2	4%	6%
7	3	6%	12%
8	3	6%	18%
9	2	4%	22%
10	1	2%	24%
11	0	0%	24%
12	0	0%	24%
13	1	2%	26%
14	2	4%	30%
15	7	14%	44%
16	25	50%	94%
17	3	6%	100%
total	50	100%	100%

4.3.4 Utility of Dioxin/Furan Congener Data for Fingerprinting

Based on the data presented in Tables 7, 8, and 9, it is clear that dioxin/furan data are not highly censored (less than 1% of the data were non-detect). In addition, a significant percentage of the un-annotated positive results are greater than three times the PQL.

Assuming, for discussion purposes only, that a minimum of five congeners must be present in a sample at concentrations above three times the PQL, then approximately 98 per cent of the stations would have sufficient data to fingerprint dioxin/furan congeners using relative ratios of the congener concentrations.

Dioxin/furan fingerprinting would be appropriate for Hammersley Inlet, Oakland Bay, and Shelton Harbor.

Visual comparisons of relative ratios of dioxin/furan congener concentrations to published ratios from sources such as wood burning may provide some indication of the nature of potential source material.

5. Summary

Based on the available data, fingerprinting is not possible for TPH in Oakland Bay, Hammersley Inlet, or Shelton Harbor.

Again, based on the available data, fingerprinting is not possible for PAHs in Oakland Bay, Hammersley Inlet, or Shelton Harbor.

Oakland Bay, Hammersley Inlet, and Shelton Harbor sediment dioxin/furan data are amenable to fingerprinting. The Oakland Bay Sediment Investigation Report will include comparisons of relative dioxin/furan congener sediment concentrations with relative dioxin/furan congener concentrations from sources such as wood burning, automotive exhaust, and pulp and paper mill effluent. Sediment dioxin/furan data will also be compared with the recently released Puget Sound Dioxin/PCB Survey, OSV Bold, 2008 (DMMP 2009)data, data provided by Ecology for sediment samples collected from Goose Lake (where Rayonier pumped sulfite waste liquor during a portion of its operating period), and if available, data from salt-laden hog fuel boiler emissions.

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