Oakland Bay
Sediment Dioxin Source Study
Oakland Bay, WA

Final Report

Prepared for

DEPARTMENT OF
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List of Acronyms

ALS	Alternating Least Squares
COPC	chemical of potential concern
dioxin	polychlorinated dibenzo-*p*-dioxin
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management
EPA	Environmental Protection Agency
E & E	Ecology and Environment, Inc.
FWEC	Foster Wheeler Environmental Corporation
furan	polychlorinated dibenzofuran
HCA	Hierarchical Cluster Analysis
HFB	hog fuel boiler
IEP	Institute of Environmental Protection
MCDD	monochlorodibenzo-*p*-dioxin
MCDF	monochlorodibenzofuran
NCASI	National Council for Air and Stream Improvement
DMMP	Dredged Material Management Program
OCDD	octachlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
PCA	principal components analysis
PCB	polychlorinated biphenyl
PCP	pentachlorophenol
PSAMP	Puget Sound Ambient Monitoring Program
Simpson	Simpson Timber Company
SMS	Sediment Management Standards
TCDD	tetrachlorodibenzo-*p*-dioxin
TEF	toxicity equivalency factor
TEQ	toxic equivalency
WPCC	Washington Pollution Control Commission
WWTP	wastewater treatment plant

1.0 Introduction

Oakland Bay was selected as one of several embayments targeted for investigation and potential cleanup of sediment contamination by the Washington State Department of Ecology (Ecology) under Puget Sound Initiative. Oakland Bay, located in Mason County, was of particular interest for investigation because of both its industrial history and productive shellfish aquaculture.

In 2008 Ecology's Toxics Cleanup Program directed a sediment investigation in Oakland Bay to support prioritization of cleanup and restoration. The study generally reported contaminants of concern below Ecology's Sediment Management Standards (SMS) across the study area. However, polychlorinated dibenzo-*p*-dioxin (dioxin) and polychlorinated dibenzofuran (furan) congeners (not addressed by SMS) were identified as specific contaminants of concern. High levels of dioxin/furan toxic equivalency (TEQ) were identified as extending across the entire study area, with the highest concentrations found in subsurface sediments of Shelton Harbor (Herrera 2010).

The Oakland Bay Sediment Dioxin Source Study was initiated by Ecology to increase understanding of dioxin/furan contamination in Shelton Harbor and Oakland Bay sediments, with an objective of identifying potential upland sources and transport pathways. This study documents the chemometric evaluation and interpretations of sediment dioxin/furan congener data. The report presents an in-depth discussion of the data evaluation process, results, and conclusions regarding probable sources of dioxin/furan contamination currently found in both surface and subsurface sediments of the study area.

1.1 Overview of Dioxins/Furans

Dioxins and furans are two classes of chemicals that are structurally similar in that they both contain two carbon ring structures. All dioxins include two oxygen atoms, while all furans include one oxygen atom, as shown in Figure 1. There are 210 unique dioxin/furan compounds, each called a "congener" (75 dioxin and 135 furan congeners), which differ from each other in the number and position of chlorine atoms on the carbon rings.

Dioxin/furan congeners contain one to eight chlorine atoms, resulting in eight families, or homolog groups, ranging from those containing one chlorine atom, monochlorodibenzo-*p*-dioxins (MCDDs) and monochlorodibenzofurans (MCDFs), to those containing eight, octachlorodibenzo-*p*-dioxins (OCDDs) and octachlorodibenzofurans (OCDFs). Figure 1 shows each numbered carbon atom, corresponding to possible positions for the chlorine atoms.

Although there are 210 unique dioxin/furan congeners, only 17 of these are typically evaluated because they are considered by the U.S. Environmental Protection Agency (EPA) and the World Health Organization to be the most toxic. These 17 congeners have chlorine atoms in the 2, 3, 7, and 8 positions shown in Figure 1. In this study, the terms "dioxins" and "furans" will be used to refer to the 17 congeners of primary interest, listed in Table 1.

Concentrations of the 17 dioxins/furans of primary interest are often expressed as a TEQ relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). This means that the concentrations of the other 16 congeners have been adjusted based on a toxicity equivalency factor (TEF) that scales each congener's potency relative to 2,3,7,8-TCDD. The concentrations are presented as mass of chemical per mass of sediment, such as 1.5 nanograms of 2,3,7,8-TCDD TEQ per kilogram of sediment (1.5 ng TEQ/kg). The TEFs assigned to each congener are consistent with Ecology guidance (Ecology 2007; Van den Berg et al. 2006) and are presented in Table 1. The most potent congeners, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, are assigned a TEF of 1, while the least potent, OCDD and OCDF, have the smallest TEF, 0.0003.

Federal and state environmental regulatory and health agencies are interested in dioxins/furans because they are toxic to humans and wildlife. Once released into the environment, dioxins/furans resist degradation, do not dissolve in water, and adhere to particles such as soil, dust, and sediment. This means that they are persistent and can bioaccumulate in people and animals and can be measured in environmental media long after they have been released. Despite their persistence and ubiquitous presence, concentrations of dioxins/furans in the environment have been declining since the 1970s due to improvements in air pollution control technologies for combustion and incineration facilities and cleanup of dioxin-contaminated areas (EPA 2003).

Dioxins/furans enter the environment from a variety of sources. Except for small quantities used in research, neither compound is created intentionally. Instead, dioxins/furans are byproducts of chemical manufacturing and combustion or incineration processes involving chlorine compounds. For example, dioxins are most notorious for their presence as a contaminant in the herbicide 2,4,5-T and in Agent Orange. They can also be produced during incineration of wood, oil, and wastes. Major contributors of dioxins/furans to the environment include:

- Incineration of municipal solid waste and medical waste;
- Secondary copper smelting;
- Forest fires;
- Land applications of sewage sludge;
- Cement kilns;
- Vehicle emissions, combustion of gasoline and diesel;
- Coal-fired power plants;
- Residential wood burning;
- Chlorine bleaching of wood pulp;
- Backyard burning of household waste;
- Byproducts and derivatives of chemical production, e.g., pentachlorophenol (PCP), polychlorinated biphenyls (PCBs), 2,4,5-T; and
- Hog fuel boilers (HFBs) burning salt-laden wood.

Dioxins/furans are present at some level throughout the environment, in air, food, water, soils, and sediments. They tend to be found in higher concentrations near industrial areas but are present in various concentrations throughout urban, rural, and even remote wilderness areas. Urban soil and sediment concentrations of dioxins/furans commonly represent the combined influences of multiple sources.

1.2 Overview of Dioxin/Furan Chemometrics

Each of the dioxin/furan sources listed in Section 1.1 produces a unique mix of the 17 congeners. Some sources may preferentially produce dioxin or furan congeners, or congeners of specific molecular weight. The abundance of these congeners relative to each other is known as a congener profile, or more simply, a chemical fingerprint.

Chemometrics, often referred to as environmental forensics, is a blanket term that includes several multivariate statistical methods such as clustering, principal components analysis (PCA), and alternating least squares (ALS). While each of these methods serves a slightly different purpose, the overall goal of the analysis is to reduce the complexity of the data set for more meaningful interpretation. In the case of dioxin/furan chemometrics, a data set's underlying congener profiles can be extracted for comparison to the congener profiles of known sources.

Dioxin/furan contamination in sediment samples is generally composed of a mixture of sources. Chemometrics methods are used to reduce the mixed profiles measured in the sediment samples into a small number of modeled congener profiles, or factors. If these factors match the congener profiles of the known sources, spatial modeling can then be used to map the distribution of each source. The spatial modeling along with other lines of evidence including sediment transport processes and historical site usage are then used to reinforce the statistical results.

1.3 Study Objectives

The goal of the Oakland Bay Sediment Dioxin Source Study is to increase the understanding of dioxin/furan sediment contamination throughout the bay, including the magnitude and likely sources of contamination to surface and subsurface sediments. Specific objectives of this study include:

- Identifying distinct dioxin/furan congener factor signatures present in Oakland Bay sediments;
- Determining the relative contribution of identified dioxin/furan factors to bay-wide contamination; and
- Using the spatial patterns of sediment dioxin/furan factors, as well as characteristics of facilities in the Oakland Bay area, to identify potential upland point source locations.

The results of this study are expected to assist Ecology in identifying potential sources of the dioxins/furans in Oakland Bay. It is not Ecology's intention to use the findings to perform detailed quantitative allocations among potential point/nonpoint sources or to apportion liability to potentially liable parties.

1.4 Report Organization

This report summarizes and evaluates the results of Oakland Bay sediment dioxin/furan chemometric analysis within the context of the project scope and study objectives. Section 2.0 of this document provides background for the region, including the most likely sources of dioxins/furans to the bay and the distribution of dioxins/furans in sediments. Section 3.0 describes the methods used for chemometric data evaluation. Section 4.0 presents the results of chemometric analysis including the character and spatial patterns of the unique sediment dioxin/furan factors identified. Section 5.0 provides a discussion of the upland processes potentially responsible for the sediment dioxin/furan patterns. Section 6.0 summarizes the conclusions that can be drawn from this study. References are provided in Section 7.0.

2.0 Site Background

This section presents findings and conclusions from numerous studies of Oakland Bay relevant to understanding where in the bay sediment dioxins/furans are found and their potential fate and transport.

2.1 Potential Dioxin/Furan Sources

A comprehensive review of the potential sources of chemical contamination to Oakland Bay sediments can be found in Herrera (2008). Below is a summary of the facilities and other sources previously identified as having the greatest potential to contribute to dioxin/furan contamination.

2.1.1 Simpson Timber Company

Facilities operated by the Simpson Timber Company (Simpson) had the potential to contribute to Oakland Bay sediment dioxin/furan contamination. Site-specific activities generally associated with the production or release of dioxins/furans include:

- Application of PCP as a wood preservative;
- Storage of PCP and products treated with PCP preservatives;
- Burning of hog fuel; and
- Handling of boiler ash and baghouse residue.

Waterfront Plywood and Sawmill Facilities

Since the mid-1800s, a number of timber industries dominated Shelton Harbor. Through the early 1930s three sawmills operated along the Shelton waterfront and a shingle mill operated at Eagle Point (Figure 2). By the early 1940s, Simpson acquired all sawmills and the shingle mill, redeveloping the Shelton waterfront into an extensive sawmill and plywood/fiberboard manufacturing complex. In the mid-1940s, Simpson developed the central tideflats across the waterfront north of Goldsborough Creek and built an insulating board plant, plywood plant, railroad roundhouse, and machine shops. At this time a railroad log dump was constructed, along with the emplacement of more than 4,000 pilings in the harbor to provide mooring for rafted logs. From the 1950s to the early 1960s, Simpson further expanded their facility on the north side of Goldsborough Creek eastward, building a planing mill, the short lumber planing mill, and dry kilns. Much of the Simpson complex, both north and south of Goldsborough Creek, was built upon filled tidelands. The property currently extends eastward to a harbor bulkhead which was backfilled with dredged sediment.

Process chemicals used at the Simpson waterfront plywood and sawmill facilities, as reported to Ecology since the early 1980s, have included phenolic and urethane resins, urea/formaldehyde glues, fungicides, and waterproofing wax. PCP-containing wood preservatives were also used by Simpson, including in a dip tank on the property. PCP was used by the wood-preserving industry as early as the 1930s to prevent decay, molding, and discoloration, becoming the most widely used preservative after 1950 (EPA 1992).

In 1926, a wood-fired power plant was built between the sawmills south of Goldsborough Creek to supply power to both the Simpson sawmills and the Rayonier pulp and paper mill. This power plant was jointly owned by Simpson and Rayonier until 1962 when Simpson purchased Rayonier’s interest in the plant (Thomas and Perry 1996). The power plant’s seven boilers burned waste wood, known as hog fuel, such as bark removed from logs and rejected wood chips and debris generated by the sawmills. When necessary, fuel oil was used to supplement fuel demands. The power plant’s two stacks operated without air emission controls between 1926 and 1976.

In 1976, Simpson installed two banks of baghouses to filter particulates prior to emission. One bank of baghouses was situated between the single high-pressure boiler and the short emission stack (125-foot high), with the other between the six low-pressure boilers and the tall emission stack (244-foot high). Collectively the baghouses captured approximately 3,000 pounds per day of particulate residue when all boilers were in use (Herrera 2008). Roughly two-thirds of the collected residue consisted of salts, with the remainder composed of unburned and charred wood.

Baghouse residues were mixed into slurries and discharged to the former Pine Street wastewater treatment plant (WWTP) (1976 to 1979) and the existing Eagle Point WWTP (1979 to 1984). Settling solids collected at these WWTPs were subsequently disposed of at the Shelton “C Street” Landfill and the Mason County Landfill. After 1984, all baghouse residues generated at the power plant were mixed with wood refuse and disposed of at Simpson’s Dayton landfill. Samples from the power plant’s stack emissions, bottom ash, and baghouse residue, as well as landfill and residential soil samples were included in EPA’s national study to identify dioxin/furan sources (CH2M Hill 1987).

In 1986, the old wood-fired power plant was decommissioned and replaced with a more efficient wood-fired power plant north of Goldsborough Creek. While the new power plant has been documented as burning salt-free wood (Thomas and Perry 1996), Ecology’s dioxin source assessment reported the wood burned to consist of 20 percent salt-laden hog fuel (Ecology 1998).

Eagle Point Facility

The Eagle Point facility served as a shingle mill prior to acquisition by Simpson. Between 1941 and 1974, the facility manufactured plywood as Olympic Plywood and operated a wood-fired power plant on site. Operations were subsequently moved to the north end of the Simpson waterfront complex. Simpson then leased the property to Shelton Structures to be used as a glue laminate beam fabrication plant until the early 1990s. The property is currently owned by the Port of Shelton.

2.1.2 Rayonier Facilities

Facilities operated by Rayonier had the potential to contribute to Oakland Bay sediment dioxin/furan contamination. Site-specific activities generally associated with the production or release of dioxins/furans include:

- Chlorine bleaching of pulp;
- Use of PCP in industrial and laboratory processes;
- Processing of wood chips treated with PCP preservatives;
- Burning of hog fuel and sulfite liquor; and

- Handling of boiler ash.

Pulp Mill

From 1926 to 1957 Rayonier operated a pulp and paper sulfite mill with a wood-fired power plant on the south side of Shelton Harbor (Figure 2). The mill mostly produced pulp for manufacturing rayon and other specialty cellulose products, with limited paper pulp production (Herrera 2008). The mill processes generally consisted of the following: pulp production (cooking), bleaching, screening, washing, and drying. Pulp was produced from wood chips supplied by Shelton sawmills or brought in by trucks or barges. By the early 1950s, the pulp mill began generating its own wood chips onsite (Thomas and Perry 1996).

The calcium sulfite pulping process utilized by the Rayonier mill generated sulfite waste liquor, also known as brown liquor, as a by-product. The liquor consisted of dissolved organic compounds, such as lignins and sugars, extracted from the wood chips by the acid-digestion pulping process. Prior to the early 1930, spent sulfite liquor was either directly discharged to the harbor during outgoing tides or piped eastward to Mill Creek for discharge to Hammersley Inlet (Thomas and Perry 1996). The locations of discharge points into the harbor from the mill are unknown (Herrera 2008). Rayonier attempted alternative methods of waste liquor disposal during the mid- to late 1930s, including the treatment of Shelton roads for dust control and the production of specialty products such as plywood adhesives and linoleum paste. In addition to the sulfite liquor waste, Rayonier generated approximately 8.4 million gallons per day of untreated chlorine bleach process wastewater that was discharged to the harbor (WPCC 1954).

Impacts to the shellfish industry were apparent in both Oakland Bay and Hammersley Inlet soon after the pulp mill began releasing waste liquor to the harbor. Degradation of regional oyster beds occurred as effluent was diffused from Shelton Harbor by tidal currents (Lindsay and Simons 1997). In order to prevent further impacts, Rayonier constructed a three-mile long pipeline that ran inland from the mill to Goose Lake, a small body of water located on a Rayonier-operated property. Goose Lake, discussed below, received waste liquor between the early 1930s to the mid-1940s (Thomas and Perry 1996).

Conveyance of waste liquor to Goose Lake was discontinued by the early 1940s because of evidence that it had seeped into groundwater and a nearby creek (Thomas and Perry 1996). In 1945, Rayonier constructed a burn plant with a 325-foot high stack on the hillside above the mill for the purpose of incinerating spent liquor. Despite the existence of the new burn plant, approximately 100 truckloads of sulfite liquor residue were buried at the Bayshore Golf Course in the 1950s. Both the pulp mill and burn plant continued operation until they were shut down in 1957. Both facilities were demolished by the mid-1960s when the Manke Lumber Company purchased the pulp mill property and converted it into a sorting yard for logs brought in by trucks. Prior to the mill closure, Rayonier may have dredged 30,000 cubic yards of sediment from the “log pond” area of southern Shelton Harbor, with disposal occurring offshore of Eagle Point (Rayonier 1952).

Research Laboratory

From 1936 to 1995, Rayonier operated a laboratory located west of and adjacent to the pulp mill (Figure 2). The laboratory supported production of rayon fibers and other specialty wood products, including cellophane, cellulose acetate, and nitrocellulose used for explosives. Waste consisting of cellulose in caustic slurry and other unknown chemicals generated by the laboratory during the late 1930s and 1940s was reportedly disposed of at the Goose Lake site (Herrera 2008). A 1987 letter from Rayonier to Ecology describes the chemical loss from the research laboratory to their National Pollutant Discharge Elimination System (NPDES) discharge (Rayonier 1987). Chemicals discharges in greatest quantity include organic solvents, sodium hydroxide, and cupriethylenediamine (a cellulose solvent and aquatic herbicide).

Goose Lake Site

Between approximately 1931 and 1974, waste materials generated at Rayonier's former pulp mill and research laboratory in Shelton were disposed of at Goose Lake. Historical disposal consisted of liquid wastes discharged to both the lake and upland disposal lagoons, and solid wastes dumped in a landfill at the lake's edge. A remedial investigation of the Goose Lake Site was completed in 2012 (GeoEngineers 2012). While the Goose Lake site may not be a direct source of dioxins/furans to sediments of Oakland Bay, samples collected there may prove important for understanding the dioxin/furan signatures of waste material derived from Rayonier facilities.

At the pulp mill site, spent liquor was temporarily stored in five aboveground storage tanks located east of and adjacent to the mill before being pumped to the lake. From May 1931 to September 1934, the liquor was discharged to the Goose Lake via a pipeline. In 1934 the discharge point was moved to two diked disposal lagoons west of the lake. Liquor discharge was discontinued in August 1943.

The landfill located at the east end of Goose Lake was operational from approximately 1936 to 1974. Waste trucked to the landfill included solids wastes from the pulp mill and research laboratory, ash and char from boilers, and demolition debris from the decommissioning of the pulp mill (GeoEngineers 2012). The inactive landfill is currently covered by sand and gravel, likely from the adjacent gravel pit to the north.

2.1.3 Other Potential Sources

Johns Prairie Industrial Park

Johns Prairie Industrial Park consists of 270 acres of developed land located ¾ miles northwest of Oakland Bay (Figure 2). Johns Creek flows eastward within 850 feet of the industrial park before discharging to Oakland Bay. In the 1940s, prior to becoming an industrial park, the property was utilized by the U.S. Navy as a supply depot. Since then the property has been used by forest product businesses, such as sawmills, wood chipping companies, wood-treatment facilities, and utility pole manufacturers (Port of Shelton 2008). From the late 1970s to the mid-1990s, a variety of wood treatment chemicals including a PCP-containing preservative were used in a dip tank at the property. A 2003 site investigation identified the petroleum and PCP contamination in the soil but not in groundwater. Cleanup activities completed in 2004 included the removal of 452 tons of contaminated soil and the dip tank.

Municipal Wastewater

Prior to 1950, sewer pipes conveyed untreated sewage directly into Shelton Harbor (City of Shelton 2006). Between 1950 and 1979, the City of Shelton operated a WWTP located on Pine Street. The plant was designed for primary treatment of sewage, including grit removal, sedimentation, single-stage digestion, and chlorination (Shelton-Mason County Journal 1950). Throughout its operation the Pine Street WWTP received municipal sewage for treatment, but also received slurried baghouse residues from the Simpson power plant from 1976 to 1979. Effluent from the WWTP was discharged to an outfall pipe located offshore of the north side of the harbor (Figure 2).

Since 1979, the City of Shelton has operated a WWTP at Eagle Point. Treatment is accomplished through screening, grit removal, oxidation ditches, final clarification, and disinfection with chlorine (Ecology 2008). The Eagle Point WWTP received slurried baghouse residue from the Simpson power plant until 1984. Secondary treated wastewater is discharged from the WWTP through a deepwater outfall pipe that extends into Hammersley Inlet (Figure 2).

Wooden Marine Structures

Wood pilings and other wooden marine structures are prevalent throughout Shelton Harbor, often employed as structural supports for anchoring log rafts, vessel mooring, and as bulkheads. Marine-use wood is generally preserved with chemicals to prevent deterioration from wood-degrading marine organisms. Creosote has historically been the most commonly used chemical wood preservative worldwide. PCP was generally used as a wood preservative for non-marine applications, as its application does not make wood resistant to marine borers (Stratus 2006). While it is assumed that the majority of marine wood structures within the harbor were treated with creosote, it is possible that PCP-treated wood pilings and structures were also used in the harbor.

Surface Water Tributaries

Creeks of the Oakland Bay watershed drain a variety of land-use types including residential and industrial areas. Ecology performed a study to identify whether current or historic sources of dioxin are present in the creeks discharging to the bay (Ecology 2013). Overall, dioxin/furan concentrations in tributary sediments were much lower than those of Oakland Bay surface sediments. However, the study identified an ash mound along the northern bank of Shelton Creek across from the Simpson facility that may contribute dioxins/furans to the creek (Figure 2).

2.2 Sediment Transport

An understanding of sediment transport processes in Oakland Bay aids in interpreting sediment chemistry results when trying to identify point sources of dioxin/furans. Productive shellfish beds in Oakland Bay can be partially attributed to the presence of broad mudflat habitats. These mudflats are intertidal sedimentary features created through the deposition of silts and clays in low-energy areas. The sheltered nature of Oakland Bay promotes stable mudflats by preventing the propagation of wind-waves and associated nearshore erosion. Silts and clay particles depositing on the mudflats are initially supplied to Oakland Bay by creeks, and are then dispersed by tidal currents and estuarine circulation.

A majority of sediment input to the bay comes from creeks located in Shelton Harbor, in Chapman Cove, at Bayshore Point, and at the head of the bay, with Goldsborough Creek delivering two-thirds of the total sediment load (Figure 2). Large precipitation events efficiently deliver sediment to the bay from these creeks, as well as stormwater outfalls. In Herrera (2010), a sediment budget was developed by using a common sediment production model (Syvitski et al. 2005) and estimating accumulation rates determined from dating of sediment cores. This budget confirmed that all sediment deposited within the confines of greater Oakland Bay remains there with little likelihood to be exported from the system through Hammersley Inlet.

The sediment-trapping effect of Oakland Bay is the result of circulation patterns established by tidal motion. The restrictive nature of Hammersley Inlet causes the water of Oakland Bay to have a high amount of refluxing and retention with little flushing (Ecology 2004). Water flows into Oakland Bay from Hammersley Inlet at depth and out from the bay near the water surface (Albertson 2004). Strong flow near the bed of Hammersley Inlet occurs as marine water enters the narrow channel during a flood tide. This strong current generally prevents sediment deposition in Hammersley Inlet, allowing the seabed here to generally consist of coarse-grained material (Figure 3). At the onset of ebb tide, water begins to flow out of the bay at the water surface, containing relatively small amounts of fine-grained sediment.

Spatial patterns of surface sediment grainsize provide clues to the direction of sediment transport in the region (Figure 3). Other than within Hammersley Inlet, coarse-grained sediment is found at the creek deltas that surround Oakland Bay. Generally, sediment varies from coarse to fine moving from the sources to deeper portions of the bay. This broad distribution of predominantly fine-grained sediment across deep Oakland Bay suggests that this area, far from sediment sources, represents the depositional reservoir for many sources surrounding the bay. This deposition of fine-grained sediments is supported by acoustic tomography results, indicating the accumulation of a shallow sediment layer (generally between 1 and 3 feet) across most of the bay was subsequent to urban development of the area (Herrera 2010).

Several consequences of this sediment transport relative to the pattern of chemicals of potential concern (COPCs) and wood waste are apparent in the results reported in Herrera (2010). The majority of COPCs and sediment sources to Oakland Bay (industrial outfalls, WWTP outfalls, large creeks, etc.) are located close to the Shelton Harbor shoreline or contribute to runoff that enters the harbor. Similarly, the primary sources of wood fibers to the region are wood processing operations of Shelton Harbor. Because sediment in Hammersley Inlet is generally non-depositional, the seabed here accumulates little input from these sources. It can be assumed that COPCs and wood waste found throughout greater Oakland Bay were transported with sediment that likely originated in Shelton Harbor.

2.3 Sediment Dioxins/Furan TEQ

Interpolation of surface sediment dioxin/furan total TEQs results in distinct spatial patterns which, in conjunction with knowledge of sediment transport processes, can be used to infer likely upland source locations of dioxins/furans entering Oakland Bay. However, it is assumed that every measure of total TEQ is a composite of inputs from multiple sources. Therefore, while spatial patterns of total TEQ can identify the most impacted regions of the bay, individual source contributions responsible for the magnitude and spatial pattern of total TEQ remain unresolved.

2.3.1 Surface Sediment

Dioxins/furans were identified during numerous sampling events in all surface sediments of the study area, ranging from 1 to 175 ng TEQ/kg (Figure 4). Generalized patterns of surface sediment TEQ concentrations include:

- The highest TEQ concentrations (>50 ng/kg) were found at locations along the shoreline of Shelton Harbor where the majority of wood processing historically took place, including wood waste burning, pulp mill chlorine bleach plant effluent discharge, sulfite liquor discharge and burning, and PCP use.
- Low level TEQ concentrations (<15 ng/kg) were found to be distributed in areas of high sedimentation (creek deltas) and where fine-grained sediments do not accumulate (junction between Oakland Bay and Hammersley Inlet.
- Medium level TEQ concentrations (15-50 ng TEQ/kg) were found to be distributed across the remaining area, including outer Shelton Harbor and greater Oakland Bay.

High dioxin TEQ concentrations in Oakland Bay relative to greater Puget Sound indicate localized sources. However, the majority of potential dioxin/furan sources to the Oakland Bay region appear to be historical in nature (see Section 2.1). The continued presence of high level dioxin in surface sediments may indicate ongoing upland sources, redistribution of sediments from high level areas, or the mixing of deeper with shallower sediments by natural or anthropogenic actions.

2.3.2 Subsurface Sediment

Sediment samples of highest dioxin TEQ concentration in the study area were collected from subsurface intervals. Nine of twelve sediment cores had higher dioxin/furan TEQ concentrations at depth, indicating higher historical input levels (Figure 4). However the limited amount of sample depths analyzed do not make it possible to correlate concentration trends with time, other than to suggest that dioxin input to the bay has decreased in the recent past. Locations with higher concentrations at the surface versus the subsurface include one in the Goldsborough Creek alluvial fan with coarser-grain material at depth and a location along the southwest shoreline with a high potential for mixing associated with historical dredging activities.

2.4 Previous Dioxin/Furan Chemical Fingerprinting

Chemical fingerprinting is a technique used to differentiate potential sources of chemical contaminants. Fingerprinting of dioxin/furan congeners found in Oakland Bay sediments was pursued by Ecology in the hope of identifying regions of the study area influenced by specific industrial, municipal, or residential sources. Dioxin source assessments conducted in Washington indicate that incinerators, hog fuel boilers, bleached pulp and paper mills, cement kilns, kraft black liquor boilers, tire combustion, and sewage sludge incineration are potential sources to the environment (Ecology 1998).

Dioxin/furan fingerprinting of Oakland Bay sediments was initially evaluated by comparing the sediment profiles with 15 EPA-provided source profiles (Herrera (2010). Five of the EPA profiles were found to be similar to those of the study area:

- 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.

Of these potential sources, PCP and black liquor recovery boiler emissions appeared to be the best matches to Oakland Bay sediments. Black liquor is the waste product of the kraft (or sulfate) pulping process. Profiles were not available for sulfite waste liquor incineration; sulfite waste liquor; or boiler ash from burning salt-laden wood. Additionally, profiles of Goose Lake surface sediment samples appeared similar to those of Oakland Bay.

Herrera (2010) concluded that based on the available data and fingerprinting results, no specific dioxin/furan source can be definitively linked to those deposited in Oakland Bay sediments without additional sampling. As a result, Ecology decided to pursue a more intensive fingerprinting approach consisting of multivariate chemometric analyses (unmixing analyses) of the sediment dioxin/furan congener data. A similar approach of chemometric analysis was performed for dioxin/furan congener data of both Port Angeles soils (E & E and Glass 2011) and Port Angeles Harbor sediments (NewFields 2013). Applying chemometrics to Port Angeles Harbor sediments resulted in the identification of four dioxin/furan source profiles, each with unique spatial footprints and likely upland sources.

3.0 Methods

This section discusses the methodology used to accomplish the objectives of this study. This included the compilation of Oakland Bay dioxin/furan congener data sets, chemical unmixing analysis of these data, and spatial interpolation and analysis of chemical unmixing results.

3.1 Data Compilation

In preparation for performing a chemometric assessment of Oakland Bay/Shelton Harbor sediment dioxin/furan congener data, the usability of available and relevant site data were evaluated (Appendix A). Data evaluation required identifying all sample locations within Oakland Bay and the surrounding watershed that include dioxin/furan results. Samples collected within and in proximity to Goose Lake were also included, as the lake, an adjacent landfill, and nearby disposal lagoons received spent sulfite liquor and solid waste from the Rayonier Mill at Shelton Harbor (GeoEngineers 2012). Dioxin/furan congener data from seven individual data sets were identified for the region:

- Simpson Lumber Anti-degradation Evaluation and Upland Disposal Evaluation of Dioxins (DMMP 2012);
- Budd Inlet and Oakland By Dioxin Study (PSAMP 2011);
- Dioxin in Surface Water Sources to Oakland Bay (Ecology 2013);
- Shelton WWTP Outfall Baseline Sediment Monitoring Study (City of Shelton 2010);
- Oakland Bay Sediment Characterization Study (Herrera 2010);
- Goose Lake Remedial Investigation (GeoEngineers 2012); and
- Simpson Timber Company Dioxin Study (CH2M Hill 1987).

When available, data collected for the above studies were obtained from Ecology's Environmental Information Management (EIM) database. If not available in EIM, data were obtained directly from original project data reports (see Appendix A).

Dioxin/furan data from all of the above studies are used for one of two purposes in the chemometric process:

1. Multivariate dioxin/furan congener "un-mixing" (*Unmixing Data Set*), or
2. Comparison profiles in a source library (*Comparison Data Set*).

3.1.1 Unmixing Data Set

The process of multivariate chemical unmixing is described in Section 3.2. This process is ultimately used to determine the number of unique dioxin/furan factors that contribute to Oakland Bay sediments and the chemical profiles of those factors. The data used for these means consist of only intertidal and subtidal sediment samples of Oakland Bay, both surface and subsurface. This compiled *Unmixing Data Set*, including reported dioxin/furan congener concentrations and calculated total TEQs, is presented in Appendix B.

Table 2 lists the studies identified in Section 3.1 that contribute to the *Unmixing Data Set* as well as the number of surface and subsurface sediment samples involved. While surface sediment data generally consisted of the 0-10 cm interval, those that are from the 0-2 cm, 2-10 cm, and 0-1 foot intervals were all classified as surface sediments for interpretation purposes. The complete *Unmixing Data Set* consists of 67 surface and 14 subsurface sediment samples (Table 2). These sediment data were compiled into a project database with a single coordinate system and consistent concentration units. Screening of this data set is discussed in Section 3.2.1.

3.1.2 Comparison Data Set

Many samples from the studies identified in Section 3.1 were not included in the *Unmixing Data Set* because they do not meet the requirement of being Oakland Bay intertidal or subtidal sediments. However, these samples may be informative as potential source profiles and were therefore retained as a part of the *Comparison Data Set*. These samples consist of:

- Goose Lake Site sediments and soils collected from the lake, a drainage ravine, an inactive landfill adjacent to the lake, and former disposal lagoons (GeoEngineers 2012);
- Sediment samples collected from Oakland Bay tributary streams (Ecology 2013);
- Ash samples collected from the bank of Shelton Creek (Ecology 2013); and
- Boiler emission and ash samples from Simpson, sludge from the City of Shelton landfill, and upland residential soils (CH2M Hill 1987).

Dioxin/furan results for these samples were added to NewFields' existing library of congener profiles previously used for dioxin/furan profile comparison for sediments of Port Angeles Harbor (NewFields 2013). The library consists of dioxin/furan congener profiles from a wide range of potential source materials, industrial samples, and environmental samples. Comparison of Oakland Bay chemometric-derived dioxin/furan factor profiles to those of the *Comparison Data Set* are discussed in Section 4.3.

3.2 Chemometric Analysis

Many sources of dioxins/furans may contribute to measured concentrations in environmental samples. In general, each sample can be assumed to reflect the combined contributions from a number of unique dioxin/furan factors. Therefore, a one-to-one match of an environmental sample to a known dioxin/furan profile from a single source should not be expected. An understanding of the sources that account for measured environmental concentrations of dioxins/furans requires a decomposition, or "unmixing," of the bulk measured concentrations.

Chemometrics is the application of mathematical and statistical methods to chemical measurements. Multivariate analysis techniques were applied to the measured concentrations of seventeen 2,3,7,8-substituted dioxin/furan congeners in Oakland Bay sediments to develop an "unmixing" model for the data set. The chemometric evaluations included two equally important parts:

- The mathematical decomposition of sample dioxin/furan measurements into their components (“unmixing”); and
- Interpretation of the factors identified by the unmixing analysis.

It is notable that in the first part, development of the chemometric model, the data are treated purely as numbers stripped of all other attributes. No information on sampling locations, sediment characteristics (e.g., grain size or total organic carbon), proximity to discharge points or upland facilities, or other sample or site characteristics influence the mathematical solution to the unmixing model. All of the non-numerical attributes of samples, however, are considered in the interpretation of the results of the mathematical analyses. Those interpretations also consider the similarity of modeled factor profiles to the profiles documented for known source types. The consistency of the chemometric decomposition of the data set with the known characteristics of the samples and study area features is one important measure of the validity of data interpretations.

A summarized description of the chemometric analysis methods are provided in this section. Additional details are found in Appendix C.

3.2.1 Data Screening

The cumulative Oakland Bay *Unmixing Data Set*, as identified in Section 3.1.1, included 81 samples with results for 17 dioxin/furan congeners. Chemometric analyses use the patterns across samples in the profiles of these 17 congeners. Where samples have numerous undetected results among the 17 congeners, these dioxin/furan profiles become less well defined. The frequency of undetected results varied across the data set, becoming more pronounced for samples with very low total TEQ values. Samples from the *Unmixing Data Set* were screened from further chemometric analysis based on the following criteria:

- More the 3 non-detected congeners; or

- Non-detected congeners contributing to more than 2 percent of the total dioxin/furan TEQ concentration, when non-detected congeners are assigned a value of one-half the detection limit.

This screening resulted in a reduction from 81 to 77 samples. Of the 4 samples excluded in this manner, none had a dioxin/furan TEQ value greater than 2 ng/kg.

Further data exploration and modeling (see Appendix C, Section 3.2) revealed one sample (SH-10-SS) with a somewhat atypical profile, driven by the unusually high contribution from furan congeners. Relatively high model residuals associated with this sample compared to the remaining *Unmixing Data Set* indicated this sample as an outlier whose composition cannot be well-predicted by the modeling framework. As a result, this sample was screened from further analysis. Unlike the low TEQ samples screened because of non-detected congeners, sample SH-10-SS has moderate TEQ value of 35 ng/kg. Screening of this sample from analysis results in a final *Unmixing Data Set* consisting of 76 sediment samples.

3.2.2 Data Scaling

Evaluation of Potential Scaling Methods

Dioxin/furan sample results were reported from the lab as bulk congener concentrations, in nanograms per kilogram (ng/kg) dry weight. It was typical for certain congeners, such as OCDD, to be present at concentrations multiple orders of magnitude greater than other congeners. If multivariate analysis were to be performed on this raw concentration data in which the measurements vary by such large amounts, those compounds with the greatest concentration would drive the analysis. To allow interpretation of the differences in congener fingerprints, it is customary to scale the variables such that they are all roughly in the same order of magnitude.

There are several approaches to accomplish variable scaling; however different methods may not produce equivalent results. In most chemometric studies in which the measurements are discrete and not continuous, each measurement is scaled by either the range or standard deviation of the measure across all samples (Wold et al. 1987; Kramer 1998; Craig et al. 2006). These scaling methods are generally referred to as variance-scaling. The result is that each scaled variable will either have a range of 0 to 1 or a variance of 1. These variance-scaling methods have three major drawbacks:

1. The scaling factor is a function of the samples that are included in the calculation and would therefore change if different samples were included.
2. There is a risk that a variable of little importance with intensities in the noise level will be magnified to the same importance as variables with real, diagnostic signals.
3. Because the scaling factors are specific to the data set being scaled, the resulting congener profiles cannot be directly compared to profiles outside of the data set, such as a profile library.

Because of these variance-scaling shortcomings, the alternative method of TEF-scaling for dioxin/furan congener data has frequently been applied (Lohmann and Jones 1998; Alcock et al. 2002; Hilscherova et al. 2003; E & E and Glass 2011; NewFields 2013). This method of scaling based on congener toxicity relative to 2,3,7,8-TCDD has three distinct advantages over variance-scaling:

1. Scaling factors (congener-specific TEFs) are independent of the samples in the data set being processed.
2. Because the scaling factors can be applied universally to dioxin/furan congener data, analysis results can be compared to profile libraries scaled by the same means.
3. Chemometric analysis of TEF-scaled data identifies dioxin/furan profiles that contribute to a significant portion of sample TEQ. This is useful for decision making, as human health risk, ecological risk, and cleanup criteria are all based on TEQ.

For data exploration purposes, both variance-scaling and TEF-scaling methods were independently applied to the *Unmixing Data Set* and the full chemometric process was performed. Results for both scaling methods are presented in Appendix C. Chemometric analyses based on variance-scaling did not result in a more informative unmixing model than results performed by TEF-scaling (see Appendix C, Section 3.0). For this reason, as well as the advantages of TEF-scaling discussed above, only the evaluations using TEF-scaled data are discussed herein.

Applied Scaling Methods

Bulk dioxin/furan congener concentrations of samples in the *Unmixing Data Set* were scaled for relative toxicity using the current set of TEF values (Table 1). The order of presentation of the congeners does not impact the data analysis; however, the order customarily used in studies of this type - increasing chlorination and increasing substitution position - was imposed and is that shown in Table 1 from top to bottom.

These TEF-scaled values were summed to obtain total TEQ concentrations. Because chemometric analyses are concerned with the patterns of dioxins/furans rather than the TEQ magnitudes across samples, the 17-congener profiles for samples were normalized by dividing each congener component by the sample total TEQ. The resulting values represent the fractional contribution to total sample TEQ from each congener, with the sum over 17 congeners equal to 1 for each individual sample in the data set. These TEF-scaled and TEQ-normalized profiles serve as the input data set for the chemometric unmixing model.

3.2.3 Unmixing Model

The software Pirouette (Infometrix, Bothell, WA) was used for the application of chemometric modeling. The mathematical model of the *Unmixing Data Set* produces the following component results:

- The number of significant factors contributing to the sample measurements;
- The chemical patterns of model factors (dioxin/furan TEQ profiles);
- The fractional contribution of each model factor to each sample total TEQ; and
- A characterization of the model’s goodness-of-fit through residuals (congener-by-congener differences between modeled and measured values for every sample) and deviations of summed factor fractional contributions from 1 (non-closure deviations; see below).

Chemometric analyses are a form of receptor-oriented modeling. Starting from the receptor (sediment) measurements, and without any prior assumptions about the number or patterns of potential factors, the analyses mathematically derive a model of the factors – conceptually “working backwards” from receptors to sources. There are several similar mathematical approaches used for unmixing evaluations. In this study, a combination of Principal Component Analysis (PCA) and Alternating Least Squares (ALS) methods was used.

Principal Component Analysis

With 17 TEF-scaled dioxin/furan congeners defining the chemical patterns in the sample profiles, each sample can be visualized or mapped as a point in a 17-dimensional space. Samples with similar TEQ profiles would be located near one another in that 17-dimensional space. PCA attempts to reduce the number of dimensions required to map the data, while accounting for almost all of the variability in the data set. PCA factors, each representing some combination of the congeners, are determined with each added factor accounting for successively less of the overall variance.

The number of PCA factors required to account for nearly all of the data set variance is an indication of the number of factors to be included in the unmixing model. Diagnostic criteria can be used to evaluate the number of PCA factors, and models with different numbers of factors can be explored when the difference in total variance accounted for is small. It should be noted that the PCA factors or axes do not themselves define source profiles. Instead, visualization of PCA results can help guide an interpretation such as identifying clusters of similar samples, outliers that do not cluster with other samples, or samples located intermediate between others (implying they might be mixtures).

Alternating Least Squares

Mixture analysis algorithms are designed to extract the patterns from which sample mixtures are composed. For this study an ALS method was used for the unmixing analysis. The ALS method assumes the data set reflects the variable contributions from a fixed number of factors. Therefore, the measured values are assumed to be the product of the chemical patterns for the factors and the fraction contributed from each factor to each sample. This product is calculated iteratively using matrix algebra, with one matrix of factor profiles and a second matrix of factor contributions to samples. Starting values are assigned to both matrices to begin the calculations. As the iteration proceeds, constraints are applied; for example, one constraint is that no negative contributions from factors are allowed, because negative contributions lack physical meaning. When the iterative calculations converge, the unmixing model is complete. The solution provided consists of the chemical profiles of factors and their contributions to each sample (i.e., sample composition). The residuals of the resulting model illustrate the goodness-of-fit.

The ALS analysis was run in non-closure mode, in which the sum of the factor fractions was not constrained to equal 1. Constraining the factor fraction sum to 1 (closure mode) forces all sediment sample profiles to be composed only of the factors being considered (100 percent factor contribution). In non-closure mode, factors do not necessarily have to account for all variation in a sediment sample’s profile. This is appropriate when it cannot be assumed or demonstrated that the model includes all possible factors contributing to the measurements. Deviations from 1 that are generally small are another indication of model goodness-of-fit.

The factor fractional contributions in the model are relative measures of the sample compositions. Interpretations of the unmixing model results benefit from absolute measures of the impacts of individual factors. The contributions of individual factors to total sample TEQ are obtained by multiplying the factor fractional contributions by the total TEQ for the sample. The results are termed factor “TEQ increments.” The sum of those model TEQ increments will differ from the measured sample TEQ to the degree that the sum of factor fractional contributions differs from 1 (non-closure analysis approach).

3.2.4 Model Interpretation

A library of comparison dioxin/furan profiles was compiled to support possible interpretations of the factor profiles obtained through chemometric modeling. The “source library” included over 300 candidate profiles compiled from published literature, regional environmental samples, and site-specific studies. Examples of source types present in the source library include air emissions, effluent discharges, ash, and various chemicals known to include dioxins/furans from their manufacture. Also part of the source library was the *Comparison Data Set,* composed of samples relevant to the study area, but not included in the *Unmixing Data Set* (see Section 3.1.2).

Comparisons of factor profiles from the ALS model to those in the compiled source library were made by two means:

1. Hierarchical Cluster Analysis (HCA); and
2. Tabulation of correlation coefficients.

As the name implies, HCA is a method of evaluating similarity by organizing data into a hierarchy of clusters. The results of HCA are best represented graphically by a dendrogram, or similarity tree. This manner of representation displays highly similar sample pairs with relatively small separation distances. As applied to this study, HCA was used to identify library profiles with high similarity to the ALS-derived factor profiles.

A correlation coefficient can be calculated for sample pairs as a measure of the strength and direction of their relationship. Correlation between two samples can be either positive or negative, with perfect positive correlation having a value of +1. Correlation analyses were performed for ALS-derived profiles against the entire source library.

These two approaches for interpreting chemical patterns are complementary and provide candidate source types for further evaluation based on the known history of Oakland Bay and the likely presence of actual sources or facilities matching the candidates. It should be noted that the matching of factor and source profiles does not in and of itself identify any specific physical source. Multiple sources with the very similar dioxin/furan profiles can exist, which have to be discriminated based on other factors than just chemical pattern.

3.2.5 Uncertainties

Chemometric pattern evaluations are subject to various sources of uncertainty, as is common to all modeling efforts. As previously noted, one common source of uncertainty, chemical patterns compromised by frequent not-detected results, was partially addressed during data screening. Some additional recognized potential sources of uncertainty are:

- Laboratory analytical issues, such as co-elution of congeners, that affect reported profiles;
- An incomplete source inventory, missing comparison source profiles that are relevant to study profiles;
- Non-representativeness of source inventory profiles from literature reports or other locations for the site-specific sources of similar type;
- Variability in source profiles over time (e.g., because of changes in facility operations, processes, or pollution control systems);
- Changes in profiles between emission sources and receptor media (e.g., sediments) due to differential fate and transport processes and weathering effects; and
- Highly-correlated impacts from multiple sources that produce composite profiles, affecting comparisons to single source profiles from a source library.

For any study, the overall uncertainty associated with chemical pattern evaluations should be assessed in light of identified potential uncertainty factors. The consistency and strength of data interpretations from multiple lines of evidence should also be assessed.

3.3 Spatial Interpolation and Analysis

Spatial interpolation is the process of approximating data in unsampled locations by using known values at discrete locations. Results of the unmixing analysis (factor TEQ increments) were used to create interpolated surfaces utilizing the geostatistical toolsets of ESRI ArcGIS version 10. A spline interpolation method was used to model local spatial variation and determine the TEQ increment at unsampled locations. The aim of this method is to build a model that describes the major spatial features of the data set by fitting a polynomial between each pair of locations. The resulting data products are surfaces of dioxin/furan factor TEQ increments across the extent of Oakland Bay. These surfaces can be utilized to determine general spatial patterns and help infer underlying processes contributing to those patterns.

Spatial interpolation could not be applied to the entirety of the model results presented herein. Although both surface and subsurface sediments were used in unmixing analysis to identify dioxin/furan congener factor profiles, data interpolation and analysis of spatial patterns was restricted to surface sediment results. Both the limited spatial coverage and varying depth intervals of subsurface dioxin/furan congener data prevent the interpolation of subsurface TEQ increments throughout the study area.

In addition to interpreting spatial pattern, interpolated TEQ increment surfaces were used to determine the fractional contribution of each factor to total TEQ bay-wide. While the fractional contribution of each factor to all samples is informative, performing similar analysis on interpolated surfaces removes sampling bias caused by differences in sample density. When considering sample statistics instead of spatial models, sampling bias causes the dominant factors in densely sampled areas to appear to have a greater contribution to total TEQ bay-wide, while dominant factors in more sparsely sampled areas are under-represented.

4.0 Results

The results of chemometric unmixing analyses are summarized in this section, with additional details provided in Appendix C. The interpretation of both 3 and 2 factor model results are provided as well as justification for the final model chosen. Results for the final model are discussed in further detail, including the factor profiles, factor fractional contributions, and factor TEQ increments. The factor TEQ increments, which provide a decomposition of measured total TEQ for the sediment samples, are further summarized in terms of their comparative magnitudes and spatial patterns.

4.1 Data Exploration

After data set screening, 76 sediment samples were retained in the *Unmixing Data Set* for further chemometric evaluation. Figure 5 is a histogram of the TEQ values showing a log-normal data distribution, typical of chemical concentration data collected for a site investigation (EPA 1997). A similar log-normal data distribution was observed for sediment dioxin/furan data used in Ecology's chemometric evaluation of Port Angeles Harbor (NewFields 2013). The Oakland Bay samples have a range in dioxin/furan TEQ from 0.63 ng/kg to 900 ng/kg, with an average value of 56 ng/kg. A noticeable difference between the Oakland Bay and Port Angeles Harbor data sets is the overall higher magnitude of Oakland Bay TEQ values, with Port Angeles Harbor sediment having mean and maximum TEQs of 13 ng/kg and 120 ng/kg, respectively.

Dioxin/furan profiles of the *Unmixing Data Set* are displayed in Figure 6. The bulk congener data in these profiles have been both TEF-scaled and TEQ-normalized (see Section 3.2.1) such that each profile shows the factional contribution of each congener to that sample's total TEQ. While there are some broad consistencies among the profiles, such as the negligible TEQ contributions of multiple furan congeners, variation in the profiles are obvious for congeners with significant TEQ contributions. The most apparent variations across the data set are for TEQ contributions of the dioxin congeners 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8-HpCDD.

The information provided by PCA is helpful for determining the number of factors to consider in the chemometric unmixing model. PCA was used to re-orient the data for the 17 congener variables into factors. These factors are ranked by how much information from the input data they describe, with each subsequent factor describing less information than the previous factor. The first factor axis is oriented in the direction of maximum spread in the data. After removing the effect of this first factor, a second orthogonal factor is created in the next direction of maximum spread. This process is repeated until a whole new set of axes is defined.

Figure 7 displays the amount of cumulative data set variance that can be explained by the PCA-derived factors. The number of PCA factors required to account for nearly all of the data set variance is an indication of the number of factors to be included in the unmixing model. Generally, once 98 to 99 percent of the variability is explained, there is no need to evaluate additional factors.

In Figure 7, PCA results for three different dioxin/furan data sets are shown to provide context: Oakland Bay, Budd Inlet (NewFields 2014), and Port Angeles Harbor (NewFields 2013). Factor 1 explains nearly 96 percent of the variance of the Oakland Bay *Unmixing Data Set*. Additional factors are needed for both the Budd Inlet and Port Angeles Harbor data sets to explain a similar amount of variance. This is an indication that fewer distinct dioxin/furan factors may be required to explain the mixtures present in Oakland Bay sediments compared to those of Budd Inlet and Port Angeles Harbor.

Four different dioxin/furan factors were ultimately required to explain Port Angeles Harbor sediment mixture, with these four factors explaining 98 percent of the data variability (NewFields 2013). Comparatively, explaining 98 percent of the Oakland Bay *Unmixing Data Set* variability is accomplished by only two factors (Figure 7). Consideration of a third factor is only able to account for an additional 0.5 percent of the data set variability. This analysis demonstrates that:

- The Oakland Bay *Unmixing Data Set* is less variable than either the Budd Inlet or Port Angeles Harbor dioxin/furan chemometric data sets; and
- Only two factors may be needed to understand the comparatively simple mixture dioxins/furans present in Oakland Bay sediments.

4.2 Chemometrics

Based on the PCA results, cross-validation diagnostic criteria, and further examination of sample residuals for normalized TEQ profiles in the ALS unmixing analysis, an initial model based on 3 factors was developed. The results for the 3-factor model are summarized in Section 4.2.1 below. After examining these results, a second model based on only 2 factors was developed. The reasons for considering a second unmixing model using only 2 factors are discussed in Section 4.2.2, and those results are summarized as well. The two unmixing models are compared in Section 4.2.3. After reviewing these unmixing results, the 2-factor model was selected as the primary model for further evaluations. Results of only the 2-factor model are addressed regarding library comparisons (Section 4.3), interpretation of factor magnitudes (Section 4.4), spatial patterns for factor TEQ increments (Section 4.5), and the interpretations of model results (Section 5.0).

4.2.1 3-Factor Model

The normalized TEQ profiles for 3 factors are shown as line plots, with separate panels for each factor profile, in Figure 8a. Numerical values for these factor profiles are provided in Appendix C, Table 2. For all of the 3 profiles, the dioxin congeners are dominant, accounting for between 61 and 81 percent of the TEQ. Factor 2 has the greatest furan contribution to TEQ (39 percent).

Although the 3 factor profiles are unique, Factor 2 and Factor 3 have distinct similarities and differ greatly from Factor 1 (Figure 8a). The TEQ profiles of both Factors 2 and 3 are dominated by 1,2,3,4,6,7,8-HpCDD, constituting 32 and 35 percent of the profiles, respectively. The Factor 1 profile is composed of 6 percent of this dioxin congener, instead being dominated by 34 percent 1,2,3,7,8-PeCDD. The profile of Factor 1 is composed of lower molecular weight dioxins/furan, consisting of 92 percent tetra-, penta-, and hexa-substituted congeners. In contrast, profiles of both Factors 2 and 3 consist of 57 and 58 percent, respectively, of the heavier hepta- and octa-substituted congeners.

The fractional contributions of each factor to each of the 76 samples included after data screening are listed as numerical values in Appendix C. Some of the factor fractional contributions are zero, as not every model factor is found to contribute to every sample. Samples are shown, however, to be composed of varying contributions from multiple factors. The sum of the fractional contributions is not equal to 1 because the unmixing model was run without a closure constraint. Only 4 of the 76 samples (5.3 percent) have summed factor fractions differing from 1 by more than 5 percent. This result, as well as examination of the residuals for sample profiles, indicates good model fit to the original data set.

The factor TEQ increments calculated from the factor fractions and sample measured TEQs are listed in Table 3. The sum of factor TEQ increments does not equal the sample measured TEQ because the model was run without a closure constraint on factor fractions. Note that where the sample TEQ is relatively small, even the higher deviations from 1 for the sum of factor fractions may result in only small differences between measured and modeled sample TEQs. Conversely, relatively small differences for factor fractions may result in larger differences in sample TEQs when total TEQs are higher. Of the 76 samples included in the model, only 4 have differences in TEQ of more than 2 ng TEQ/kg. Thus, the 3-factor model produces total TEQ values within 2 ng TEQ/kg for more than 94 percent of the 76 sediment samples.

4.2.2 2-Factor Model

A detailed review of the results of the 3-factor model shows that two of the factor profiles have a substantial degree of commonality, even though there are some differences in the ranking of congener contributions. The ALS unmixing model was therefore repeated for a 2-factor model. The normalized TEQ profiles for the 2 factors are shown as line plots in Figure 8b. Numerical values for the two factor profiles are provided in Appendix C, Table 3. As was the case for the 3-factor model, the 2-factor profiles are dominated by dioxin congeners, accounting for between 76 and 68 percent of the TEQ for Factor 1 and Factor 2, respectively.

The factor fractions for the 2-factor model are listed as numerical values in Appendix C. Unlike the 3-factor model, only a single sample has a factor fraction of zero; sample SH-10-SC_2-3ft (the sample with the greatest TEQ of the data set) is composed entirely of Factor 2. Five of the 76 samples (6.6 percent) have summed factor fractions differing from 1 by more than 5 percent, only one sample more than the 3-factor model. With fewer factors, this model has somewhat higher residuals than the 3-factor model, but overall model fit is still judged to be good.

The factor TEQ increments calculated from the factor fractions and sample measured TEQs are listed in Table 4. Of the 76 samples included in the model, eight have differences in TEQ of more than 2 ng TEQ/kg. Thus, the 2-factor model still produces total TEQ values within 2 ng TEQ/kg for almost 90 percent of the 76 sediment samples.

4.2.3 Comparison of 3 and 2-Factor Models

While some differences in factor profiles and factor fractions can be identified between the two unmixing models, a comparative evaluation indicates that these differences are relatively small. The two unmixing models lead to results that are not markedly different with respect to factor profiles and spatial patterns of factor contributions.

As discussed above, both Factors 2 and 3 of the 3-factor model had the largest contribution from 1,2,3,4,6,7,8-HpCDD, with moderately elevated contributions from the same dioxin congeners (Figure 8a). Factors 2 and 3 of the 3-factor model differed mostly in relative contributions from furan congeners. While Factor 2 has a more substantial contribution from furans, the specific furan congeners most prevalent in Factors 2 and 3 are the same. The similarity of these two profiles is apparent when analyzed by HCA, with Factors 2 and 3 clustering closely and having a similarity of almost 95 percent (see Appendix C, Figure 12).

When the spatial patterns of TEQ increments were examined for the 3-factor model, Factors 2 and 3 showed a strong consistency and correlation in spatial pattern. One possibility raised by these similarities in factor profiles and spatial patterns of TEQ increments was the occurrence of subtle variations in the source over time or variations in degradation processes that slightly affected TEQ profiles after release.

The Factor 1 profiles of both the 2-factor and 3-factor models are essentially identical (Figure 8a,b). This results in Factor 2 of the 2-factor model having a profile that is a hybrid of Factors 2 and 3 of the 3-factor model. As discussed in Section 4.1, consideration of only two factors accounts for 98.6 percent of the *Unmixing Data Set* variability, and extending this to include a third factor only explains an additional 0.5 percent of the variability. These findings support the use of the 2-factor model as being most appropriate for the data set, with interpretation of a third dioxin/furan factor unnecessary and not supported by the variability of dioxin/furan patterns observed in Oakland Bay sediments. Therefore only the 2-factor model was used as the basis for all further evaluations.

4.3 Library Comparison

Factor profiles identified by the 2-factor model were compared to the source library using the two methods described in Section 3.2.4. Profile comparisons using HCA allow the analysis of sample clustering, along with a quantitative metric of profile similarity. Correlation analysis results in the calculation of a correlation coefficient (r-value) that is also a quantitative measure of profile similarity. Profiles from the 2-factor model were considered to significantly “match” that of a source library profile when either the HCA similarity metric or correlation coefficient were greater than or equal to 0.95. HCA dendrograms and a profile correlation with the source library are included in Appendix C. Matches to the 2-factor model profiles are summarized in Table 5.

4.3.1 Factor 1 Comparison

Dioxin/furan profiles of the source library that best match Factor 1 are all related to HFB sources, both emissions and ash. The best-matched library samples and associated references are provided in Table 5. These matches include:

- A soil sample from Shelton’s City Landfill, likely containing HFB ash;
- Port Angeles Harbor’s dioxin/furan Factor 4, derived from HFB sources;
- Emissions from Canadian HFBs;
- Ash from Rayonier’s Port Angeles HFB; and

- Multiple samples from the Goose Lake site.

Figure 9a presents a selection of these library profiles along with that of Factor 1. All profiles in this figure share the same most prominent congeners, including 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF as the dioxin and furan congeners that contribute most to TEQ.

4.3.2 Factor 2 Comparison

Dioxin/furan profiles of the source library that best match Factor 2 are all related to PCP sources. The best-matched library samples and associated references are provided in Table 5. These matches include:

- Chemical-grade PCP;
- Port Angeles Harbor’s dioxin/furan Factor 3, derived from PCP sources;
- PCP used as a wood preservative; and
- Multiple samples from the Goose Lake site.

Figure 9b presents a selection of these library profiles along with that of Factor 2. All profiles in this figure share 1,2,3,4,7,8-HpCDD and 1,2,3,4,7,8-HxCDD as the most prominent dioxin congeners, with little contribution from other dioxins. The Goose Lake landfill soil sample shown in Figure 9b has a greater relative TEQ contribution from 2,3,7,8-TCDD and OCDD than the others, suggesting that the sample may contain other sources. Two furans are prevalent in the Factor 2 profile, 1,2,3,4,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF. While the latter is a consistently moderate component to the library profiles displayed, the former is quite variable among the library profiles.

4.4 Factor Increment Magnitudes

The magnitude of dioxins/furans in Oakland Bay sediment samples can be determined by the calculated TEQ increments for each factor based on the 2-factor model. Figure 10 provides box-and-whisker plots for the numerical distributions of surface and subsurface sediment sample TEQ increments for each of the 2 factors. These box-and-whisker plots are accompanied by histograms for each factor.

By inspection of Figure 10 and associated tabulated values by sample (Table 4), it is apparent that Factor 1 and 2 contributions to surface sediment are approximately equal, with similar means and distributions. Factor 2 has a slightly greater contribution to surface samples, having the greater factor increment in 58 percent of samples.

Overall subsurface sediment samples have higher TEQ increment concentrations of both Factors 1 and 2 compared to surface sediments (Figure 10). Subsurface sediments have especially high concentrations of Factor 2, with more than half of subsurface samples having a Factor 2 increment greater than 50 ng TEQ/kg. Factor 2 is the dominant TEQ increment in 64 percent of subsurface sediment samples.

While the preceding discussion of factor increment magnitudes identifies Factors 2 as having dominant factor increments in both surface and subsurface sediment samples, spatial modeling is required to quantitatively determine the fractional contribution of each factor increment to total

TEQ bay-wide. Spatial modeling accounts for sampling bias caused by differences in sample density. For example, despite the greatest number of sediment samples having Factor 2 as their maximum TEQ increment, Factor 2 may not be the dominant factor to bay-wide total TEQ if samples high in Factor 2 were mostly located in a relatively small region. Considering the spatial extent of Oakland Bay shown in Figure 13, modeling results indicate that Factors 2 contributes slightly more to the bay-wide surface sediment dioxin/furan concentrations than Factor 1, comprising 52 percent of the total TEQ.

4.5 Factor Increment Spatial Patterns

The unmixing analysis of the Oakland Bay sediment data supports a more focused and useful evaluation of spatial patterns than an analysis based on total TEQ results (Section 2.3). The contribution to each sample from individual factors (factor increments) identified by the unmixing modeling can be spatially displayed to aid in the identification of patterns. Spatial interpretation of the TEQ increments from individual factors illustrates the relative scale of impact of the separate factors and thereby provides more detailed information than that of total TEQs before unmixing (Figure 4).

Surface and subsurface sediment TEQ increments for the individual factors derived from the 2-factor unmixing model are presented independently in Figures 11 and 12. The surface sediment TEQ increment data displayed in Figures 11 and 12 are also presented as interpolated surfaces in Figure 13. For all of these figures TEQ increments are shown using the same scale among the two factors such that the relative magnitude of factors can be visually compared.

Sediment samples collected for the PSAMP (2011) study consisted of both the 0-2 cm and 2-10 cm intervals for the 10 locations sampled. Although both of these intervals were considered surface sediments in the *Unmixing Data Set*, only the interval with the greater total TEQ increment concentration is displayed in Figures 11 and 12.

4.5.1 Factor 1 Pattern

The extent of Factor 1 across Oakland Bay consists of spatially distinct high TEQ increment areas in Shelton Harbor, areas of relatively low TEQ increments in regions of coarse-grained sediment, and moderate TEQ increments throughout much of greater Oakland Bay (Figure 11 and 13a). Five of the seven surface sediment samples with the highest Factor 1 TEQ increments (30 – 61 ng/kg) are all closely clustered in the southwest corner of southern Shelton Harbor in the vicinity of the former Rayonier pulp mill and Simpson’s former seven-boiler power plant and sawmill #4. Two of the seven locations with the highest Factor 1 TEQ increments (30 and 34 ng/kg) are found in northern Shelton Harbor near the outflow of Shelton Creek. These two regions in southern and northern Shelton Harbor are spatially distinct areas containing sample clusters with the greatest Factor 1 TEQ increments. These clusters likely define localized depositional areas, as sediments in these location are finer-grained than those of surrounding samples.

The lowest Factor 1 TEQ increments in the harbor are all associated with areas where coarse-grained sediments are found. All surface sediment samples with Factor 1 TEQ increments less than 4 ng/kg are located either within intertidal channels of Goldsborough Creek and Shelton Creek, the deltas of these creeks, or the junction between Oakland Bay and Hammersley Inlet. While the deltas are depositional zones for coarse-grained sediments, strong flow near the bed of

Hammersley Inlet generally prevents sediment deposition at the Oakland Bay/Hammersley Inlet junction.

Surface sediment samples east of the Oakland Bay/Hammersley Inlet Junction have Factor 1 TEQ increments ranging from 5 to 26 ng/kg, with an average of 18 ng/kg. In this region, the magnitude of the Factor 1 TEQ increment is correlated with grainsize. Coarser-grained sediments of the creek deltas have lower Factor 1 TEQ increments than those of finer-grained sediments of the deeper bay. Implications of this grainsize correlation are further discussed in Section 5.

4.5.2 Factor 2 Pattern

The Factor 2 spatial pattern (Figures 12 and 13b) exhibits much of the same structure as that of Factor 1. As with Factor 1, Factor 2 TEQ increments less than 4 ng/kg are restricted to intertidal channels of Goldsborough Creek and Shelton Creek, the deltas of these creeks, and the junction between Oakland Bay and Hammersley Inlet. Also, sediment east of the Oakland Bay/Hammersley Inlet junction have a similar Factor 2 TEQ increment range (4 to 30 ng/kg) and mean (20 ng/kg) as those determined for Factor 1.

The samples with the highest Factor 2 TEQ increments fall within the same spatial clusters as those with the highest Factor 1 TEQ increments. As was noted for Factor 1, the locations with the greatest Factor 2 TEQ increment are found in the southwest corner of southern Shelton Harbor and near the outlet of Shelton Creek.

Two very localized regions of Shelton Harbor exist where the surface sediments are generally enriched in Factor 2 relative to Factor 1. The first is the former Simpson saw pond located in the northwestern-most corner of northern Shelton Harbor. The second is a small area of southern Shelton Harbor immediately adjacent to an outfall from the former Rayonier pulp mill and an outfall from the former Rayonier Research Laboratory. A more complete discussion of relative factor contributions is presented in Section 5.2.

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5.0 Discussion

In this section each of the two factors to Oakland Bay sediments identified through unmixing analysis are discussed. First, the distinctive chemical profiles of the identified dioxin factors are discussed, including evaluation of dioxin-containing materials with analogous profiles. Spatial patterns of the factor are then described in relation to likely sediment transport pathways driving these patterns. Finally, comprehensive interpretations of the factors are presented, incorporating supplementary information regarding the history of upland industrial activities and locations of potential point sources.

5.1 Dioxin/Furan Factor Profiles

Chemometric evaluation identified two distinct dioxin/furan congener factor profiles that account for the vast majority of profile variability observed in both surface and subsurface sediment of Oakland Bay. These two factors profiles match well with source library profiles, upland samples collected within the Oakland Bay watershed, and the results of a similar chemometric study of Port Angeles Harbor sediment.

5.1.1 Factor 1

The Factor 1 TEQ profile has the largest contribution from one dioxin congener, 1,2,3,7,8-PeCDD (31 percent), with a “hump” of additional moderate contributions from several higher chlorinated dioxin congeners (Figure 8b). The furan congener 2,3,7,8-TCDF accounts for most of the furan contribution to total TEQ. The pattern of dominant 1,2,3,7,8-PeCDD and 2,3,7,8-TCDF contribution was previously noted in the Port Angeles Harbor sediment dioxin/furan source study as being characteristic of HFB sources (NewFields 2013). In fact, Oakland Bay’s Factor 1 and the Port Angeles Harbor chemometric-determined HFB profile were found to be 98 percent similar (Table 5). Further comparison of the Factor 1 profile to the source library identified numerous HFB-related samples as having considerable similarity. Similar patterns were found in both air emissions and ash from burning salt-laden wood.

Particularly pertinent to potential dioxin/furan sources to Oakland Bay are the comparisons between Factor 1 and regional samples. A number of samples at Rayonier’s Goose Lake site have similar profiles to Factor 1 including:

- Sediment collected behind Dam #1 of the Goose Lake drainage ravine; and
- Subsurface soil from the former Goose Lake landfill.

Samples associated with Simpson also have high similarity to that of Factor 1. A soil sample from the City Landfill, accepting WWTP sludge and Simpson baghouse residues, was found to have the greatest similarity to Factor 1 of all the library profiles. This soil sample is of interest as it has a total dioxin/furan TEQ of 3900 ng/kg. Slightly less similarity (correlation coefficients between 0.8 – 0.9) was found between Factor 1 and:

- Two ash samples collect on the bank of Shelton Creek directly across from the Simpson property (Ecology 2013); and

- Ash collected from Simpson's low pressure baghouse (CH2M Hill 1987).

The high degree of similarity between the Factor 1 profile and a wide range of HFB-related profiles identify HFB sources as a major contributor to dioxins/furans in Oakland Bay sediments.

5.1.2 Factor 2

Overall the Factor 2 profile is composed of higher molecular weight dioxin and furan congeners than Factor 1. The Factor 2 TEQ profile has the largest contribution from one dioxin congener, 1,2,3,4,6,7,8-HpCDD (35 percent), with additional contributions of 13 and 11 percent from two additional dioxin congeners. Two furan congeners, 1,2,3,4,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF, account for the majority of furan contributions (Figure 8b). While this general pattern was previously noted in the Port Angeles Harbor sediment dioxin/furan source study as being characteristic of PCP sources (NewFields 2013), the relatively high contribution of 1,2,3,4,7,8-HxCDF was not evident in the Port Angeles Harbor sediment profile.

Comparison of the Factor 2 profile to that of the source library identified PCP-related samples as having the greatest similarity. Similar patterns to Factor 2 include a number of PCP formulations for wood preservation (both oil and water soluble forms). Among these similar profiles the congener with the greatest variability is 1,2,3,4,7,8-HxCDF, which is the same congener present in Oakland Bay's Factor 2 but absent from Port Angeles Harbor's sediment PCP profile. While the variable presence of this furan congener may be a diagnostic indicator for specific PCP source types, it may also just have inherent variability and should not be a distraction in comparative analysis.

5.2 Distribution of Factors in Sediments

Factors 1 and 2 have relatively similar contributions of 48 and 52 percent, respectively, to bay-wide TEQ. Additionally, the spatial patterns of Factor 1 and 2 are remarkably similar. These parallels include highest sediment concentrations within station clusters of Shelton Harbor, lowest concentration on the coarse-grained deltas and in the Oakland Bay/Hammersley Inlet junction, and moderate concentrations throughout greater Oakland Bay. Such commonalities in spatial patterns reflect common source regions and transport mechanisms for Factors 1 and 2, linking their depositional fates in Oakland Bay sediments.

5.2.1 Shelton Harbor

Both the highest and lowest surface sediment TEQ increment of Factors 1 and 2 are found at locations in Shelton Harbor (Figure 13a,b). This patchiness is because of the complex mix of both contaminant and sediment sources to the confines of the harbor, as well as harbor morphology driven by natural sediment transport processes and human modifications.

Since development of the region, municipal and industrial input of contaminants to the Oakland Bay system has been mostly localized to the shoreline of Shelton Harbor and WWTP outfalls. Due to concentration of potential dioxin/furan sources one would expect to find localized sediment hot-spots, especially in proximity to shoreline outfalls and within nearby fine-grained sediment depositional zones.

Goldsborough Creek is the dominant source of freshwater and sediment to the Oakland Bay system. The impact of Goldsborough Creek on the morphology of Shelton Harbor is apparent at low tidal stages when its vast intertidal delta is exposed (Figure 2). The delta is composed predominantly of coarse-grained sediment delivered to the harbor by the creek. At low tidal stages, fine-grained suspended sediment of the creek is expected to be transported beyond the eastern extent of the delta. At higher tidal stages, fine-grained sediments may deposit within the inner harbor, including relatively deep depositional pockets in the northwest and southwest corners of the harbor.

A combination of the above natural and anthropogenic factors has led to three localized hot-spots of Factors 1 and 2 within Shelton Harbor:

- Northwestern Shelton Harbor;
- Southwestern Shelton Harbor; and
- Goldsborough Creek Pro-delta.

Northwestern Shelton Harbor

The northwestern-most corner of Shelton Harbor served as a saw pond for Simpson and is immediately adjacent to Shelton Creek’s discharge point. Two sediment cores were analyzed within this region of the harbor: SH-04 (west of Shelton Creek within the Simpson saw pond) and SH-02 (east of Shelton Creek). Both Factors 1 and 2 are found in relatively high concentration in both surface and subsurface sediments of SH-04 (Figures 11 and 12), but with higher concentrations of both factors in the subsurface interval. Factor 2 is the dominant form of dioxins/furans in the surface interval at this location, but Factor 1 is the dominant form at depth. In contrast, both factors are found in higher concentrations in surface compared to subsurface sediments in core SH-02. Factor 1 is the dominant form of dioxins/furans in both depth intervals at this location.

Southwestern Shelton Harbor

The dioxin/furan hot-spot in the southwestern-most corner of Shelton Harbor is larger in spatial extent than that of the northwestern corner. Two sediment cores were analyzed within this region of the harbor: SH-12 (adjacent to the former Simpson power plant) and SH-13 (adjacent to the former Rayonier pulp mill). Similar to the core SH-04 in the northwestern corner of the harbor, core SH-12 has relatively high concentrations of Factors 1 and 2 in both surface and subsurface sediment intervals, with higher concentrations of both factors in deeper intervals (Figures 11 and 12). At this location, Factor 1 is the dominant form of dioxins/furans in all sediment intervals. In contrast, core SH-13 has higher concentrations of both factors in surface intervals, and all intervals are dominated by Factor 2.

Goldsborough Creek Pro-delta

The Goldsborough Creek pro-delta is the subtidal delta slope east of the intertidal delta. This type of deltaic feature generally experiences high rates of fine-grained sediment accumulation. Inspection of Factor 1 and 2 surface sediment TEQ increments in Figures 11, 12, and 13 do not indicate the pro-delta as a hot-spot for either factor. However, the subsurface sample collected at location SH-10 (2-3 feet) is unique in that it has the highest total TEQ (900 ng/kg) of all sediment samples of Oakland Bay and it is composed entirely of Factor 2.

Subsurface sediment at SH-10 suggests that the pro-delta was historically a depositional zone for pure PCP-like dioxin likely transported from upland sources. Because fine-grained sediment transported by Goldsborough Creek deposits at this deltaic feature, this PCP-like dioxin may have originated from industrial outfalls discharging directly to the creek. The lower TEQ of surface sediment of the pro-delta suggest the magnitude of this source may have greatly diminished in more recent times. Importantly, such a high TEQ sample being located distant from point sources provides evidence for a Factor 2 transport mechanism linking historic Shelton Harbor sources to greater Oakland Bay.

5.2.2 Greater Oakland Bay

While sediments are delivered to Oakland Bay by all tributary creeks, Goldsborough Creek provides two-thirds of the total sediment load (Herrera 2010). The fine-grained sediment fraction is dispersed throughout the bay in freshwater plumes and by tidal currents. The prevalence of broad mudflats that support productive shellfish habitat can be attributed to the dispersion of fine-grained sediments away from their sources and the protected nature of the bay that prevents the propagation of wind-waves. The conditions created allow virtually all sediment introduced to Oakland Bay to deposit with little likelihood to be exported from the system through Hammersley Inlet (Ecology 2004; Albertson 2004).

The broad distribution of predominantly fine-grained sediment across deep Oakland Bay suggests that this area, far from sediment sources, represents the depositional reservoir for many sources surrounding the bay (Figure 3). The modern deposition of fine-grained sediments in greater Oakland Bay is supported by acoustic tomography results of Herrera (2010), indicating the accumulation of a shallow sediment layer (generally between 1 and 3 feet) subsequent to urban development in the area.

The magnitude of both Factor 1 and 2 TEQ increments in surface sediments are strongly correlated with fine-grained content throughout greater Oakland Bay, but not in Shelton Harbor (Figure 14). Because Shelton Harbor contains likely point sources of Factor 1 and 2, locations in close proximity to upland sources are likely to have elevated TEQ increments regardless of grainsize. Therefore, proximity to source is an important factor for Shelton Harbor locations that prevents strong correlation with grainsize (Figure 14). The strong relationship between Factor 1 and 2 TEQ increments and grainsize through greater Oakland Bay indicates that sediment transport processes rather than proximity to source are the dominant factor affecting TEQ. Additionally, the consistency in this relationship for both Factor 1 and 2 indicates that they have similar locations of origin, likely Shelton Harbor, and are transported in the same manner prior to deposition in greater Oakland Bay.

Further evidence that dioxins/furans deposited in greater Oakland Bay are derived from a common source area is the small variability in congener profiles found here. In Figure 15a the contributions of Factors 1 and 2 to total dioxin/furan TEQ are shown as pie-charts for each surface sediment sampling location, with the size of the chart being proportional to total TEQ. In Figure 15b the Factor 1 fraction is plotted versus location longitude, providing a simplified representation of factor mixing from Shelton Harbor in the west to greater Oakland Bay in the east. These figures show that surface sediment factor compositions vary considerably within

Shelton Harbor, but those of greater Oakland Bay are consistently composed of between 40 to 65 percent Factor 1. On average, surface sediments of greater Oakland Bay are an exact 50/50 mixture of Factors 1 and 2. Subsurface sediment compositions are equally consistent for samples of greater Oakland Bay. However, the subsurface mixture contains a greater proportion of Factor 2, averaging 70 percent (Figure 15b). These results indicated that a homogenous mixture of dioxin/furan sources deposits throughout all of greater Oakland Bay, though the character of this mixture historically contained a greater relative amount of Factor 2.

The magnitude of factor TEQ increments in sediment core samples can be used to infer historical changes in the loadings of Factors 1 and 2. Surface sediments (0-10 cm) and a subsurface interval (1-2 feet) have been analyzed in five sediment cores of greater Oakland Bay (Herrera 2010). In all of these cores the Factor 2 TEQ increment is lower for surface sediments, with a decrease of 40 – 80 percent from subsurface concentrations (Figure 12). The change is not as consistent for Factor 1 (Figure 11). While three of the five cores display decreases in Factor 1 of 20 – 60 percent from subsurface to surface sediments, the two remaining cores have relatively consistent Factor 1 TEQ increments in both depth intervals.

Collectively, chemometric results for greater Oakland Bay can be used to identify the source location of dioxins/furans transported to the bay prior to deposition and historical changes in the source composition. The homogenous congener profile of deposited surface sediments and strong relationship between Factor 1 and 2 TEQ increments and grainsize suggest Shelton Harbor as the ultimate source area. Total TEQ of surface sediments is less than those of subsurface sediments. While the TEQ increments of Factors 1 and 2 are both lower in surface than subsurface sediments, the overall surface decrease is driven by less contribution of the PCP-like Factor 2. Existing surface sediments of greater Oakland Bay consist of an approximately equal mixture of Factors 1 and 2.

5.3 Source Interpretations

The preceding analysis identifies Shelton Harbor as the dominant source area of both Factor 1 and 2 for all of Oakland Bay sediments. Although their fates are closely linked after discharge, Factor 1 and 2 production mechanisms, source materials, and upland point sources differ. Below Factors 1 and 2 are discussed independently in regard to the likely activities responsible for their discharge to Shelton Harbor.

5.3.1 Factor 1

As discussed in Section 5.1.1, the chemical pattern of Factor 1 is most similar to that of emissions and ash from HFBs burning salt-laden wood. HFBs burning salt-laden wood were previously identified as a major contributor of dioxins/furans to sediments of Port Angeles Harbor (NewFields 2013). Shelton Harbor and Port Angeles Harbor are analogous in that they both have supported waterfront wood processing facilities and pulp mills throughout their industrialized histories. Because of these parallels, common dioxin/furan sources to regional sediments are expected.

Wood-fired power plants have operated in Shelton Harbor for the past century, supplying power to Simpson sawmills, the Rayonier pulp mill, and the Olympic Plywood plant. Due to the location of facilities in Shelton Harbor and the abundance of wood as a source of fuel for onsite burners, burning salt-laden hog fuel such as bark and sawmill debris was a common practice.

Using salt-laden wood in HFBs can result in significantly higher emissions of dioxins/furans than can burning salt-free wood (Duo and Leclerc 2004; Lavric et al. 2004; Luthe et al. 1997; Luthe et al. 1998; Pandompatam et al. 1997; Preto et al. 2005; Uloth et al. 2005).

Transport of HFB-Related Dioxin Prior to Entering the Marine Environment

Dioxin/furan TEQ profiles for HFB stack emissions and boiler ash are indistinguishable. Additionally, the different facilities in Shelton Harbor burning salt-laden wood wastes in HFBs are likely to have had similar emission and ash TEQ profiles. Therefore the Factor 1 TEQ increments of Oakland Bay may reflect contributions from more than one HFB source and also mixtures of boiler ash and stack emissions. Additionally, Factor 1 may be introduced to the harbor through a variety of transport pathways that are physically disconnected from the HFBs themselves. Prior to deposition in the bay, transport of Factor 1 dioxin may involve:

- Aerial deposition of HFB emissions onto the bay surface;
- Aerial deposition of HFB emissions in the uplands and subsequent delivery to the bay in stormwater runoff and municipal effluent;
- Erosion/runoff of HFB ash from industrial properties and disposal sites;
- Incorporation of HFB ash into industrial process water and effluent;
- Incorporation of HFB ash into municipal wastewater;
- Direct disposal of HFB ash into the bay; and
- Dredging and disposal of Shelton Harbor sediments.

HFB emissions and ash may have a long and complex transport history before being introduced to the marine environment. Published studies have shown that impacts on nearby soils from dioxin in air emissions decrease relatively rapidly as distance from the source increases. Therefore the greatest amount of dioxin aerial deposition (both on-water and upland) is expected to be in close proximity to the HFB. Once deposited on the land surface, emission-related dioxin is susceptible to transport in stormwater runoff. Such runoff is delivered to the harbor by local creeks, WWTP outfalls, and stormwater outfalls. Therefore creeks and outfalls may appear as point sources for Factor 1 even though the dioxin is initially derived from HFBs.

Boiler ash is generally handled as solid waste by the HFB operators. Currently, boiler ash produced by wood-fired power plants is generally removed from the properties and disposed of in landfills. Little is known about ash disposal procedures during the early history of industrial activities in Shelton Harbor. Unknown amounts of ash may have been used as fill at the properties or intentionally dumped into the harbor. Prior to removal from a property, exposed boiler ash at a facility may be introduced to the marine environment through transport by wind and stormwater runoff. Additionally, boiler ash may be incorporated into process water or incorporated into wastewater effluent as a means of disposal.

Overall, multiple HFB point sources and the complexity of possible transport mechanisms prior to deposition in sediments make the partitioning of Factor 1 between the different HFBs challenging. Regardless, the spatial pattern of Factor 1 in Oakland Bay surface sediments suggests the southwestern-most corner of Shelton Harbor, where both Simpson’s former power plant and Rayonier’s former pulp mill were located, as the predominant source area to the region. Below is a discussion of the two facilities most likely to contribute to the Factor 1 dioxin signature found throughout Oakland Bay sediments; the former Simpson power plant and the former Rayonier pulp mill.

Former Simpson Power Plant

In 1926 Simpson began operating seven HFBs at its power plant south of Goldsborough Creek to supply power to both the Simpson sawmills and the Rayonier pulp and paper mill. The power plant was jointly owned by Simpson and Rayonier until Simpson bought out Rayonier's interest in 1962. The plant's two stacks operated without air emission controls until 1976 when baghouses were installed. The HFBs utilized wood waste including bark removed from logs, rejected wood chips, and debris generated by the sawmills. During this time of operation it is unknown how boiler ash was handled.

In 1976, Simpson installed two banks of baghouses to filter particulates prior to emission. Collectively these baghouses captured approximately 3,000 pounds per day of particulate residue when all boilers were in use (Herrera 2008). Roughly two-thirds of the collected residue consisted of salts, with the remainder composed of unburned and charred wood. The baghouse residues were mixed into slurries and discharged to the former Pine Street WWTP (1976 to 1979) and the existing Eagle Point WWTP (1979 to 1984). Settling solids collected at these WWTPs were subsequently disposed of at the Shelton "C Street" Landfill and the Mason County Landfill. After 1984, all baghouse residues generated at the power plant were mixed with wood refuse and disposed of at Simpson's Dayton landfill.

Simpson's wood-fired power plant was decommissioned in 1986 and replaced with a more efficient wood-fired power plant north of Goldsborough Creek. Despite upgrading the power plant, the wood burned at the new facility was reported to consist of 20 percent salt-laden hog fuel (Ecology 1998).

Numerous samples associated with Simpson have the characteristic Factor 1 dioxin/furan congener profile. In 1986, samples of the plant's boiler ash and baghouse residue, as well as Shelton landfill and residential soil samples were included in EPA's national study to identify dioxin/furan sources (CH2M Hill 1987). Samples from the new power plant and all residential soil samples had total dioxin/furan TEQs less than 10 ng/kg and far too many non-detected congeners to be of use in profile analysis. Baghouse residue (TEQ = 25,000 ng/kg) and boiler emissions (TEQ = 740 ng/kg) from the plant's old, low pressure system match well with the Factor 1 profile, with correlation coefficients of 0.87 and 0.82, respectively. An even better match to the Factor 1 profile (correlation coefficient of 0.97) was the soil samples collected from the Shelton Landfill (TEQ = 3900 ng/kg), that received WWTP sludge and baghouse residues from Simpson.

As a part of Ecology's *Dioxin in Surface Water Sources to Oakland Bay* study (Ecology 2013), two subsurface soil samples were collected from fill mound rising from the northern bank of Shelton Creek, directly across the creek from the Simpson property (Figure 2). Based on visual observations of sparse vegetative cover and gray-colored surface, the mound was characterized as being composed of ash and clinker. The source of this material is uncertain, but its location along the rail line suggests it may have been dumped from rail cars. These two ash samples have similar dioxin/furan TEQ profiles, both correlating well with Factor 1 (correlation coefficients of 0.90 and 0.88).

Former Rayonier Pulp Mill

From 1926 to 1957 Rayonier operated a pulp and paper sulfite mill with a wood-fired power plant on the south side of Shelton Harbor. This mill also received power from the power plant on Simpson property jointly owned by Simpson and Rayonier. Pulp was produced at the mill from wood chips supplied by Shelton sawmills or brought in by trucks or barges. While the source of fuel burned at Rayonier's pulp mill power plant is undocumented, it is likely that it consisted of the same salt-laden sources utilized by the jointly owned power plant during this time period.

Additionally, Rayonier constructed a burn plant in 1945 with a 325-foot high stack on the hillside above the mill for the purpose of incinerating spent brown liquor, the by-product of the sulfite pulping process. While the burn plant also produced stack emissions and boiler ash, it is unknown if the dioxin/furan profile produced by burning brown liquor differs from that of burning salt-laden hog fuels. The source library includes a single profile from a black liquor recovery boiler that is considerably different than HFB sources. However, black liquor is produced from a sulfate (kraft) process rather than the sulfite process utilized by Rayonier. Therefore the brown liquor burn-plant cannot be ruled out as a source of Factor 1 or Factor 2 dioxin.

There are no known records of samples collected directly from the Shelton Harbor Rayonier facility that have been analyzed for dioxins/furans. Despite this, samples from Rayonier's former Port Angeles facilities and the Goose Lake site can be used to evaluate the dioxin/furan composition of wastes produced at Rayonier's former Shelton Harbor mill. A significant difference between Rayonier's Shelton Harbor and Port Angeles facilities is that the Shelton Harbor mill effluent did not receive treatment prior to release; while treatment at the Port Angeles facility began in 1974. Seven effluent samples collected from the former Rayonier Mill in Port Angeles between 1989 and 1992 (FWEC 1997) have TEQ profiles similar to that of Factor 1, with correlation coefficients ranging from 0.83 to 0.94. It is not known whether these samples were collected from the chlorine bleaching, sulfite liquor, or mixed waste process stream. While the chemical profiles of these effluent samples are not characteristic of the dioxin/furan congener pattern created during the chlorine bleaching process (NCASI 1990), they do imply the presence of HFB ash in the mill's effluent.

A number of samples collected at the Goose Lake site also match the TEQ profile of Factor 1. The Goose Lake site samples with correlation coefficients greater than 0.94 include subsurface soils samples of the former landfill and sediment collected behind a dam in Goose Lake's drainage ravine.

5.3.2 Factor 2

As discussed in Section 5.1.2, the chemical pattern of Factor 2 is most similar to that of PCP. PCP is notable for having among the highest dioxin/furan TEQ content among manufactured chemicals, with dioxins/furans created as an impurity during production. The production of PCP for wood preservation purposes began in the 1930s, used to prevent discoloration (sap-stain), molding, and decay. PCP became one of the most widely used biocides in the United States before regulatory actions to cancel and restrict certain uses in 1987. Approximately 80 percent of PCP production in the United States has been used for commercial wood treatment, 6 percent for slime control in pulp and paper production, and 3 percent for non-industrial purposes (IEP 2008).

The remaining 11 percent was converted to Na-PCP, the sodium salt of PCP, also commonly used as a wood preservative and slimicide.

It is expected that sediments of Oakland Bay have a dioxin component derived from PCP because of the long-term existence of both lumber and pulp mills along the Shelton Harbor waterfront. Despite PCP being a likely source of dioxin in harbor sediments, PCP itself has not recently been detected in any surface sediments of the Oakland Bay (Herrera 2010). This absence is likely due to the rapid degradation rate of PCP (Kao et al. 2004) compared to its associated dioxin. Additionally, the lack of PCP in bay sediments may indicate that Factor 2 dioxin is relatively old and not associated with current upland activities.

Similar to the HFB-like dioxin of Factor 1, PCP-like dioxin was previously identified as a major contributor of dioxins/furans to sediments of Port Angeles Harbor (NewFields 2013). The presence of PCP-like dioxin in Port Angeles Harbor sediments was mostly attributed to its use a slimicide by pulp and paper mills. Throughout the history of the pulp and paper industry, slimicides have been used to prevent the uncontrolled growth of microorganisms that can result in slime deposits. When unchecked, slime can clog filters, screens, and pipelines, and result in spots and breaks in the paper sheet. The use of slimicides, in addition to good housekeeping, is the only practical way to prevent slime formation during the papermaking process (Sanborn 1965).

Potential pathways for Factor 2 dioxin to enter Oakland Bay are fewer and less complex than those of Factor 1. Transport of Factor 2 dioxin may involve:

- Runoff of PCP from industrial properties;
- Incorporation of PCP into industrial process water and effluent;
- Direct disposal of PCP containing materials into the bay; and
- Dredging and disposal of Shelton Harbor sediments.

The spatial pattern of Factor 2 in Oakland Bay surface sediments suggests sources in the southern and northern Shelton Harbor, as well as possibly sources in the Johns Creek watershed (Figure 13b). Below is a discussion of the most likely to contributors to the Factor 2 dioxin signature found throughout Oakland Bay sediments; the Simpson Timber Company, the former Rayonier pulp mill and research laboratory, and Johns Creek/Bayshore Point.

Simpson Timber Company

None of the upland samples collected at the Simpson property as a part of EPA's national dioxin/furan source study match the profile of Factor 2. However, this sampling was focused on combustion sources and not effluent. Despite the lack of effluent samples from Simpson, the historical importance of PCP as a wood preservative is acknowledged.

Process chemicals used at the Simpson waterfront plywood and sawmill facilities, as reported to Ecology since the early 1980s, have included phenolic and urethane resins, urea/formaldehyde glues, fungicides, and waterproofing wax. Tanks containing resin and caustic chemicals associated with the plywood plant were located at the northwest corner of the building near Shelton Creek (Herrera 2008). In this area Simpson had three outfalls for discharging effluent and stormwater directly to Shelton Creek. Additionally, a wood preservative dip tank was referred to in a 1981 Ecology file letter stating that approximately 9,400 gallons of the PCP-containing Permatox 200 wood preservative was removed and disposed of by spraying it across the Dayton dry log sort yard (Herrera 2008).

Rayonier Pulp Mill and Research Facility

Similar to Simpson, there are no effluent sample results from Rayonier's Shelton Harbor facilities that can be used to compare to the chemometric-derived TEQ profiles. However, results from the Port Angeles Harbor sediment dioxin study (NewFields 2013) in the vicinity of the former Rayonier Mill provide a comparison. Surface sediments in the immediate vicinity of Rayonier's former Port Angeles mill contained relatively high levels of PCP-like dioxin. This dioxin footprint was attributed to Rayonier's effluent, possibly resulting from the use of PCP-containing slimicides or wood chips treated with PCP preservatives.

The case may be similar for Rayonier's former Shelton Harbor pulp mill, as a similar Factor 2 footprint is observed in the southwestern-most corner of the harbor near historic outfalls for the pulp mill and research laboratory (Figure 13b). There are no known records of the mill's slime control program. It is known that the Shelton Harbor mill produced pulp from wood chips supplied by Shelton sawmills, potentially treated with PCP as a preservative.

Samples from the Goose Lake site also suggest Rayonier's Shelton Harbor facilities as possible sources of Factor 2 dioxin to Oakland Bay. A number of Goose Lake landfill samples match the TEQ profile of Factor 2 with correlation coefficients as high as 0.93. Landfill samples with the highest correlation to Factor 2 were generally described in core logs as containing wood chip debris. This may be an indication that wood chips utilized at the pulp mill were treated with PCP.

Johns Creek/Bayshore Point

The possibility that Johns Creek and the uplands in the vicinity of Bayshore Point contributed Factor 2 dioxin to Oakland Bay sediments is primarily driven by two data points: OB-10 nearest to the Johns Creek delta, and OB-12 just north of Bayshore Point (Figure 12). These locations have relatively high Factor 2 TEQ increments compared to their neighbors.

As a part of Ecology's *Dioxin in Surface Water Sources to Oakland Bay* study (Ecology 2013), two sediment samples were collected from Johns Creek to determine if dioxin is currently being discharged to Oakland Bay. The low total TEQ and numerous congener non-detects of these samples prevent a meaningful comparison to the Factor 2 TEQ profile. While these results suggest that Johns Creek may not currently be a significant source of dioxin to Oakland Bay, historic sources may have existed within the watershed.

Johns Prairie Industrial Park, described in Section 2.1.3, does not discharge directly to Oakland Bay but is within the Johns Creek watershed. The property may have contributed Factor 2 dioxins/furans to Johns Creek, as it has been utilized by industries in which PCP use was common: sawmills, wood chipping companies, wood-treatment facilities, and utility pole manufacturers (Port of Shelton 2008). As late as the mid-1990s, a variety of wood treatment chemicals including a PCP-containing preservative were used in a dip tank at the property. Following a site investigation, cleanup activities completed at the site in 2004 included the removal of the dip tank and 452 tons of soil contaminated with PCP and petroleum.

Johns Creek flows through Bayshore Point prior to discharging to Oakland Bay. Bayshore Point was home to the Bayshore Golf Course, a nine-hole public golf course, between 1948 and 2013. Records state that Rayonier disposed of approximately 100 truckloads of sulfite liquor residue at the Bayshore Golf Course during the 1950s. As noted above, the Factor 2 dioxin/furan profile was evident in many samples from Rayonier's Goose Lake sulfite liquor disposal site. Disposal of sulfite liquor waste in the vicinity of Bayshore Point may have contributed to elevated Factor 2 TEQ increments in greater Oakland Bay.

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6.0 Conclusions

In an effort to increase the understanding of dioxin/furan sediment contamination throughout Oakland Bay, specific objectives of the Oakland Bay Sediment Dioxin Source Study included:

- Identifying distinct dioxin/furan congener factor signatures present in Oakland Bay sediments;
- Determining the relative contribution of identified dioxin/furan factors to bay-wide contamination; and
- Using the spatial patterns of sediment dioxin/furan factors, as well as characteristics of facilities in the Oakland Bay area, to identify potential upland point source locations.

The results of this study are expected to assist Ecology in identifying potential sources of the dioxins/furans in Oakland Bay. It is not Ecology's intention to perform detailed quantitative allocations among potential point/nonpoint sources or to apportion liability to potentially liable parties.

The chemometric evaluation of Oakland Bay sediment dioxin/furan congeners identified two factor patterns that provide a good model for measured TEQ values. Each of the two proposed factor patterns has an analog in known dioxin-producing materials:

- Factor 1 – Emissions and ash related to the burning of salt-laden wood in HFBs; and
- Factor 2 – Pentachlorophenol.

Spatial interpolation of dioxin factor TEQ increments allowed for the determination of the relative contribution of each factor to bay-wide surface sediment dioxin contamination. Factors 1 and 2 contribute relatively equal amounts, 48 and 52 percent, respectively. While TEQ concentrations of both dioxin factors are lower in surface sediments than subsurface sediments, a more drastic modern decrease in Factor 2 is apparent.

The two dioxin factors have somewhat unique spatial patterns in Shelton Harbor sediments, but these differences become marginal in sediments of greater Oakland Bay. Consistencies between the spatial patterns of Factor 1 and 2 and their strong correlation with grainsize throughout greater Oakland Bay suggest common transport mechanisms. It is likely that the vast majority of sedimentary dioxins/furans deposited in sediments of greater Oakland Bay originated in Shelton Harbor and were subsequently dispersed along with fine-grained sediments within freshwater plumes and by tidal currents.

Spatial patterns of Factor 1 and 2 in bay sediments along with supplemental information can be used to identify potential upland source locations and understand mechanisms by which the dioxin was introduced to Oakland Bay:

Factor 1 dioxin, derived from emissions and ash related to the burning of salt-laden wood in HFBs, is slightly less abundant in Oakland Bay surface sediments than Factor 2. Its spatial pattern is indicative of predominant point sources in the southwestern-most corner of Shelton Harbor. This is the former location of the HFBs jointly owned and operated by Simpson and Rayonier.

Factor 2 dioxin is characteristic of PCP, a chemical used extensively by both lumber and pulp and paper mills. The spatial pattern of Factor 2 implies upland sources in both northern and southern Shelton Harbor, as well as possibly within the Johns Creek watershed. The use of PCP as a wood preservative at both Simpson’s facilities and Johns Prairie Industrial Park has been documented (Herrera 2008). PCP may have been utilized by the Rayonier facilities as a slimicide during pulp production or as a laboratory chemical in the research facility. Wood chips sourced from local sawmills and used by Rayonier for pulp may have also been treated with PCP and subsequently released in the mill’s effluent.

More ubiquitous and diffuse dioxin/furan source types such as vehicle emissions, forest fires, and residential wood burning were not apparent in sediments of Oakland Bay. Also, a dioxin/furan profile consistent with that of chlorine bleaching was not identified.

A main deduction of this study is that the majority of dioxin contamination in bay sediments appears to be derived from industrial practices that are no longer occurring. The majority of dioxin found in the bay is associated with the use of PCP, a chemical currently banned from most industrial uses. HFBs in the vicinity of Shelton Harbor have either been decommissioned or are no longer thought to be fueled by salt-laden wood. However, any ongoing activities in Shelton Harbor that result in resuspension of surface sediments may cause harbor sediments to be an ongoing dioxin/furan source to sediments throughout Oakland Bay.

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Figures

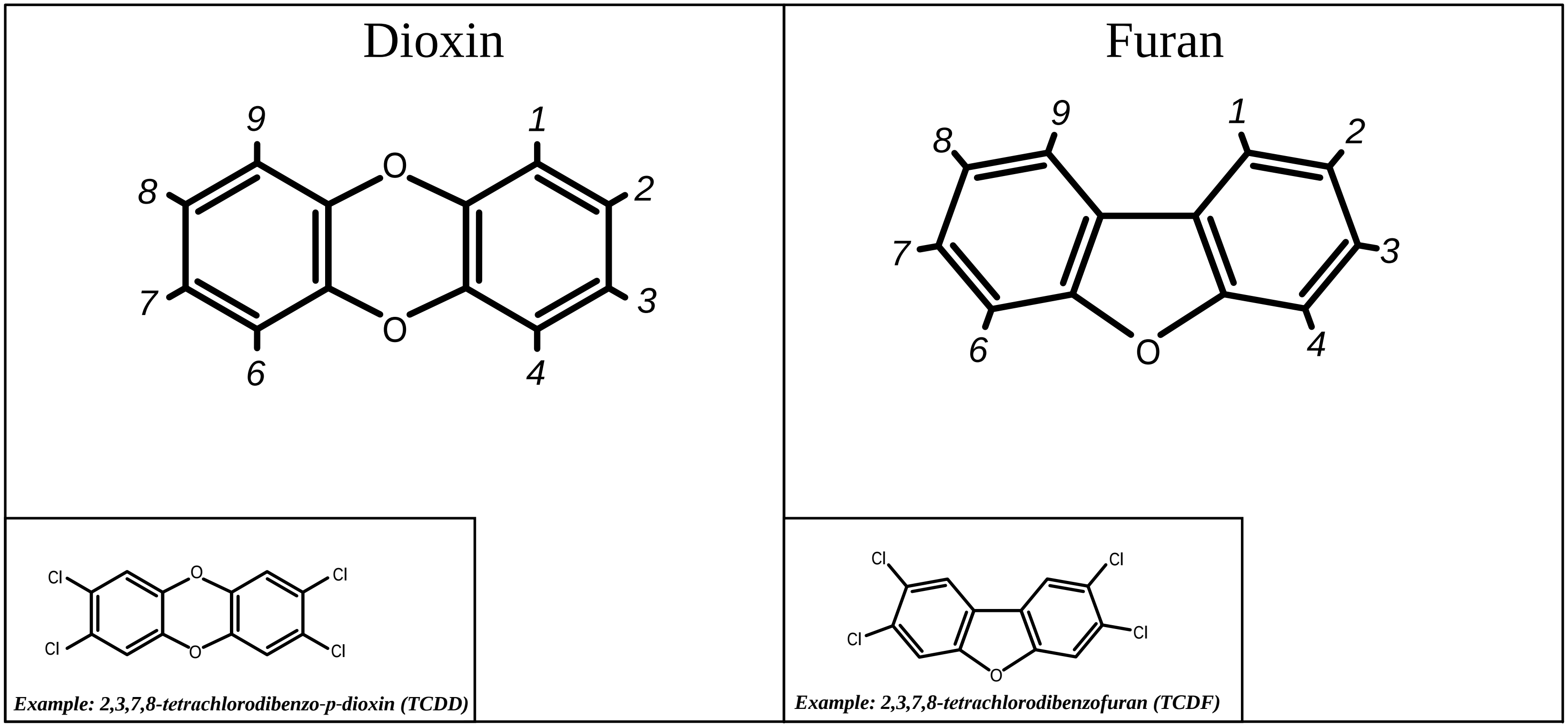

Figure 1. Structure and Chlorine Substitution Locations for Dioxins and Furans

N

Legend

⊗ outfall

● historic emission stack

Figure 2. Site Map of Shelton Harbor and Oakland Bay

0 500 1,000 2,000 Feet

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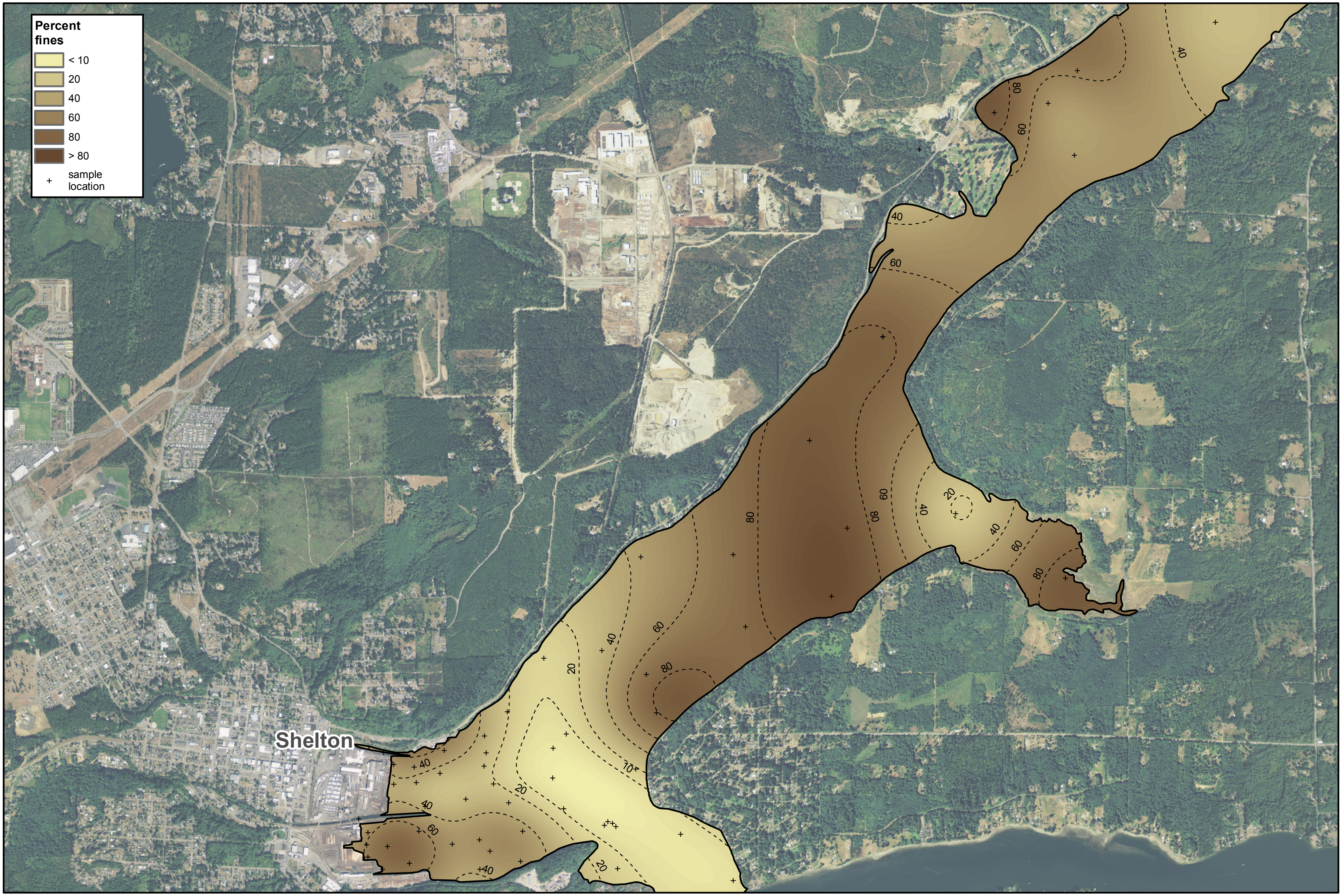

Figure 3. Interpolation of Surface Sediment Fines Content

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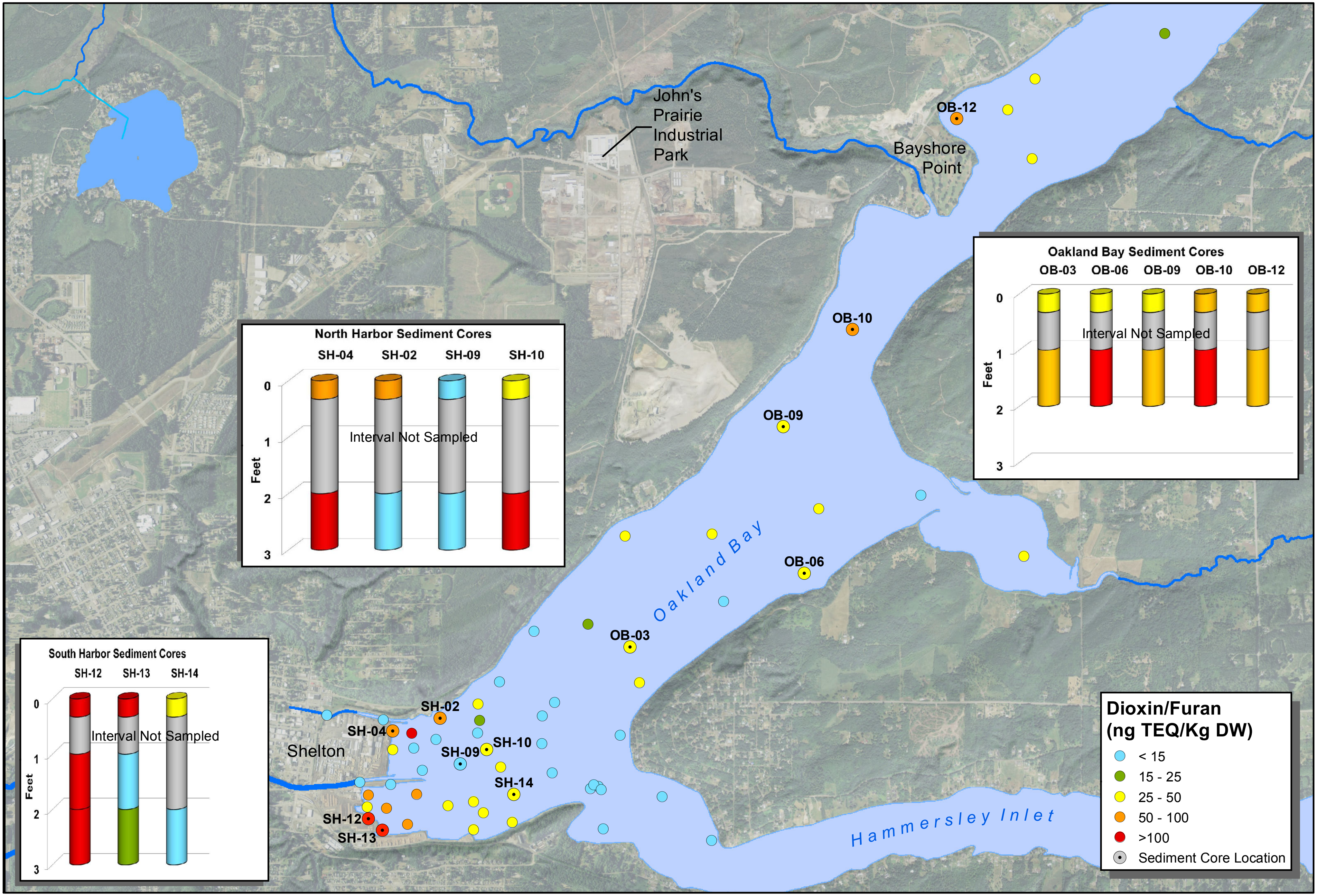

Figure 4. Dioxin/Furan Total TEQs of Surface and Subsurface Sediments

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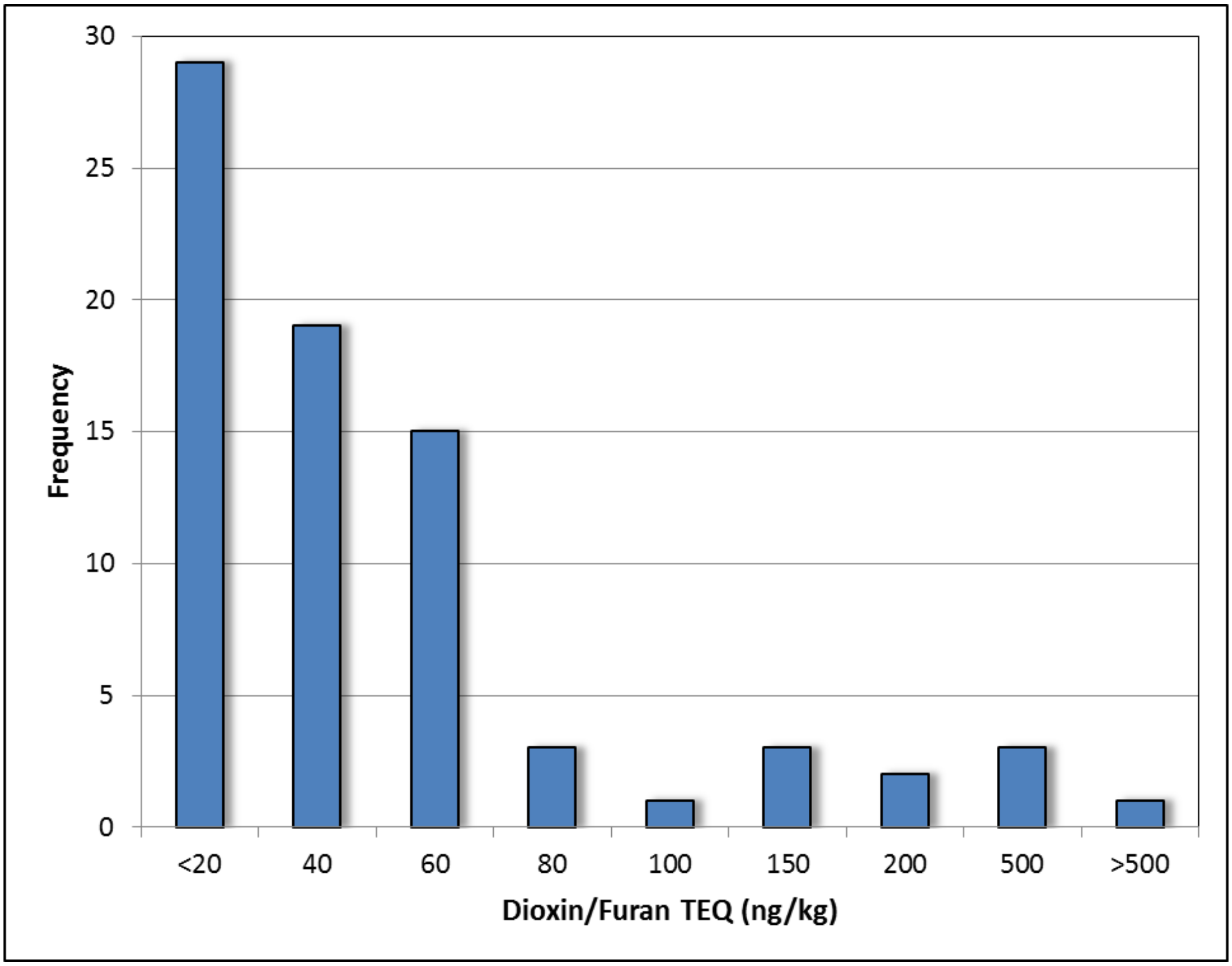

Figure 5. Dioxin/Furan TEQ Histogram of the Unmixing Data Set

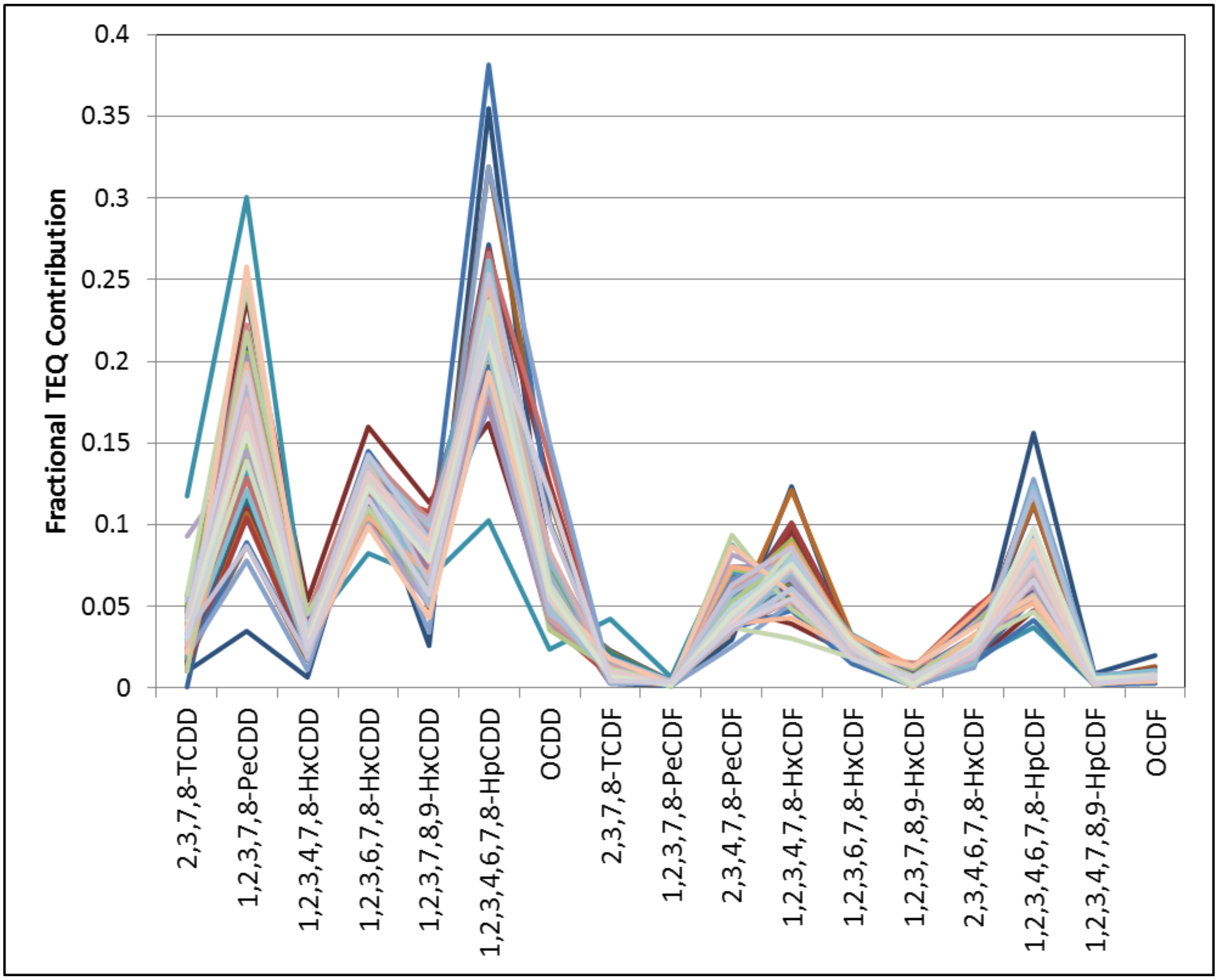

Figure 6. Normalized Dioxin/Furan Sample Profiles of the Unmixing Data Set

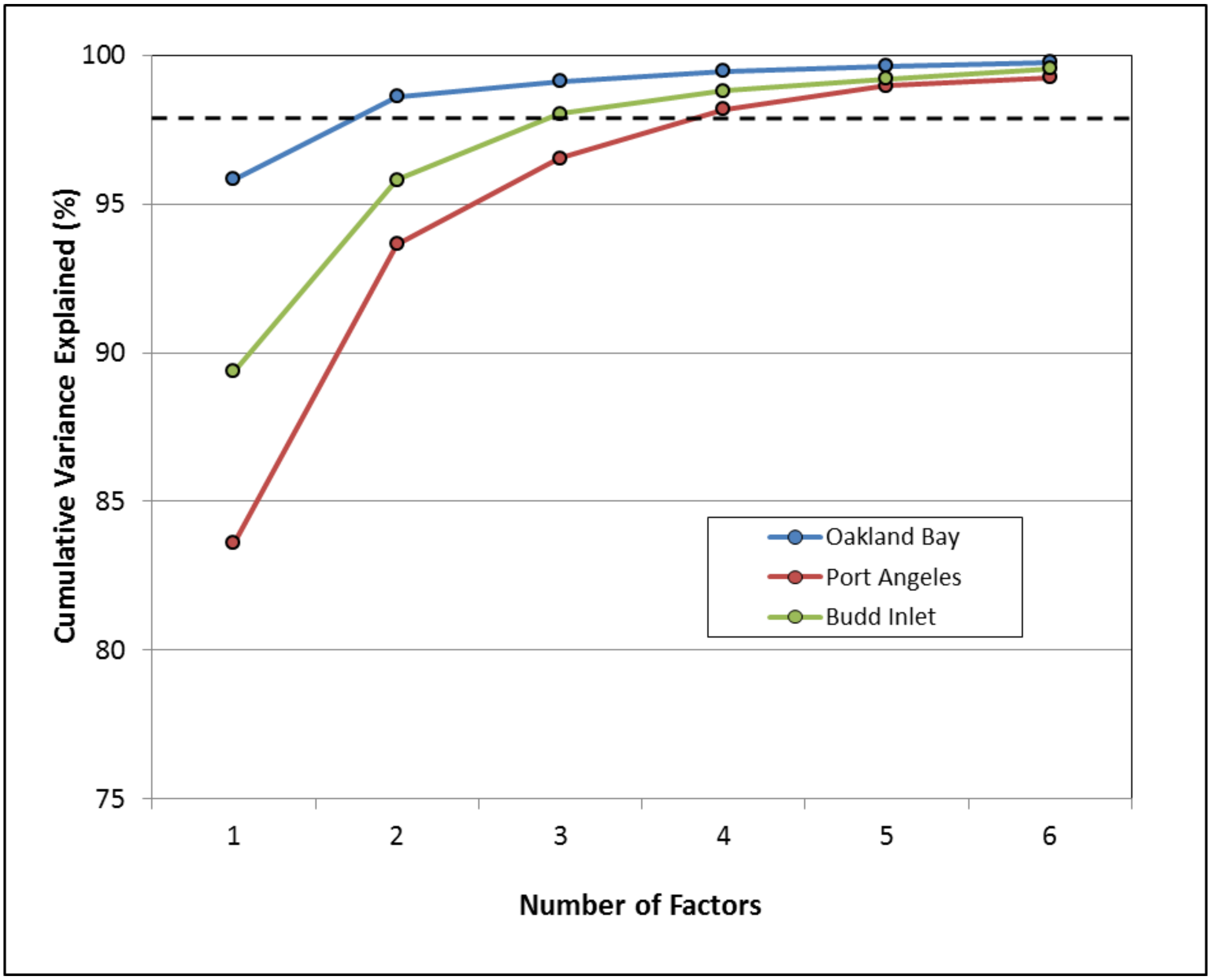

Figure 7. Data Set Variance Explained by PCA Factors

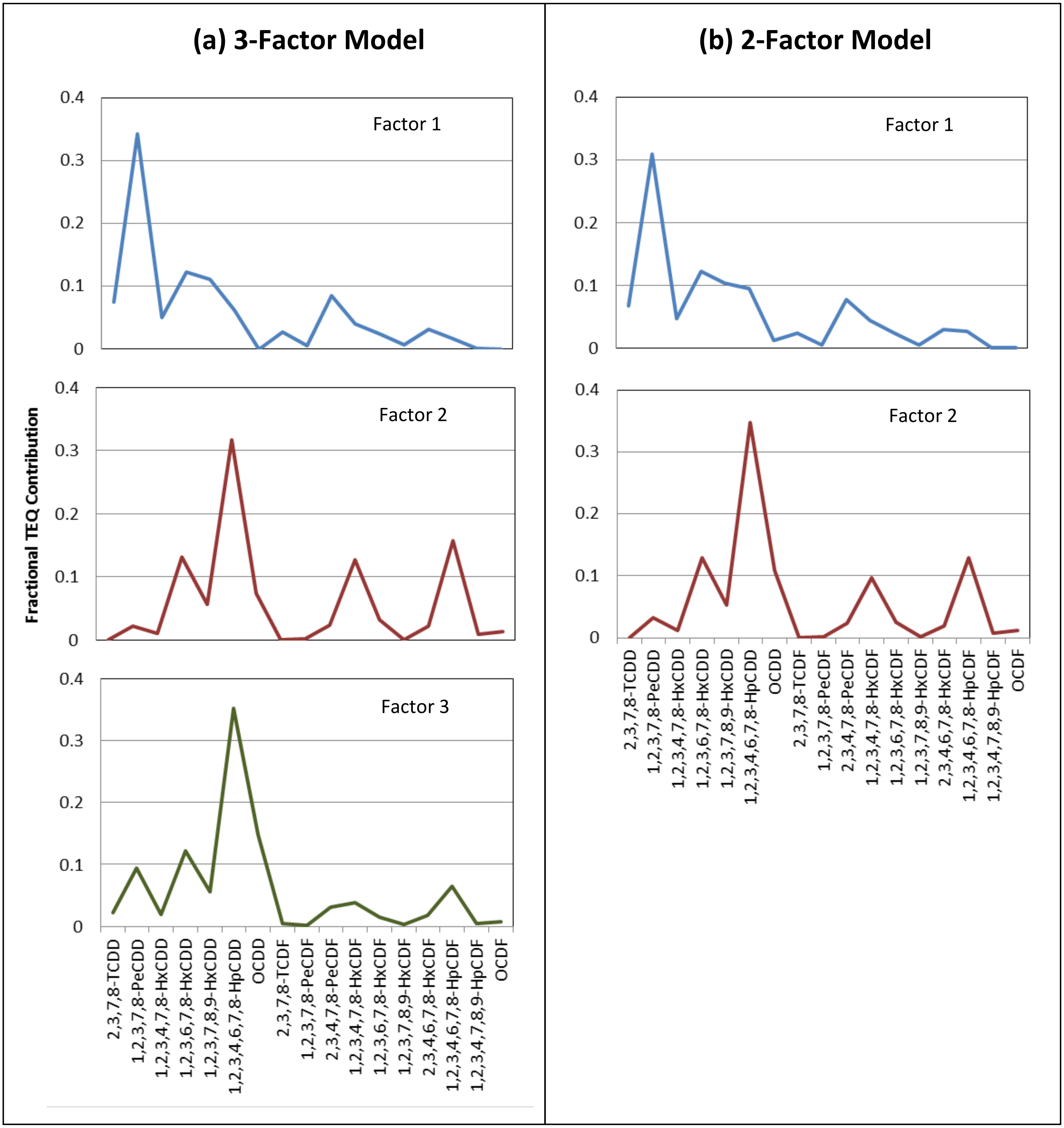

Figure 8. Dioxin/Furan Factor Profiles derived from the 3-Factor (a) and 2-Factor Model (b)

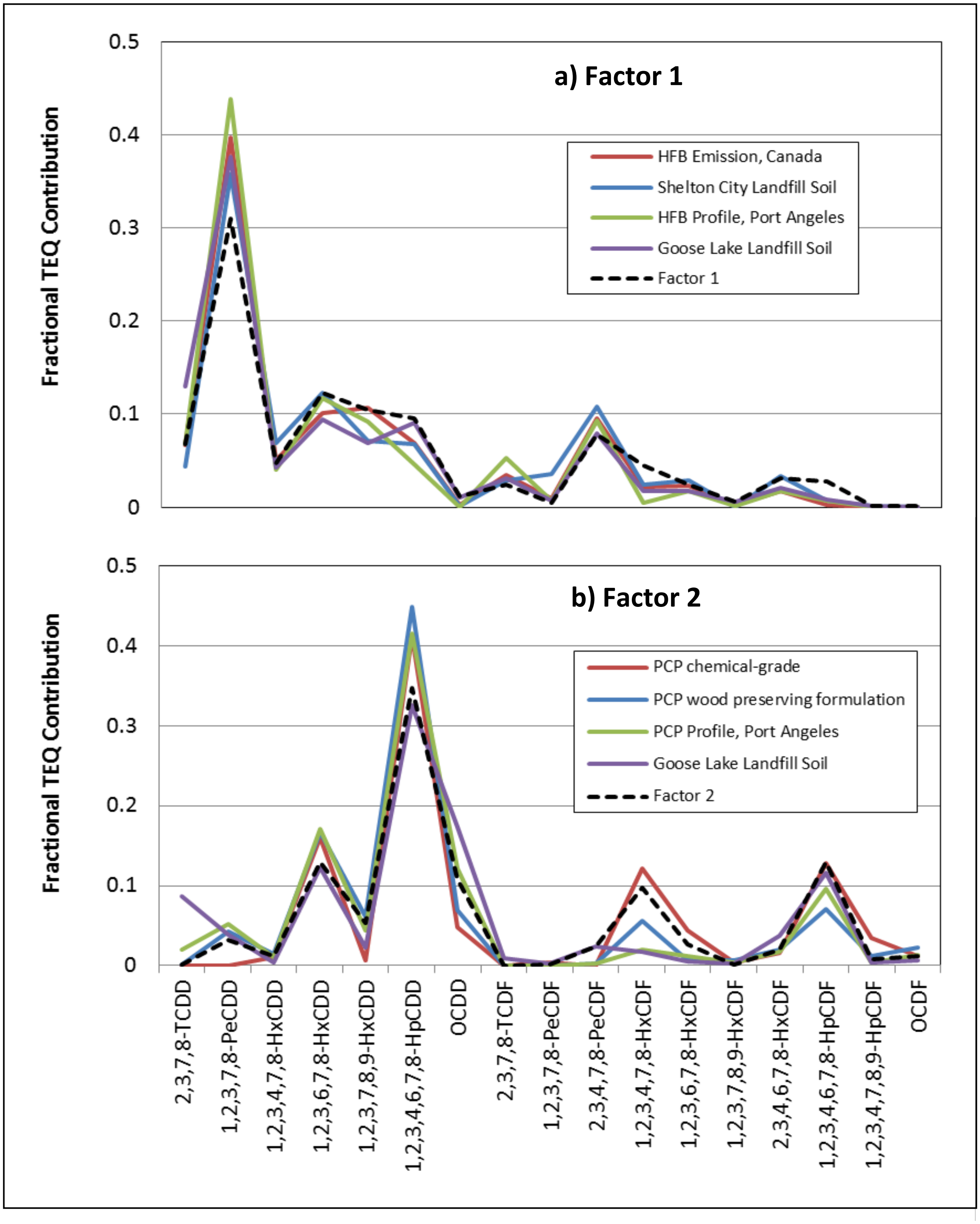

Figure 9. Source Library Profile Matches to Factor 1 (a) and Factor 2 (b)

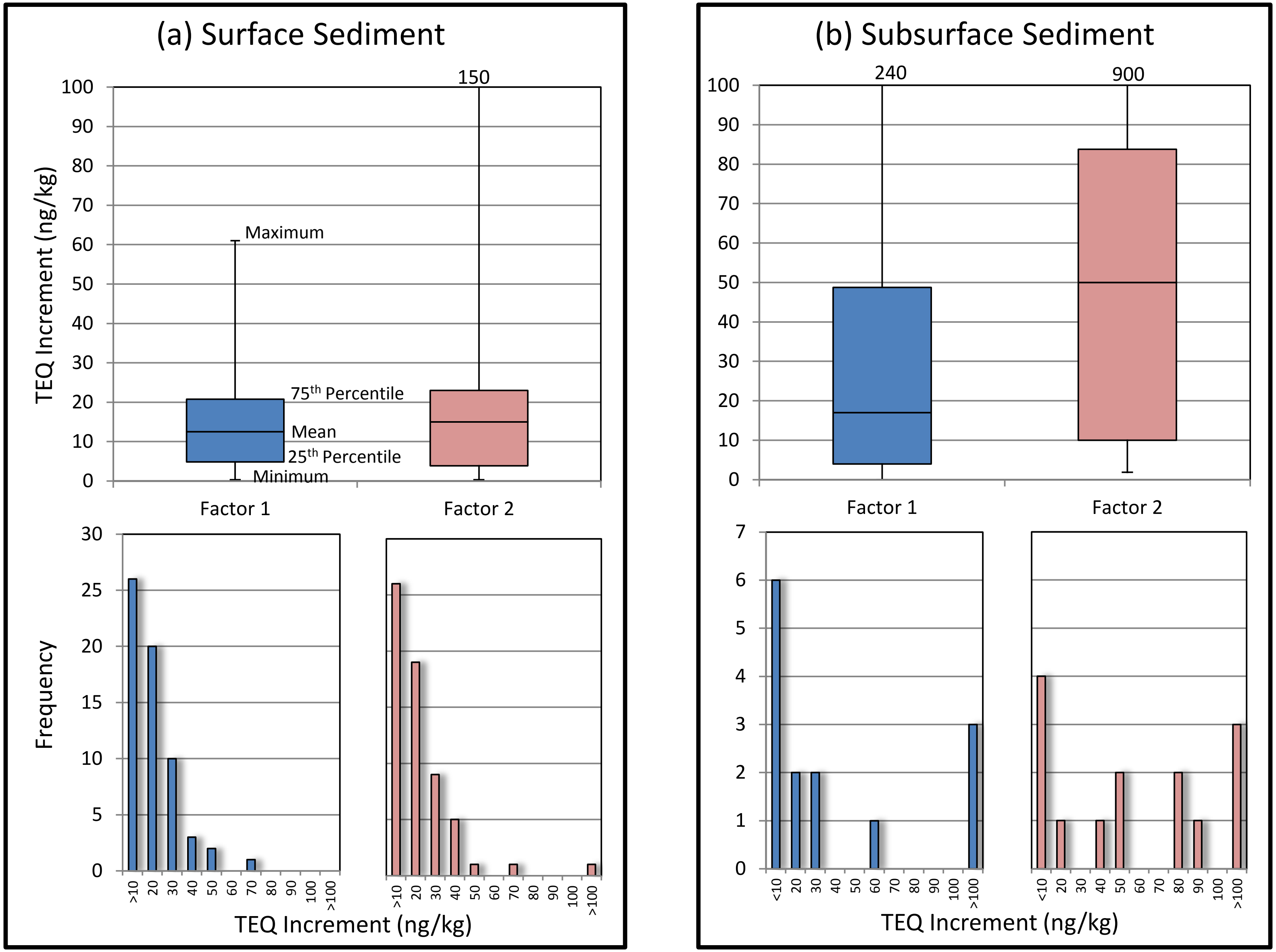

Figure 10. Comparison of Sample Factor TEQ Increments for Surface Sediments (a) and Subsurface Sediments (b)

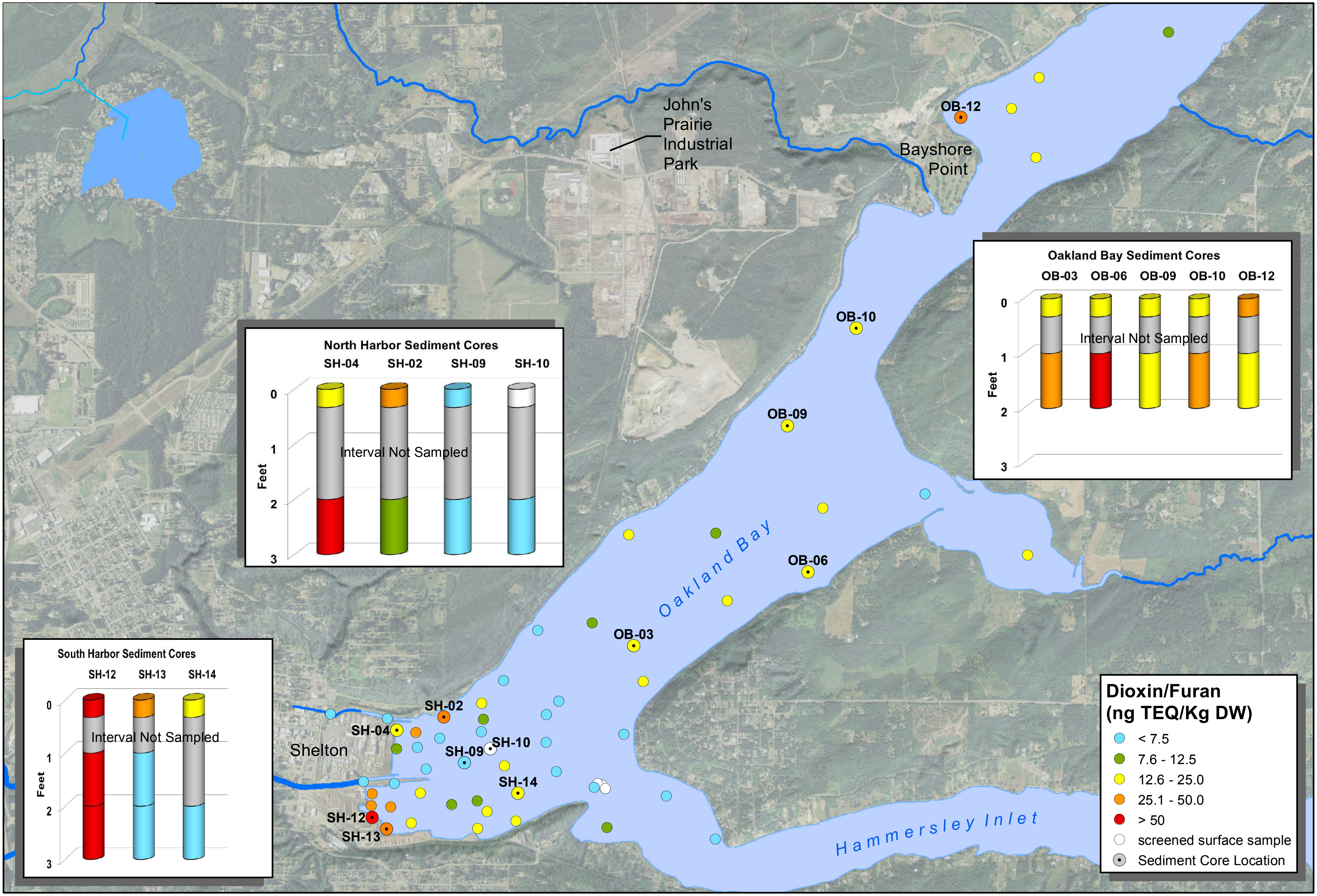

Figure 11. Factor 1 Dioxin/Furan TEQ Increments of Surface and Subsurface Sediments

N

0 0.5 1 2 Miles

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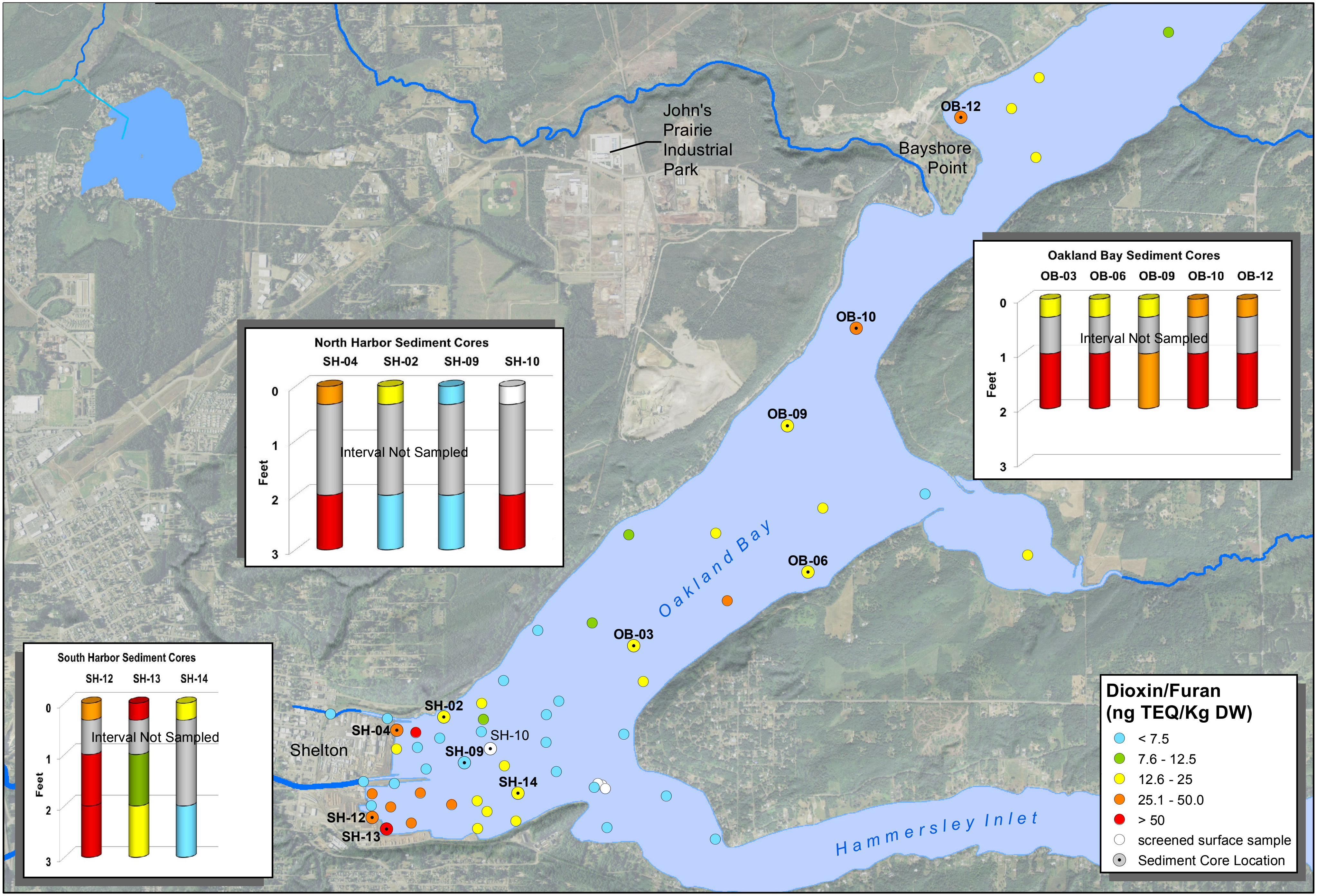

Figure 12. Factor 2 Dioxin/Furan TEQ Increments of Surface and Subsurface Sediments

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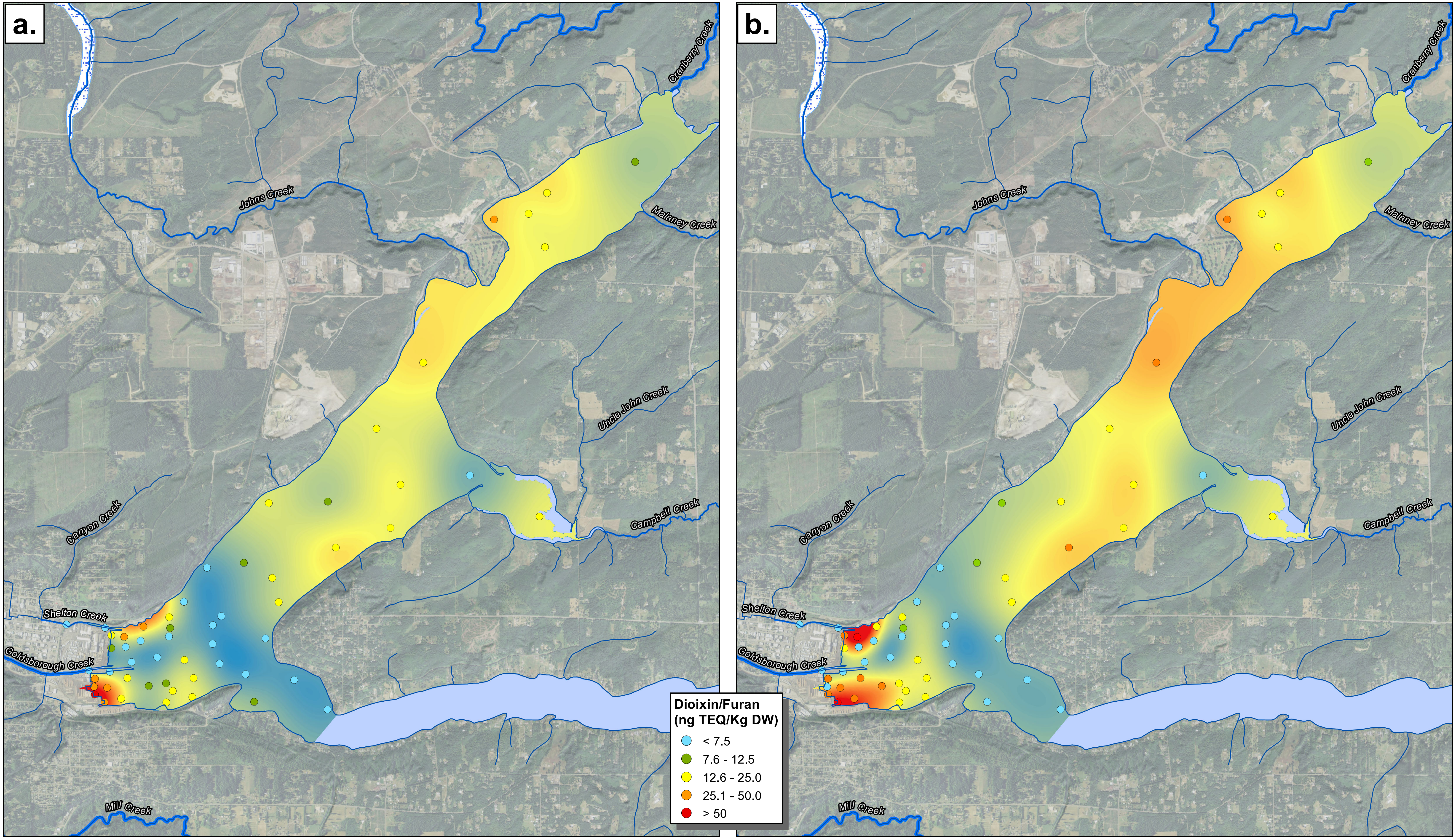

Figure 13. Interpolations of Surface Sediment Factor 1 TEQ (a) and Factor 2 TEQ (b)

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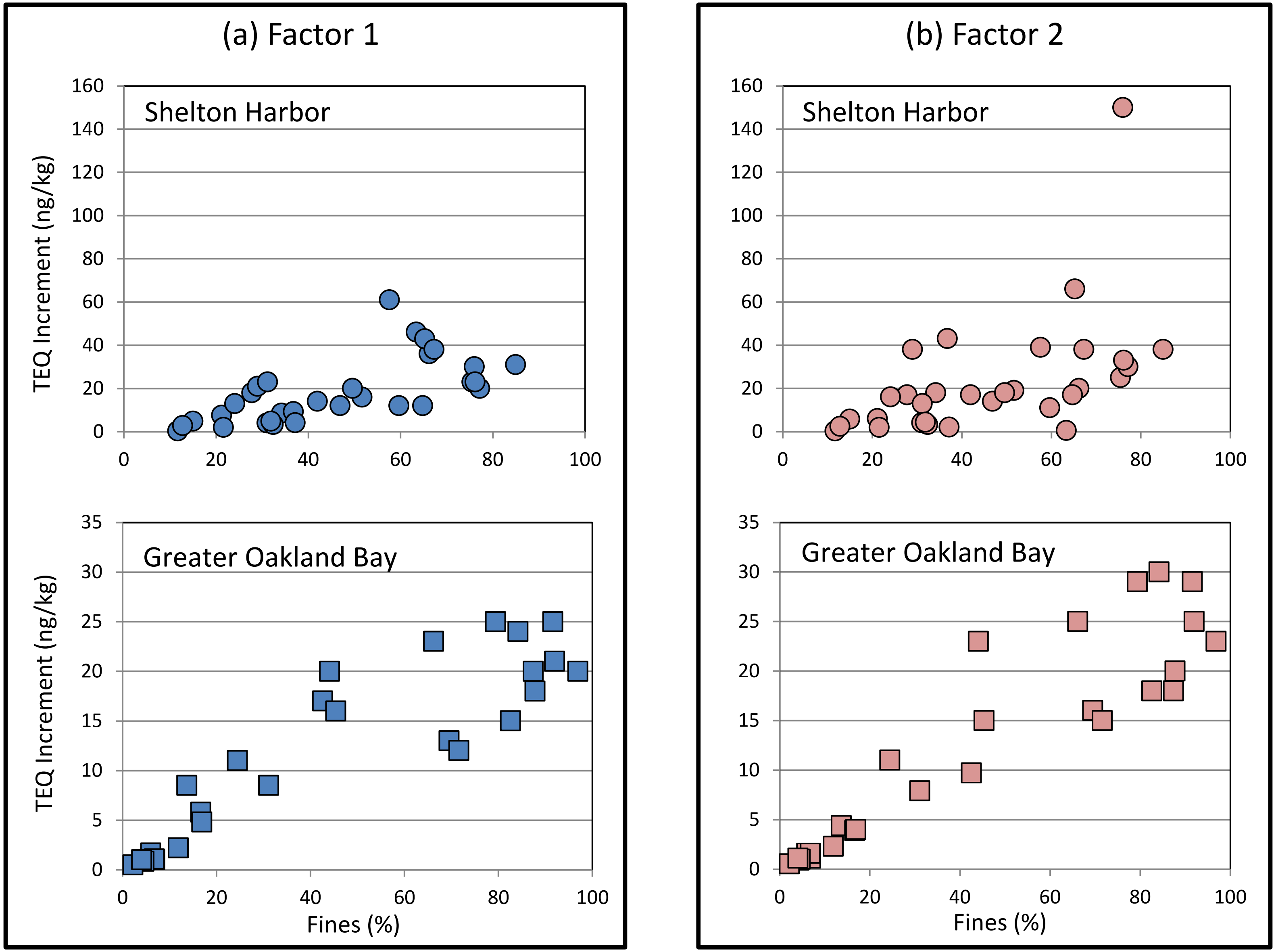
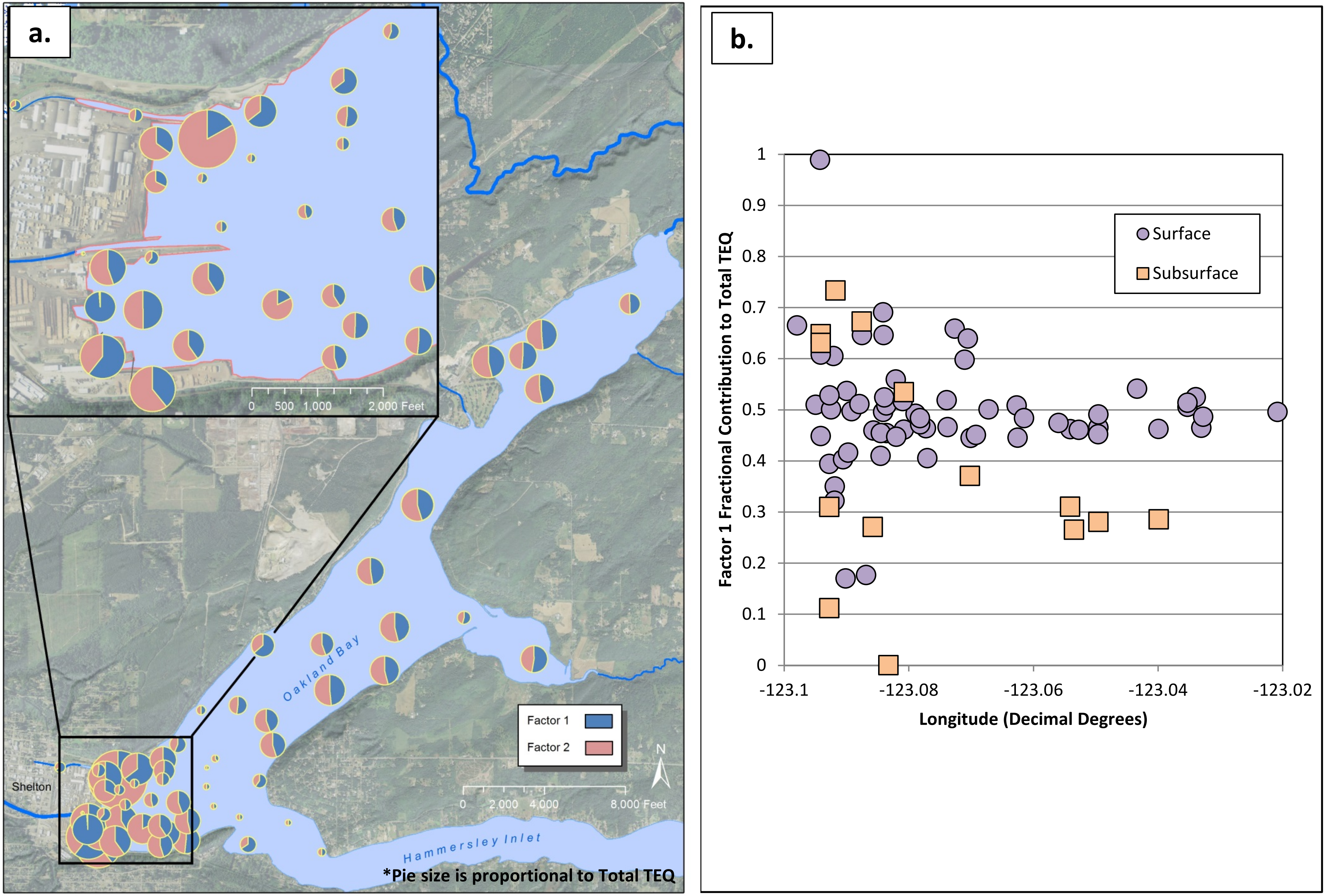


Figure 14. Relationship between TEQ Increment and Fines in both Shelton Harbor and Greater Oakland Bay for Factor 1 (a) and Factor 2 (b)



*Pie size is proportional to Total TEQ

Figure 15. Factor Contributions to Total TEQ for Surface Sediments (a) and both Surface and Subsurface Sediments (b)

Tables

Table 1. Dioxin/Furan Homologue Groups and 17 Congeners of Greatest Concern

Homologue Group	Congener	Abbreviation	TEF
Dioxins			
Tetrachlorodibenzo-p-dioxins		TCDD	--
	2,3,7,8-tetrachlorodibenzo-p-dioxin	2,3,7,8-TCDD	1
Pentachlorodibenzo-p-dioxins		PeCDD	--
	1,2,3,7,8-pentachlorodibenzo-p-dioxin	1,2,3,7,8-PeCDD	1
Hexachlorodibenzo-p-dioxins		HxCDD	--
	1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	1,2,3,4,7,8-HxCDD	0.1
	1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	1,2,3,6,7,8-HxCDD	0.1
	1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	1,2,3,7,8,9-HxCDD	0.1
Heptachlorodibenzo-p-dioxins		HpCDD	--
	1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	1,2,3,4,6,7,8-HpCDD	0.01
Octachlorodibenzo-p-dioxin	Octachlorodibenzo-p-dioxin	OCDD	0.0003
Furans			
Tetrachlorodibenzofurans		TCDF	--
	2,3,7,8-tetrachlorodibenzofuran	2,3,7,8-TCDF	0.1
Pentachlorodibenzofurans		PeCDF	--
	1,2,3,7,8-pentachlorodibenzofuran	1,2,3,7,8-PeCDF	0.03
	2,3,4,7,8-pentachlorodibenzofuran	2,3,4,7,8-PeCDF	0.3
Hexachlorodibenzofurans		HxCDF	--
	1,2,3,4,7,8-hexachlorodibenzofuran	1,2,3,4,7,8-HxCDF	0.1
	1,2,3,6,7,8-hexachlorodibenzofuran	1,2,3,6,7,8-HxCDF	0.1
	1,2,3,7,8,9-hexachlorodibenzofuran	1,2,3,7,8,9-HxCDF	0.1
	2,3,4,6,7,8-hexachlorodibenzofuran	2,3,4,6,7,8-HxCDF	0.1
Heptachlorodibenzofurans		HpCDF	--
	1,2,3,4,6,7,8-heptachlorodibenzofuran	1,2,3,4,6,7,8-HpCDF	0.01
	1,2,3,4,7,8,9-heptachlorodibenzofuran	1,2,3,4,7,8,9-HpCDF	0.01
Octachlorodibenzofuran	Octachlorodibenzofuran	OCDF	0.0003

Notes:

TEF – toxicity equivalency factor

Table 2. Oakland Bay Dioxin/Furan Congener Sediment Samples

Study Name	EIM Study ID	Surface Samples	Subsurface Samples
Simpson Lumber anti-degradation evaluation and upland disposal evaluation of dioxins	SIMPS12	1	--
Budd Inlet and Oakland Bay Dioxin Study	BuddOakDioxins	10	--
Dioxin in Surface Water Sources to Oakland Bay	RCOO0012	3	--
Shelton WWTP Outfall Baseline Sediment Monitoring Study	SHELTON WWTP	3	--
Oakland Bay Sediment Characterization Study	OAKSED08	50	14
Total		**67**	**14**

Table 3. TEQ Increments derived from the 3-Factor Model

Location ID	TEQ Increment (ng/kg)			Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2	Factor 3			
Surface Samples						
G1_0-1ft	4.7	1.4	3.3	9.4	9.3	-0.18
Gold-1_0-2cm	0.24	0.03	0.36	0.62	0.63	0.01
HI-02-SS_0-10cm	1.4	1.2	0.73	3.3	3.2	-0.07
HI-03-SS_0-10cm	7.4	4.3	1.3	13	13	-0.03
HI-04-SS_0-10cm	0.77	0.73	0.34	1.8	1.8	-0.01
HI-05-SS_0-10cm	0.83	0.91	0.42	2.2	2.2	0.00
HI-06-SS_0-10cm	5.1	4.0	0.79	9.9	9.7	-0.13
HI-07-SS_0-10cm	0.90	1.3	0.47	2.7	2.7	0.01
OB-01-SS_0-10cm	1.9	1.9	0.72	4.5	4.4	-0.05
OB-02-SS_0-10cm	7.4	7.9	1.3	17	17	0.03
OB-03-SS_0-10cm	11	13	5.1	29	29	-0.09
OB-04-SS_0-10cm	15	11	0.69	27	27	-0.11
OB-05-SS_0-10cm	10	14	3.9	28	28	-0.19
OB-06-SS_0-10cm	17	21	5.6	44	43	-0.33
OB-07-SS_0-10cm	4.1	3.6	1.2	8.9	8.7	-0.18
OB-08-SS_0-10cm	17	14	7.3	39	37	-1.6
OB-09-SS_0-10cm	15	18	5.2	39	38	-0.25
OB-10S_0-2cm	20	21	12	54	55	1.5
OB-10S_2-10cm	4.3	4.3	2.1	11	11	0.31
OB-10-SS_0-10cm	20	23	11	54	54	-0.65
OB-11-SS_0-10cm	17	22	5.3	44	44	-0.63
OB-12.5S_0-2cm	13	11	6.9	31	32	0.84
OB-12.5S_2-10cm	17	15	6.6	39	40	1.3
OB-12-SS_0-10cm	21	27	6.6	55	54	-0.25
OB-13-SS_0-10cm	20	25	4.0	49	48	-0.79
OB-14-SS_0-10cm	9.3	9.8	3.1	22	22	-0.31
OB-17-WS_0-10cm	6.6	5.7	1.4	14	13	-0.30
OB-18-WS_0-10cm	12	15	6.4	33	33	-0.48
OB-19-WS_0-10cm	17	19	9.6	46	45	-0.61
OB-227S_0-2cm	3.2	2.1	2.8	8.0	8.8	0.71
OB-227S_2-10cm	2.5	0.40	1.5	4.4	4.3	-0.10
OB-232S_2-10cm	19	17	12	48	49	1.2
OB-636S_0-2cm	9.3	8.6	7.8	26	27	0.97
OB-636S_2-10cm	14	12	8.6	35	36	0.95
SH-01-SS_0-10cm	9.8	7.8	4.9	22	23	0.28
SH-02-SS_0-10cm	30	11	15	55	53	-1.8
SH-03-SS_0-10cm	11	63	100	180	180	0.06
SH-04-SS_0-10cm	12	6.2	38	57	58	0.89
SH-05-SS_0-10cm	4.8	2.7	18	26	27	0.92
SH-07-SS_0-10cm	2.5	1.0	3.0	6.5	6.5	-0.04
SH-09-SS_0-10cm	4.0	3.8	3.0	11	11	-0.13
SH-11-SS_0-10cm	40	0.00	7.0	47	49	1.4
SH-12-SS_0-10cm	50	22	27	100	100	0.81
SH-13-SS_0-10cm	30	24	53	110	110	-0.68

Table 3. (Continued)

Location ID	TEQ Increment (ng/kg)			Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2	Factor 3			
SH-14-SS_0-10cm	13	13	8.7	35	35	-0.27
SH-15-SS_0-10cm	0.73	0.88	0.27	1.9	1.9	0.00
SH-16-SS_0-10cm	0.41	0.49	0.13	1.0	1.0	0.01
SH-18-WS_0-10cm	25	27	17	69	67	-1.8
SH-19-WS_0-10cm	33	33	12	78	79	1.00
SH-20-WS_0-10cm	16	21	14	50	51	0.34
SH-21-WS_0-10cm	17	16	23	55	54	-1.2
SH-22-WS_0-10cm	1.3	4.3	44	50	47	-2.4
SH-23-WS_0-10cm	9.3	11	8.2	29	29	0.15
SH-24-WS_0-10cm	12	15	4.6	32	32	-0.10
SH-25-WS_0-10cm	16	14	7.8	38	38	-0.47
SH-26-WS_0-10cm	2.3	1.5	1.4	5.3	5.2	-0.08
SH-27-WS_0-10cm	1.6	1.3	0.96	3.9	3.8	-0.05
SH-28-WS_0-10cm	11	15	3.1	30	30	0.11
SH-29-WS_0-10cm	0.85	0.92	0.32	2.1	2.1	-0.01
SH-30-WS_0-10cm	20	10	6.1	36	36	-0.01
Shelton-1_0-2cm	3.7	1.0	4.3	9.0	8.7	-0.37
Shelton-2_0-2cm	3.2	0.00	2.8	6.1	5.8	-0.27
Subsurface Samples						
OB-03-SC_1-2ft	26	54	2.0	82	82	-0.21
OB-06-SC_1-2ft	48	120	11	180	180	-0.32
OB-09-SC_1-2ft	12	37	4.5	53	52	-0.63
OB-10-SC_1-2ft	24	69	11	100	100	-0.82
OB-12-SC_1-2ft	18	54	0.00	73	71	-1.7
SH-02-SC_2-3ft	8.50	3.90	2.3	15	14	-0.34
SH-04-SC_2-3ft	200	46	76	320	310	-8.8
SH-09-SC_2-3ft	0.48	1.2	0.90	2.5	2.7	0.15
SH-10-SC_2-3ft	0.00	880	73	950	900	-50
SH-12-SC_1-2ft	110	48	43	200	200	1.1
SH-12-SC_2-3ft	170	80	67	310	310	-4.5
SH-13-SC_1-2ft	3.0	6.60	3.0	13	13	-0.04
SH-13-SC_2-3ft	0.00	5.10	11	16	16	0.25
SH-14-SC_2-3ft	3.8	4.6	0.00	8.4	8.0	-0.34

Notes:

Δ TEQ = (Measured TEQ) – (Sum of TEQ Increments)

Table 4. TEQ Increments derived from the 2-Factor Model

Location ID	**TEQ Increment (ng/kg)**		**Sum of TEQ Increments (ng/kg)**	**Measured TEQ (ng/kg)**	**Δ TEQ[1] (ng/kg)**
	Factor 1	**Factor 2**			
Surface Samples					
G1_0-1ft	5.8	3.8	9.6	9.3	-0.31
Gold-1_0-2cm	0.33	0.31	0.64	0.63	-0.01
HI-02-SS_0-10cm	1.7	1.6	3.3	3.2	-0.06
HI-03-SS_0-10cm	8.5	4.4	13	13	0.11
HI-04-SS_0-10cm	0.91	0.91	1.8	1.8	0.00
HI-05-SS_0-10cm	1.0	1.1	2.1	2.2	0.02
HI-06-SS_0-10cm	5.8	3.9	9.7	9.7	0.01
HI-07-SS_0-10cm	1.1	1.6	2.7	2.7	0.04
OB-01-SS_0-10cm	2.2	2.3	4.4	4.4	-0.01
OB-02-SS_0-10cm	8.5	7.9	16	17	0.31
OB-03-SS_0-10cm	13	16	29	29	0.19
OB-04-SS_0-10cm	17	10	27	27	0.40
OB-05-SS_0-10cm	12	15	27	28	0.17
OB-06-SS_0-10cm	20	23	43	43	0.27
OB-07-SS_0-10cm	4.8	4.0	8.8	8.7	-0.08
OB-08-SS_0-10cm	20	18	38	37	-1.3
OB-09-SS_0-10cm	18	20	38	38	0.24
OB-10S_0-2cm	25	29	54	55	1.7
OB-10S_2-10cm	5.2	5.4	11	11	0.38
OB-10-SS_0-10cm	24	30	54	54	-0.33
OB-11-SS_0-10cm	20	23	44	44	0.01
OB-12.5S_0-2cm	16	15	31	32	0.94
OB-12.5S_2-10cm	20	19	38	40	1.6
OB-12-SS_0-10cm	25	29	54	54	0.53
OB-13-SS_0-10cm	23	25	48	48	0.07
OB-14-SS_0-10cm	11	11	22	22	-0.06
OB-17-WS_0-10cm	7.6	6.0	14	13	-0.12
OB-18-WS_0-10cm	15	18	33	33	-0.23
OB-19-WS_0-10cm	21	25	46	45	-0.35
OB-227S_0-2cm	4.0	4.1	8.1	8.8	0.65
OB-227S_2-10cm	3.1	1.4	4.4	4.3	-0.16
OB-232S_2-10cm	23	25	48	49	1.3
OB-636S_0-2cm	12	14	26	27	0.89
OB-636S_2-10cm	18	17	35	36	0.96
SH-01-SS_0-10cm	12	11	22	23	0.35
SH-02-SS_0-10cm	36	20	55	53	-2.2
SH-03-SS_0-10cm	30	150	180	180	-3.6
SH-04-SS_0-10cm	21	38	59	58	-1.1
SH-05-SS_0-10cm	8.6	18	27	27	-0.06
SH-07-SS_0-10cm	3.3	3.3	6.6	6.5	-0.17
SH-09-SS_0-10cm	4.9	5.8	11	11	-0.14
SH-11-SS_0-10cm	46	0.52	47	49	1.9
SH-12-SS_0-10cm	61	39	100	100	0.34
SH-13-SS_0-10cm	43	66	110	110	-2.8

Table 4. (Continued)

Location ID	TEQ Increment (ng/kg)		Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2			
SH-14-SS_0-10cm	16	19	35	35	-0.19
SH-15-SS_0-10cm	0.86	1.0	1.9	1.9	0.03
SH-16-SS_0-10cm	0.48	0.53	1.0	1.0	0.03
SH-18-WS_0-10cm	31	38	68	67	-1.6
SH-19-WS_0-10cm	38	38	77	79	1.8
SH-20-WS_0-10cm	20	30	50	51	0.43
SH-21-WS_0-10cm	23	33	56	54	-1.8
SH-22-WS_0-10cm	9.3	43	52	47	-5.0
SH-23-WS_0-10cm	12	17	29	29	0.15
SH-24-WS_0-10cm	14	17	32	32	0.30
SH-25-WS_0-10cm	20	18	38	38	-0.28
SH-26-WS_0-10cm	2.8	2.4	5.3	5.2	-0.09
SH-27-WS_0-10cm	2.0	1.9	3.9	3.8	-0.05
SH-28-WS_0-10cm	13	16	29	30	0.60
SH-29-WS_0-10cm	1.0	1.1	2.1	2.1	0.02
SH-30-WS_0-10cm	23	13	36	36	0.14
Shelton-1_0-2cm	4.9	4.4	9.3	8.7	-0.58
Shelton-2_0-2cm	4.1	2.1	6.2	5.8	-0.42
Subsurface Samples					
OB-03-SC_1-2ft	30	50	80	82	2.0
OB-06-SC_1-2ft	55	120	180	180	4.1
OB-09-SC_1-2ft	14	38	52	52	0.64
OB-10-SC_1-2ft	29	74	100	100	1.4
OB-12-SC_1-2ft	20	50	70	71	1.1
SH-02-SC_2-3ft	9.8	4.8	15	14	-0.28
SH-04-SC_2-3ft	240	87	330	310	-11
SH-09-SC_2-3ft	0.69	1.9	2.5	2.7	0.14
SH-10-SC_2-3ft	0.00	910	910	900	-11
SH-12-SC_1-2ft	130	71	200	200	0.98
SH-12-SC_2-3ft	200	120	310	310	-4.5
SH-13-SC_1-2ft	3.9	8.7	13	13	0.05
SH-13-SC_2-3ft	1.8	14	16	16	-0.14
SH-14-SC_2-3ft	4.1	3.6	7.7	8.0	0.32

Notes:

Δ TEQ = (Measured TEQ) – (Sum of TEQ Increments)

Table 5. Factor Profile Matches to Source Library

Oakland Bay Sediment Profile	Source Library Match		HCA Similarity (fractional %)	Correlation Coefficient (r-value)
	Description	Reference		
Factor 1	Shelton City Landfill Soil	CH2M Hill (1987)	0.99	0.97
	Port Angeles HFB Source 4	NewFields (2013)	0.98	0.97
	HFB Stack Emission (CANST58)	DeAbreu (2009)	0.98	0.98
	Goose Lake Sediment (SED-09, 0-0.4 ft)	GeoEngineers (2012)	0.96	0.94
	Goose Lake Landfill Soil (MW-17, 3-4 ft)	GeoEngineers (2012)	0.95	0.97
	Rayonier HFB Ash (Port Angeles)	FWEC (1997)	0.94	0.95
Factor 2	PCP chemical-grade	Masunaga et al. (2001)	0.98	0.97
	Goose Lake Landfill Soil (TP-35, 15 ft)	GeoEngineers (2012)	0.96	0.91
	Port Angeles PCP Source 3	NewFields (2013)	0.94	0.96
	PCP treated utility pole	Lorber et al. (2002)	0.94	0.96
	PCP wood preservative	Christmann et al. (1989)	0.94	0.95

Notes:

HCA = hierarchical cluster analysis

Appendix A

Oakland Bay Dioxin/Furan Data Screening Memo

NewFields
Perspective. Vision. Solutions.

Technical Memorandum

To: Washington State Department of Ecology
300 Desmond Drive SE
Lacey, WA 98503

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

Date: January 17, 2014

Subject: Oakland Bay/Shelton Harbor Sediment Chemometrics - Data Screening

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In preparation for performing a chemometric assessment of Oakland Bay/Shelton Harbor sediment dioxin/furan congener data, the usability of available and relevant site data were evaluated. This memo describes the data selection criteria, the data screening process, and the identification of any data anomalies. All data evaluated were accessed through Ecology's Environmental Information Management (EIM) database, which was used as a tool to query and download existing data. While the usable data identified in this memo will be utilized for chemometric evaluation, further analysis may deem some of these data unfit for the chemometric process.

1.0 Existing Dioxin/Furan Data

Data evaluation required identifying all sample locations within Oakland Bay and the surrounding watershed that include dioxin/furan results. Samples collected within and in proximity to Goose Lake were also included, as the lake, an adjacent landfill, and nearby disposal lagoons received spent sulfite liquor and solid waste from the Rayonier Mill at Shelton Harbor. Tissue samples were not included, as metabolism can alter the dioxin/furan profile between sediments and receptor organisms. Only one study, *Evaluation of Dioxins in Shellfish from the Oakland Bay Site* (EIM Study_ID DOH05Oakland Bay) exclusively contained tissue samples.

The studies reviewed and their associated samples are listed in Table 1. Figure 1 presents the dioxin/furan sampling locations by EIM Study_ID, while Figure 2 presents the sample matrix and depth interval for all samples. Complete analytical results for these studies were downloaded from EIM and were subsequently reviewed relative to the dates of sample collection, sample depths, data validation levels, and detection limits. Short narratives of each study are presented below, beginning with the most recent study.

Simpson Lumber anti-degradation evaluation and upland disposal evaluation of dioxins

A 2012 beneficial re-use characterization was conducted to determine the suitability of 135 cubic yards of woody debris for recycling into mulch and topsoil. The single surface sediment sample consisted of the 0-1 foot interval collected from the south side of the Goldsborough Creek jetty where log handling activities occur (Figure 1). Dioxin/furan congener analysis was conducted for the bulk sample as well as the >0.5 inch and <0.5 inch size fractions. Dioxin/furan method detection limits (MDLs) were generally less than 1 ng/kg for all non-detected congeners. No parameters other than dioxins/furans were present in EIM. According to the EIM study information, the analyzed sediment was approved for removal.

Budd Inlet and Oakland Bay Dioxin Study

Sediment samples were collected both within Budd Inlet and Oakland Bay during June 2011. The 5 dioxin/furan sediment sampling locations within Oakland Bay had the 0-2 cm and 2-10 cm intervals analyzed, both within the 0-10 cm depth generally classified as surface sediments. Dioxin/furan MDLs were less than 1 ng/kg for all non-detected congeners. In addition to dioxin/furan congener results, both grain size and total organic carbon (TOC) results were available for all samples.

Dioxin in Surface Water Sources to Oakland Bay

This study includes 9 surface sediment samples collected from Shelton, Goldsborough, and Johns Creeks during 2011. Shelton and Goldsborough Creeks are the largest sources of surface water discharging within the urban/industrial area of Shelton Harbor. Johns Creek discharges to upper Oakland Bay and drains an area that includes an industrial park where wood-treating facilities were once located. Although all of the sediment samples were classified in EIM as freshwater sediments, three sampling locations appear to be intertidal and will be considered as marine/intertidal sediments. Two subsurface soil samples from an ash mound along Shelton Creek were also included in the study. Sediment samples consist of the 0-2 cm interval. Soil samples of the ash mound were from the 10-15 cm interval. Dioxin/furan MDLs were generally less than 0.1 ng/kg for all non-detected congeners. While no results for the furan congener 2,3,7,8-TCDF were present in EIM, these results were found in the study data report (Ecology 2013).

Shelton Wastewater Treatment Plant Outfall Baseline Monitoring Study by City of Shelton

Sediment samples were collected in the vicinity of the new City of Shelton outfall and diffuser in order to establish 2010 baseline sediment quality conditions. The 3 dioxin/furan surface sediment sampling locations consist of the 0-10 cm interval and were located at the junction of Oakland Bay and Hammersley Inlet. Dioxin/furan MDLs were generally less than 0.1 ng/kg for all non-detected congeners. In addition to dioxin/furan congener results, grain size, TOC, and Sediment Management Standards (SMS) contaminants of concern were available for all samples.

2008 Oakland Bay Sediment Characterization of intertidal and subtidal areas from Hammersley Inlet to upper Oakland Bay

This sediment characterization includes surface and subsurface sediment samples collected in Oakland Bay, Shelton Harbor, and Hammersley Inlet, as well as reference samples collected Carr Inlet. The 50 surface sediment dioxin/furan results were consistently from the 0-10 cm interval. The 14 subsurface dioxin/furan results were from either the 1-2 or 2-3 foot interval. Low MDLs were achieved, generally less than 0.1 ng/kg, and all congeners were detected in the non-reference samples. In addition to dioxin/furan congener results, grain size, TOC, and SMS contaminants of concern were available for some samples.

Goose Lake Remedial Investigation

Freshwater sediment and soil were collected at the Goose Lake site between 2002 and 2010 for dioxin/furan congener analysis. Samples were collected from the lake, a drainage ravine, an inactive landfill adjacent to the lake, and former disposal lagoons. Sediment data include dioxin/furan results from 5 surface and 6 subsurface samples collected in 2002 and 2003 from the lake and a drainage ravine. Surface samples from the lake were collected from a black silty layer, while subsurface samples were from native peat. For the sediment data, practical quantitation limits (PQLs) rather than MDLs were reported for non-detected congeners. These PQLs were as high as 5 ng/kg for some congeners. Anomalous concentration units were noticed in the EIM data. These errors were corrected in the reviewed data after consulting the original laboratory reports.

EIM contains dioxin/furan results for 1 surface and 26 subsurface soil samples collected from the disposal lagoons, landfill, and ravine. The draft Goose Lake Remedial Investigation (RI) Report (GeoEngineers 2012), classified many of these samples as either waste, peat, glacial, or cover material. For the soil data, PQLs rather than MDLs were reported for non-detected congeners. These PQLs were generally less than 1 ng/kg for all congeners.

In addition to the Goose Lake site soil data present in EIM, the Goose Lake RI also includes dioxin/furan results for 9 additional soil samples (1 surface and 8 subsurface). Neither laboratory reports nor data validation reports for these samples were available in the RI report (GeoEngineers 2012). Some of these samples may prove to be important for understanding the dioxin/furan signature associated with Rayonier Mill solid waste, as many were collected from the former landfill and were classified as waste material in the RI. These 9 soil samples were not displayed on Figure 1, as coordinates of the sampling locations were not available in either EIM or the RI report. However, these sampling locations were displayed on figures within the RI report and can be approximated.

2.0 Data Screening

Results from the above studies constitute the relevant and available dioxin/furan congener data for Oakland Bay, Shelton Harbor, Hammersley Inlet, Goose Lake site, and their watersheds. Review of the data did not indicate that any particular results currently present in EIM should be screened from further evaluation.

Dioxin/furan results for 9 soil samples not currently present in EIM were discovered in the Goose Lake RI report (GeoEngineers 2012). These soil data will not be used for chemometric un-mixing analysis, but will be further evaluated for comparison purposes (see Section 3.0). Further information to verify the analytical results presented in the RI for these 9 soil samples are desirable.

Dioxin/furan data from the reviewed studies are recent, with the oldest results from 2002, and are of sufficient quality to not interfere in the chemometric process. At a minimum, all data reviewed underwent a Level 2 QA assessment (Table 1). The Level 2, or QA1, validation is based on information summarized by the laboratory of its quality control forms but includes no, or minimal, raw data review.

MDLs and PQLs for dioxin/furan congeners are generally low for non-detected congeners, and therefore are not likely to drive pattern identification. However, early in the chemometric process both a maximum number of non-detected congeners and a minimum dioxin/furan toxic equivalency (TEQ) value will be used to further screen samples from analysis. Determination of these screening limits will require further evaluation of the data using chemometric software.

3.0 Data Utilization

Dioxin/furan data from the reviewed studies will be used for one of two purposes in the chemometric process, either for sediment profile “un-mixing” (source identification) or as profiles in a comparison library. Only marine and intertidal sediment samples, both surface and subsurface, will be used for chemometric source analysis and identification. While surface sediment data generally consists of the 0-10 cm interval, those that are from the 0-2 cm, 2-10 cm, and 0-1 foot intervals will all be considered surface sediments for interpolation purposes. The total dioxin/furan congener dataset consists of 67 surface and 14 subsurface sediment samples (Table 1). These sediment data will be compiled into a project database with a single coordinate system and consistent concentration units. Additional sample parameters such as grain size and TOC will also be maintained in the database.

The remaining dioxin/furan data from upland samples will be added to NewFields’ existing library of congener profiles. Comparison between data-derived Oakland Bay/Shelton Harbor sediment profiles with library profiles will aid in the identification of potential dioxin/furan sources.

The library currently consists of dioxin/furan congener profiles from a wide range of potential source materials, industrial samples, and environmental samples. The Goose Lake site data will be especially important for comparison to sediment data-derived profiles as sediment and soil from the site may be representative of solid waste, effluent, and local background signatures depositing in Oakland Bay/Shelton Harbor. Because non-detected congeners of Goose Lake sediment samples were reported as PQLs rather than MDLs, the relatively high influence of non-detects on their profiles must be considered when comparing them to data-derived Oakland Bay/Shelton Harbor sediment profiles.

4.0 References

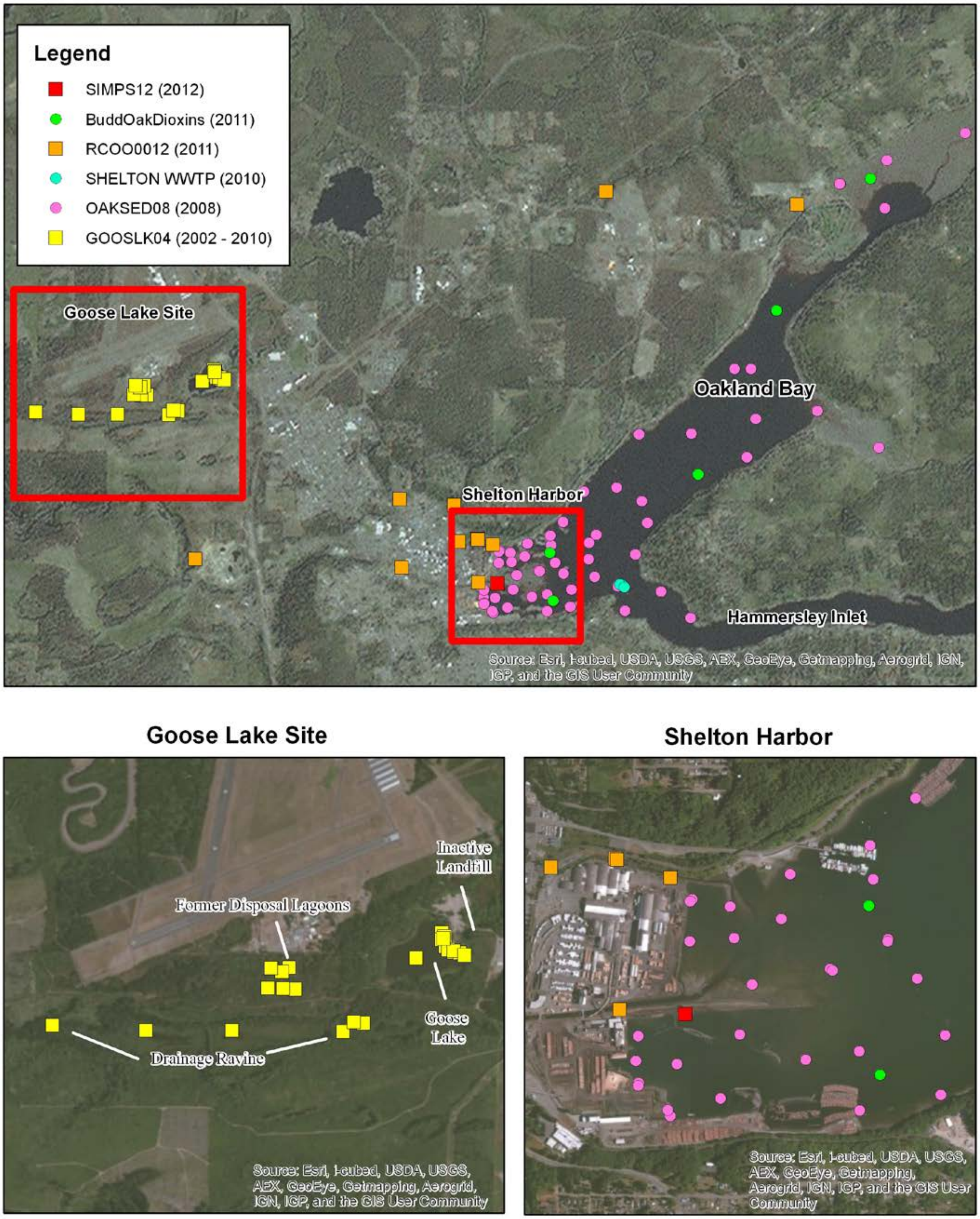
Ecology. 2013. Dioxin in Surface Water Sources to Oakland Bay, Mason County. Washington State Department of Ecology, Olympia, WA. May 2013. Publication No. 13-03-022. https://fortress.wa.gov/ecy/publications/SummaryPages/1303022.html

GeoEngineers. 2012. Goose Lake Site, Shelton, Washington. Final Remedial Investigation Report: Public Review Draft. Prepared for Rayonier Properties, LLC by GeoEngineers. July 2012.

.

Table 1. Oakland Bay Regional Dioxin/Furan Studies

Study Name	EIM Study ID	EIM Data Entry Review Status	Study QA Level Assessment	Field Collection Start Date	Field Collection End Date	Marine/Intertidal Sediment		Freshwater Sediment		Upland Soil	
						Surface Samples	Subsurface Samples	Surface Samples	Subsurface Samples	Surface Samples	Subsurface Samples
Simpson Lumber anti-degradation evaluation and upland disposal evaluation of dioxins	SIMPS12	Not Reviewed	Level 2 - Data Verified	27-Aug-12	27-Aug-12	1	--	--	--	--	--
Budd Inlet and Oakland Bay Dioxin Study	BuddOakDioxins	Reviewed	Level 3 - Data Verified and assessed for usability	1-Jun-11	21-Jun-11	10	--	--	--	--	--
Dioxin in Surface Water Sources to Oakland Bay	RCOO0012	Reviewed	Level 5 - Data Verified and Assessed for Usability in a Peer-Reviewed Study Report	6-Dec-11	13-Dec-11	3	--	6	--	--	2
Shelton WWTP Outfall Baseline Sediment Monitoring Study by City of Shelton	SHELTON WWTP	Not Reviewed	Level 2 - Data Verified	23-Sep-10	23-Sep-10	3	--	--	--	--	--
2008 Oakland Bay Sediment Characterization of intertidal and subtidal areas from Hammersley Inlet to upper Oakland Bay	OAKSED08	Not Reviewed	Level 2 - Data Verified	29-Sep-08	20-Oct-08	50	14	--	--	--	--
Goose Lake Remedial Investigation	GOOSLK04	Not Reviewed	Level 4 - Data Verified and Assessed for Usability in a Formal Study Report	25-Jun-02	1-Dec-10	--	--	5	6	2	34
TOTAL						**66**	**14**	**11**	**6**	**2**	**36**



Legend
🟥 SIMPS12 (2012)
● BuddOakDioxins (2011)
🟧 RCOO0012 (2011)
● SHELTON WWTP (2010)
● OAKSED08 (2008)
🟨 GOOSLK04 (2002 - 2010)
Goose Lake Site
Oakland Bay
Shelton Harbor
Hammersley Inlet
Source: Esri, i-cubed, USDA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community
Goose Lake Site
Inactive Landfill
Former Disposal Lagoons
Goose Lake
Drainage Ravine
Source: Esri, i-cubed, USDA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community
Shelton Harbor
Source: Esri, i-cubed, USDA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community

Appendix B

Oakland Bay
Sediment Dioxin/Furan Congener Data Set

Appendix B. Oakland Bay Sediment Dioxin/Furan Congener Data Set

Study	EIM Study ID	Sample ID	Latitude	Longitude	Upper Depth (cm)	Lower Depth (cm)	Total TEQ[1] (ng/kg)	Dioxin Congeners[2] (ng/kg)							Furan Congeners[2] (ng/kg)									
								2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-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	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
DMMP 2012	SIMPS12	G1_0-1ft	47.20937	-123.09205	0	30.5	9.30	-0.19	2.02	4.23	10.2	5.45	203	1540	1.56	-0.34	2.9	4.5	2.16	-1.4	2.93	53.3	3.25	139
PSAMP 2011	BuddOakDioxins	OB-10S_0-2cm	47.23762	-123.04956	0	2	55.00	1.54	8.61	16.9	63.1	35.7	1240	10700	5.18	5.23	11.5	37.8	15.7	6.55	25.6	459	24.9	1230
PSAMP 2011	BuddOakDioxins	OB-10S_2-10cm	47.23762	-123.04956	2	10	11.00	-0.271	1.8	3.76	11.5	7.55	240	1940	1.51	1.25	2.71	7.62	3.52	1.44	4.94	89	4.6	261
PSAMP 2011	BuddOakDioxins	OB-12.5S_0-2cm	47.25125	-123.03525	0	2	32.00	1.37	5.39	9.47	33.1	20.6	711	5150	3.36	3.15	6.94	21.9	8.83	4.08	15.4	249	14	618
PSAMP 2011	BuddOakDioxins	OB-12.5S_2-10cm	47.25125	-123.03525	2	10	40.00	1.51	6.58	11.6	43.8	25.3	844	6360	3.63	4.08	9.4	29.8	12.9	5.03	19.4	296	17.8	734
PSAMP 2011	BuddOakDioxins	OB-227S_0-2cm	47.21257	-123.08407	0	2	8.80	0.818	1.27	1.83	8.89	4.45	188	1820	1.46	0.948	2.38	5.79	1.84	1.14	3.34	55	3.49	162
PSAMP 2011	BuddOakDioxins	OB-227S_2-10cm	47.21257	-123.08407	2	10	4.30	-0.186	1.1	1.04	4.22	1.85	82.6	814	0.771	0.457	1.24	2.47	0.948	0.585	1.59	23.8	1.33	61.8
PSAMP 2011	BuddOakDioxins	OB-232S_0-2cm	47.22068	-123.06149	0	2	2.10	-0.269	-0.347	-0.747	2.45	1.43	49.6	415	0.55	-0.371	0.546	1.65	-0.317	-0.701	0.988	16.2	1.28	45.1
PSAMP 2011	BuddOakDioxins	OB-232S_2-10cm	47.22068	-123.06149	2	10	49.00	1.61	7.88	14.9	56.7	32.2	1110	8740	6.04	5.67	11.3	32.4	14.1	5.87	21.1	375	19.5	989
PSAMP 2011	BuddOakDioxins	OB-636S_0-2cm	47.20758	-123.08358	0	2	27.00	1.29	4.03	6.86	28.8	14.2	625	5270	3.73	3.12	6.47	17.8	6.81	3.21	10.4	203	11.1	579
PSAMP 2011	BuddOakDioxins	OB-636S_2-10cm	47.20758	-123.08358	2	10	36.00	1.55	5.31	12.7	50	33.6	764	5590	4.44	4.12	7.92	20.6	7.72	3.42	11.3	215	11.9	599
Ecology 2013	RCOO0012	Gold-1_0-2cm	47.20950	-123.09490	0	2	0.63	0.0275	0.122	0.15	0.733	0.362	13.9	250	-0.0577	0.0796	0.0805	0.347	0.111	0.0401	0.158	4.18	0.195	14.1
Ecology 2013	RCOO0012	Shelton-1_0-2cm	47.21340	-123.09270	0	2	8.70	0.313	1.72	2.7	11.8	6.72	215	1820	0.607	1.05	1.14	3.77	1.9	-0.184	2.84	45.1	2.09	185
Ecology 2013	RCOO0012	Shelton-2_0-2cm	47.21370	-123.09790	0	2	5.80	0.333	1.42	1.76	7.25	4.9	123	1080	0.678	0.598	0.723	1.77	1.09	-0.164	1.62	27.1	1.14	136
City of Shelton 2010	SHELTON WWTP	SH-D1_0-10cm	47.20920	-123.07302	0	10	0.41	-0.0309	-0.0242	-0.0529	0.552	0.222	12.2	110	-0.0843	-0.0414	-0.0401	0.453	0.149	-0.0891	0.204	4.86	-0.078	19
City of Shelton 2010	SHELTON WWTP	SH-D2_0-10cm	47.20930	-123.07342	0	10	0.37	-0.0667	-0.0336	-0.0778	0.428	0.172	11.3	95.8	-0.0519	-0.0549	-0.0552	0.326	-0.0934	-0.129	-0.112	4.42	-0.111	13.6
City of Shelton 2010	SHELTON WWTP	SH-D3_0-10cm	47.20900	-123.07275	0	10	0.37	-0.0592	-0.0374	-0.0816	0.423	0.224	10.6	83.6	0.269	-0.0502	-0.05	-0.191	-0.185	-0.257	-0.216	3.9	-0.114	12.6
Herrera 2010	OAKSED08	HI-02-SS_0-10cm	47.20582	-123.06266	0	10	3.20	0.085	0.574	0.954	4.29	2.87	72.1	629	0.301	0.304	0.477	2.39	0.789	0.079	0.728	24.2	1.53	66.9
Herrera 2010	OAKSED08	HI-03-SS_0-10cm	47.20655	-123.07260	0	10	13.00	0.515	2.65	3.51	18.5	12.4	224	1790	1.86	1.79	3.22	9.8	3.27	0.318	2.9	71.7	4.96	193
Herrera 2010	OAKSED08	HI-04-SS_0-10cm	47.20854	-123.06716	0	10	1.80	0.068	0.305	0.538	2.41	1.59	40	330	0.19	0.183	0.279	1.37	0.457	0.048	0.442	14.2	0.911	41.4
Herrera 2010	OAKSED08	HI-05-SS_0-10cm	47.20907	-123.07374	0	10	2.20	0.068	0.34	0.684	2.63	1.8	48.8	420	0.199	0.213	0.358	1.64	0.523	0.048	0.55	18.3	1.15	53.1
Herrera 2010	OAKSED08	HI-06-SS_0-10cm	47.21238	-123.07101	0	10	9.70	0.277	1.86	2.85	13.4	9.59	184	1370	1.2	1.12	1.96	7.96	2.59	0.229	2.24	64.1	3.98	152
Herrera 2010	OAKSED08	HI-07-SS_0-10cm	47.21444	-123.07699	0	10	2.70	0.082	0.377	0.708	3.44	2.22	64.2	577	0.197	0.23	0.369	2.31	0.717	0.078	0.684	24.7	1.59	73.8
Herrera 2010	OAKSED08	OB-01-SS_0-10cm	47.21888	-123.07887	0	10	4.40	0.125	0.749	1.37	5.67	3.92	97.4	833	0.387	0.445	0.566	3.54	1.17	0.12	1.14	36.8	2.21	112
Herrera 2010	OAKSED08	OB-02-SS_0-10cm	47.21931	-123.07390	0	10	17.00	0.567	2.8	5.09	20.3	14.6	345	2570	2.19	2.16	2.84	14.7	4.59	0.408	4.29	133	7.99	350
Herrera 2010	OAKSED08	OB-03-SS_0-10cm	47.21790	-123.07007	0	10	29.00	0.828	4.41	8.23	37.3	24.6	664	5830	2.41	2.88	3.95	22.9	8.04	0.689	7.56	256	13.9	783
Herrera 2010	OAKSED08	OB-04-SS_0-10cm	47.22479	-123.07050	0	10	27.00	1.19	5.44	7.09	38.8	21.5	467	3480	3.87	3.37	5.99	22.8	7.07	0.514	7.06	186	10.1	488
Herrera 2010	OAKSED08	OB-05-SS_0-10cm	47.22489	-123.06252	0	10	28.00	0.734	4.26	8.06	34	22.7	634	5240	2.25	2.58	3.76	24.1	7.95	0.596	7.27	246	12.9	759
Herrera 2010	OAKSED08	OB-06-SS_0-10cm	47.22245	-123.05407	0	10	43.00	1.1	6.83	13.4	55.4	38.6	965	8080	3.06	4.23	5.62	34.2	12	0.964	11.3	405	21.3	1230
Herrera 2010	OAKSED08	OB-07-SS_0-10cm	47.22726	-123.04334	0	10	8.70	0.233	1.58	2.91	12.1	8.69	181	1410	0.692	0.914	1.15	6.31	2.36	0.229	2.2	68.6	3.94	171
Herrera 2010	OAKSED08	OB-08-SS_0-10cm	47.22345	-123.03392	0	10	37.00	0.756	6.84	14	45.3	40	856	4860	2.8	3.5	4.5	25.8	10.5	0.763	9.71	269	16.5	529
Herrera 2010	OAKSED08	OB-09-SS_0-10cm	47.23157	-123.05593	0	10	38.00	0.982	6.2	12.5	48.2	35.3	849	7230	2.85	3.55	4.83	32	10.9	0.925	10.4	333	18.3	938
Herrera 2010	OAKSED08	OB-10-SS_0-10cm	47.23761	-123.04958	0	10	54.00	1.07	8.66	17	64	47.5	1250	11600	3.6	5.23	6.75	43.5	15.3	1.28	13.5	455	26.3	1180
Herrera 2010	OAKSED08	OB-11-SS_0-10cm	47.24819	-123.03303	0	10	44.00	0.84	7.03	13.8	55.8	40.5	982	7890	2.64	4.22	5.27	35.9	13.7	1.07	11.9	397	21.9	1060
Herrera 2010	OAKSED08	OB-12-SS_0-10cm	47.25071	-123.03991	0	10	54.00	1.21	8.44	18.1	68	53.8	1210	9710	3.68	5.24	6.81	41.9	16.8	1.47	15.2	502	28.2	1180
Herrera 2010	OAKSED08	OB-13-SS_0-10cm	47.25315	-123.03273	0	10	48.00	1.16	8.01	15.5	57.3	48.8	1070	7220	3.18	4.58	5.47	41.6	14.6	1.06	13.9	427	28.1	1220
Herrera 2010	OAKSED08	OB-14-SS_0-10cm	47.25595	-123.02082	0	10	22.00	0.473	3.75	6.69	27.5	19.8	478	4060	1.59	2.07	2.95	18.1	6.7	0.645	5.93	182	11	412
Herrera 2010	OAKSED08	OB-17-WS_0-10cm	47.21575	-123.08204	0	10	13.00	0.519	2.48	3.96	17.5	11.8	280	1580	1.57	1.61	2.37	10.9	3.48	0.34	3.15	95.6	5.36	268
Herrera 2010	OAKSED08	OB-18-WS_0-10cm	47.21567	-123.06921	0	10	33.00	0.793	5.21	9.86	42.9	28.7	768	6490	2.68	3.12	4.16	24.8	8.82	0.72	8.46	290	15.7	867
Herrera 2010	OAKSED08	OB-19-WS_0-10cm	47.22643	-123.05271	0	10	45.00	0.984	7.3	13.6	60.7	40.6	1040	9640	3.49	4.22	5.78	34.4	12.4	1.09	10.8	379	21.6	1130
Herrera 2010	OAKSED08	SH-01-SS_0-10cm	47.21335	-123.08389	0	10	23.00	0.978	3.88	4.74	30.3	16.7	468	4850	3.78	2.85	4.91	15.7	5.15	0.482	4.52	176	10	652
Herrera 2010	OAKSED08	SH-02-SS_0-10cm	47.21350	-123.08750	0	10	53.00	2.45	11.6	21	76.8	50.6	1040	8030	5.21	5.5	8.17	27.2	10.5	0.98	9.37	290	16.2	947
Herrera 2010	OAKSED08	SH-03-SS_0-10cm	47.21254	-123.09011	0	10	180.00	2.88	15.4	29.3	220	85.9	5590	67600	7.47	12.6	20.4	126	37.4	4.04	29.9	1700	98.8	7660
Herrera 2010	OAKSED08	SH-04-SS_0-10cm	47.21270	-123.09184	0	10	58.00	1.33	7.91	15.9	75.2	44	1550	24200	3.89	4.76	6.84	31.2	11.9	1.15	10.7	368	24.1	1210
Herrera 2010	OAKSED08	SH-05-SS_0-10cm	47.21152	-123.09187	0	10	27.00	0.621	3.44	6.73	31.7	19.2	712	12500	1.66	2.31	3.22	16.1	5.8	0.556	4.71	179	11.5	607
Herrera 2010	OAKSED08	SH-07-SS_0-10cm	47.21024	-123.08914	0	10	6.50	0.295	1.17	1.97	8	5.09	152	1810	0.581	0.592	0.801	3.46	1.33	0.132	1.2	42.8	2.91	157
Herrera 2010	OAKSED08	SH-09-SS_0-10cm	47.21065	-123.08565	0	10	11.00	0.351	1.72	2.95	14	8.67	247	2470	0.341	1.01	1.47	7.27	2.63	0.225	2.25	87.4	5.4	292

Appendix B. (Continued)

Study	EIM Study ID	Sample ID	Latitude	Longitude	Upper Depth (cm)	Lower Depth (cm)	Total TEQ[1] (ng/kg)	Dioxin Congeners[2] (ng/kg)							Furan Congeners[2] (ng/kg)									
								2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-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	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
Herrera 2010	OAKSED08	SH-11-SS_0-10cm	47.20798	-123.09420	0	10	49.00	5.72	14.6	16.8	40.1	32.7	498	3900	20.5	10.8	14.2	24.4	10.4	1.04	8.71	180	10.7	562
Herrera 2010	OAKSED08	SH-12-SS_0-10cm	47.20726	-123.09411	0	10	100.00	5.67	20.1	32	122	71.3	1980	18600	22.1	15.5	21.2	64.3	22	1.94	18	605	33.6	1970
Herrera 2010	OAKSED08	SH-13-SS_0-10cm	47.20636	-123.09272	0	10	110.00	4.09	15.6	28.8	121	79.8	2870	28900	13.4	12.7	17	72.4	20.9	2.48	18.3	652	38.9	1880
Herrera 2010	OAKSED08	SH-14-SS_0-10cm	47.20874	-123.08076	0	10	35.00	1.23	5.67	8.38	44.5	24.1	815	7300	3.68	3.73	6.44	24.6	8.38	0.669	7.49	300	15.2	1160
Herrera 2010	OAKSED08	SH-15-SS_0-10cm	47.21006	-123.07723	0	10	1.90	0.061	0.297	0.525	2.34	1.59	41.6	373	0.138	0.177	0.271	1.43	0.521	0.047	0.505	18.2	1.13	45
Herrera 2010	OAKSED08	SH-16-SS_0-10cm	47.21361	-123.07812	0	10	1.00	0.043	0.162	0.288	1.28	0.811	22.2	203	0.079	0.077	0.157	0.786	0.296	0.026	0.284	10.2	0.579	22.4
Herrera 2010	OAKSED08	SH-18-WS_0-10cm	47.20872	-123.09410	0	10	67.00	-0.0976	11.2	18.2	85.4	48.8	1610	14600	11.5	8.43	12.5	51.6	16.5	1.26	13.6	558	29.1	1820
Herrera 2010	OAKSED08	SH-19-WS_0-10cm	47.20789	-123.09243	0	10	79.00	3.69	13	17.6	99.8	45.1	1660	14500	16.3	10.9	16.6	61.4	19.1	1.51	16.7	688	36.3	2260
Herrera 2010	OAKSED08	SH-20-WS_0-10cm	47.20688	-123.09053	0	10	51.00	1.62	7.26	13.4	62.8	35.9	1230	12400	5.35	5.29	7.88	39.4	12.9	1.1	10.6	447	24.8	1750
Herrera 2010	OAKSED08	SH-21-WS_0-10cm	47.20877	-123.08970	0	10	54.00	1.72	8.34	15.7	70.8	43.2	1420	12900	5.08	5.62	7.56	33.4	11.4	1.02	11	393	22.2	1230
Herrera 2010	OAKSED08	SH-22-WS_0-10cm	47.20802	-123.08683	0	10	47.00	0.885	4.23	9.27	61.6	39.5	1810	16100	4.59	4.18	5.81	22.5	7.18	0.792	7.41	197	11	490
Herrera 2010	OAKSED08	SH-23-WS_0-10cm	47.20827	-123.08448	0	10	29.00	1.19	3.93	7.04	36.1	28.6	712	6340	2.3	2.65	4.27	22	7.13	0.611	6.2	217	13.5	634
Herrera 2010	OAKSED08	SH-24-WS_0-10cm	47.20653	-123.08447	0	10	32.00	1.05	5.01	8.19	42.3	22.1	717	6430	2.92	3.25	5.22	26.5	8.21	0.666	7.51	298	16.1	1030
Herrera 2010	OAKSED08	SH-25-WS_0-10cm	47.20699	-123.08094	0	10	38.00	1.59	6.82	9.34	48.5	26.9	820	7400	4.01	4.12	6.23	26.2	9.18	0.715	8.07	330	16.7	1020
Herrera 2010	OAKSED08	SH-26-WS_0-10cm	47.21162	-123.08993	0	10	5.20	0.211	0.951	1.88	6.56	5.34	113	1030	0.325	0.433	0.602	3.16	1.29	0.111	1.02	37.5	2.42	105
Herrera 2010	OAKSED08	SH-27-WS_0-10cm	47.21218	-123.08789	0	10	3.80	0.143	0.657	1.34	5.48	3.48	83.7	756	0.284	0.373	0.488	2.32	0.878	0.075	0.896	29.2	1.53	80.2
Herrera 2010	OAKSED08	SH-28-WS_0-10cm	47.21042	-123.08198	0	10	30.00	0.813	4.39	6.82	40.3	21.8	654	5860	3.89	3.14	5.74	27.1	7.86	0.66	6.41	262	15.3	735
Herrera 2010	OAKSED08	SH-29-WS_0-10cm	47.21188	-123.07818	0	10	2.10	0.073	0.339	0.606	2.6	1.85	45.4	394	0.163	0.179	0.279	1.56	0.595	0.052	0.5	18.7	1.07	50
Herrera 2010	OAKSED08	SH-30-WS_0-10cm	47.21435	-123.08402	0	10	36.00	1.84	7.39	9.84	48.4	31.1	649	5720	5.51	4.56	8.02	25.5	8.77	0.785	7.39	204	12.4	586
Herrera 2010	OAKSED08	OB-03-SC_1-2ft	47.21790	-123.07014	30.5	61	82.00	1.34	10.7	20.5	106	55.2	1910	16400	6.67	7.8	12.6	83.1	24.1	2.14	17.7	921	48.3	2320
Herrera 2010	OAKSED08	OB-06-SC_1-2ft	47.22244	-123.05409	30.5	61	180.00	2.62	20.8	39.1	232	115	4470	40800	11.8	14.3	23.7	181	51.1	5.89	39.4	2170	109	6010
Herrera 2010	OAKSED08	OB-09-SC_1-2ft	47.23157	-123.05345	30.5	61	52.00	0.707	5.48	10.2	66.2	32.5	1410	11100	3.2	4.15	6.94	52.9	15.2	1.18	12.1	644	30.1	1760
Herrera 2010	OAKSED08	OB-10-SC_1-2ft	47.23762	-123.04956	30.5	61	100.00	1.25	11.4	22.3	132	65.4	2730	23500	5.41	8.34	12.9	99.4	31	2.91	22.1	1270	70.1	4020
Herrera 2010	OAKSED08	OB-12-SC_1-2ft	47.25072	-123.03988	30.5	61	71.00	0.818	7.57	15.7	91.5	44.9	1840	13000	2.42	4.52	9.46	85.7	22.2	1.11	18.7	803	39.1	1740
Herrera 2010	OAKSED08	SH-02-SC_2-3ft	47.21351	-123.08751	61	92	14.00	0.387	3.19	6.51	20.4	14.8	255	1860	1.8	1.42	2.3	7.53	2.79	2.28	2.51	95.4	4.26	220
Herrera 2010	OAKSED08	SH-04-SC_2-3ft	47.21276	-123.09175	61	92	310.00	9.1	75.1	169	502	357	5100	48700	38.2	32.2	51.1	124	65	8.17	51.2	1500	76.3	4230
Herrera 2010	OAKSED08	SH-09-SC_2-3ft	47.21071	-123.08575	61	92	2.70	0.092	0.233	0.517	3.63	1.74	67.9	894	0.217	0.31	0.564	2.31	0.683	0.089	0.545	22.3	1.38	56.7
Herrera 2010	OAKSED08	SH-10-SC_2-3ft	47.21158	-123.08324	61	92	900.00	9.51	31.4	61.6	1170	237	32000	171000	23.1	40.7	88.7	1110	211	15.7	118	14100	801	59400
Herrera 2010	OAKSED08	SH-12-SC_1-2ft	47.20734	-123.09408	30.5	61	200.00	9.93	43	66.9	251	152	3680	34900	46.8	27.5	38.2	127	41.4	3.67	55.5	1270	72.7	4380
Herrera 2010	OAKSED08	SH-12-SC_2-3ft	47.20734	-123.09408	61	92	310.00	12.7	65.3	135	415	268	5820	53400	54.1	34.1	49.2	173	59.9	5.13	46.9	2200	98.8	6170
Herrera 2010	OAKSED08	SH-13-SC_1-2ft	47.20636	-123.09272	30.5	61	13.00	0.337	1.53	2.78	16.4	7.27	330	3290	1.25	1.04	1.57	8.85	2.73	0.563	1.89	156	8.05	475
Herrera 2010	OAKSED08	SH-13-SC_2-3ft	47.20636	-123.09272	61	92	16.00	0.321	1.26	1.74	20.3	5.53	516	8090	1.07	0.795	1.35	8.46	2.84	0.219	2.03	207	12.6	556
Herrera 2010	OAKSED08	SH-14-SC_2-3ft	47.20875	-123.08078	61	92	8.00	0.433	1.4	1.44	10.2	4.04	149	1220	1.46	1.15	1.55	6.48	1.97	0.17	1.76	96.9	3.95	242
Herrera 2010	OAKSED08	SH-10-SS_0-10cm	47.21152	-123.08326	0	10	35.00	0.477	2.1	3.41	48.3	11.2	754	3500	1.75	4.01	14.3	73.1	12.5	1.21	7.06	336	31.7	1230

Notes:

1. Total TEQ to 2,3,7,8-TCDD, with non-detected congeners equal to 0.5*MDL

2. Non-detected congeners are listed as negative values equivalent to the MDL

Appendix C

Chemometric Evaluation of Oakland Bay Dioxin/Furan Data

Table of Contents

Figures

Tables

Appendices

List of Acronyms

ALS	Alternating Least Squares
dioxin	polychlorinated dibenzo-*p*-dioxin
DMMP	Dredged Material Management Program
EIM	Environmental Information Management
E & E	Ecology and Environment, Inc.
FWEC	Foster Wheeler Environmental Corporation
furan	polychlorinated dibenzofuran
HCA	Hierarchical Cluster Analysis
HFB	hog fuel boiler
PCA	principal components analysis
PCP	pentachlorophenol
PSAMP	Puget Sound Ambient Monitoring Program
RI	remedial investigation
TEF	toxicity equivalency factor
TEQ	toxic equivalency

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1.0 Introduction

The chemometric evaluation process involves extracting information from chemical systems by data-driven means, typically through the application of multivariate statistics. When a data analysis scenario includes the collection of more than one or two measurements, interpretation of the results in a univariate sense can become tedious if not misleading. Often these measurements are correlated rather than being completely independent. Univariate analysis is incapable of detecting these correlations and can misrepresent trends and relationships that result from correlation. A multivariate approach utilizes tools and techniques from mathematics and statistics to guide interpretation of complex and potentially correlated data.

In this chemometric study, multivariate methods were applied to evaluate important congeners of polychlorinated dibenzo-p-dioxins (dioxins) and dibenzofurans (furans) obtained from chemical analysis of Oakland Bay sediment samples. The chemometric process consisted of the following steps:

1. Data compilation and screening;
2. Data scaling;
3. Multivariate chemical source unmixing
4. Source interpretation

This appendix provides a detailed description of these chemometric analysis steps. The results of this evaluation reveal several patterns apparent in the sediments of Oakland Bay that suggest dioxin/furan contributions from specific source types.

2.0 Data Compilation and Screening

2.1 Data Compilation

The data used for chemometric evaluation consist of analytical results for the 17 priority dioxin/furan congeners from samples collected within Oakland Bay and the surrounding watershed. Samples collected within and in proximity to Goose Lake were also included, as the lake, an adjacent landfill, and nearby disposal lagoons received spent sulfite liquor and solid waste from the Rayonier Mill at Shelton Harbor. Tissue samples were not included for evaluation, as metabolism can alter the dioxin/furan profile between sediments and receptor organisms.

The majority of dioxin/furan data evaluated were accessed through Ecology's Environmental Information Management (EIM) database, which was used as a tool to query and download existing data. Complete analytical results for these studies were downloaded from EIM and were subsequently reviewed relative to the dates of sample collection, sample depths, data validation levels, and detection limits (see Appendix C1 of the study report). The relevant studies and their EIM Study ID's are presented below:

- SIMPS12 - Simpson Lumber Anti-degradation Evaluation and Upland Disposal Evaluation of Dioxins (DMMP 2012);
- BuddOakDioxins - Budd Inlet and Oakland By Dioxin Study (PSAMP 2011);
- RCOO0012 - Dioxin in Surface Water Sources to Oakland Bay (Ecology 2013);
- SHELTON WWTP - Shelton WWTP Outfall Baseline Sediment Monitoring Study (City of Shelton 2010);
- OAKSED08 - Oakland Bay Sediment Characterization Study (Herrera 2010);
- GOOSLK04 - Goose Lake Remedial Investigation (GeoEngineers 2012); and

Because of their potential importance in understanding the signature of dioxin/furan sources to Oakland Bay, dioxin/furan data not present in EIM were also evaluated:

- 9 soil samples collected from the former Goose Lake landfill. Analytical results were reported in the Remedial Investigation (RI) report (GeoEngineers 2012), but are not present in EIM. Neither laboratory reports nor data validation reports for these samples were available in the final report.

- Ash, sludge, soil, and sediment samples from the Simpson Timber Company Dioxin Study, collected as part of the USEPA National Dioxin Study of the Shelton area (CH2M Hill 1987). Neither laboratory reports nor data validation reports for these samples were available in the final report.

Dioxin/furan data from all of the above studies were segregated into two data sets, each used for different purposes during evaluation:

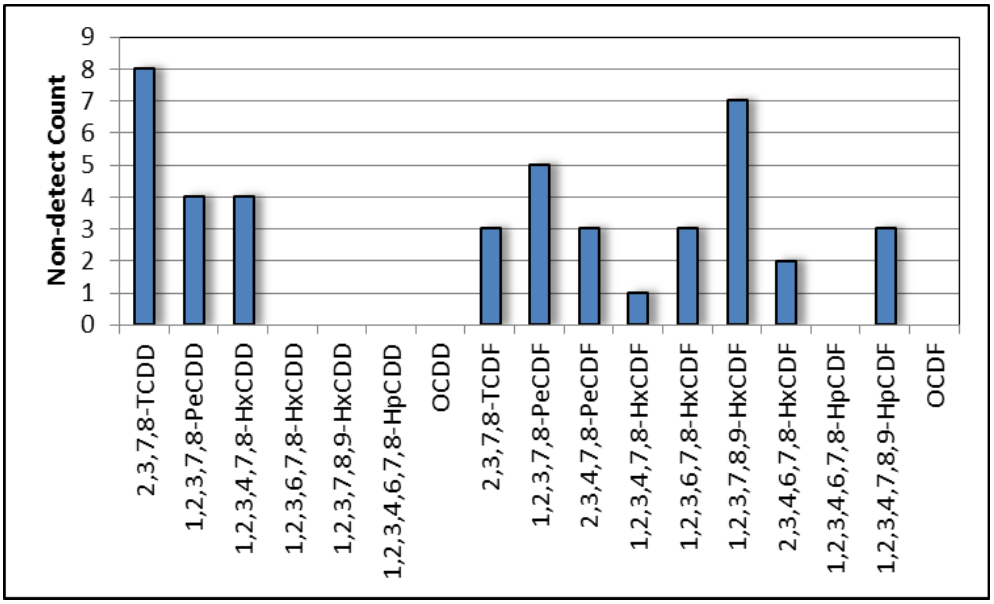
3. *Unmixing Data Set* – consists only on intertidal and subtidal sediment samples from the above references, both surface and subsurface, from Oakland Bay. This data set is used for dioxin/furan congener “unmixing” to derive chemical profiles.
4. *Comparison Data Set* – the remaining samples from the above references. This data set was added to the existing dioxin/furan source library used for comparative purposes in NewFields (2013). The combined source library is used to evaluate the likely source types contributing to profiles of the Unmixing Data Set.

2.2 Data Screening

Chemometric analyses use the patterns across samples in the profiles of the 17 dioxin/furan congeners. Where samples have numerous non-detected congeners, or where non-detected congeners contribute to a large percentage of the dioxin/furan toxic equivalency (TEQ), these profiles become less well defined. For these reasons it is important to screen samples from chemometric analysis whose profiles are biased by non-detects.

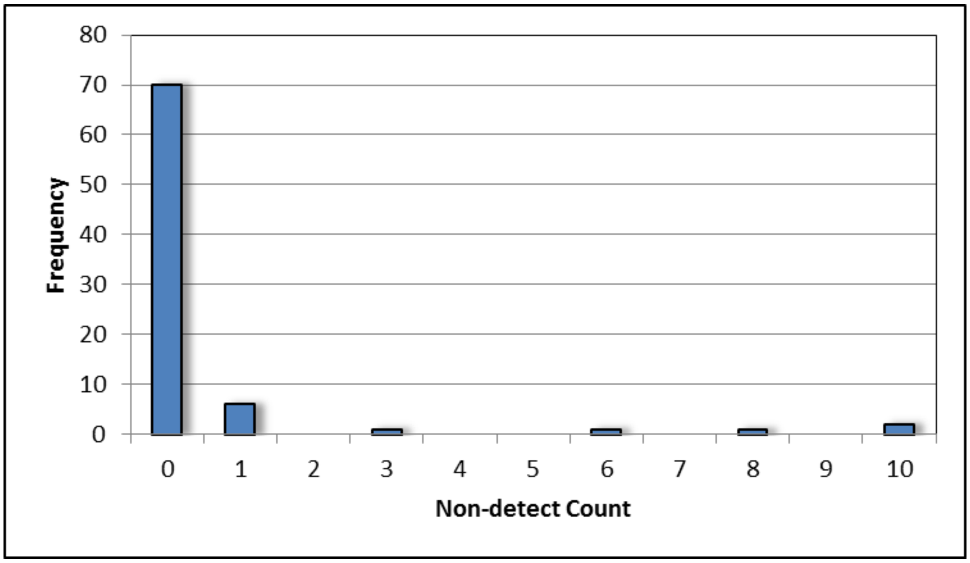
Dioxin/furan congener concentrations of the un-screened Unmixing Data Set are presented in Appendix C2 of the study report. Of the 81 samples in this data set for which 17 congeners were measured, there were a total of 43 non-detect values, approximately 3 percent. However, these non-detects were not uniformly distributed. The two congeners for which non-detects were most frequent were 2,3,7,8-TCDD (8 samples) and 1,2,3,7,8,9-HxCDF (7 samples). The distribution of non-detects is shown in Figure 1.

Figure 1. Distribution of Non-Detects across Congeners



The frequency of non-detects within samples is shown in Figure 2. All congeners were detected in the majority (86 percent) of sediment samples. The frequency of non-detects becomes more pronounced for samples with very low TEQ values.

Figure 2. Frequency of Non-Detects in Unmixing Data Set samples



Samples were screened from further chemometric analysis based on the following criteria:

- More the 3 non-detected congeners; or
- Non-detected congeners contributing to more than 2 percent of the total dioxin/furan TEQ concentration, when non-detected congeners are assigned a value of one-half the detection limit.

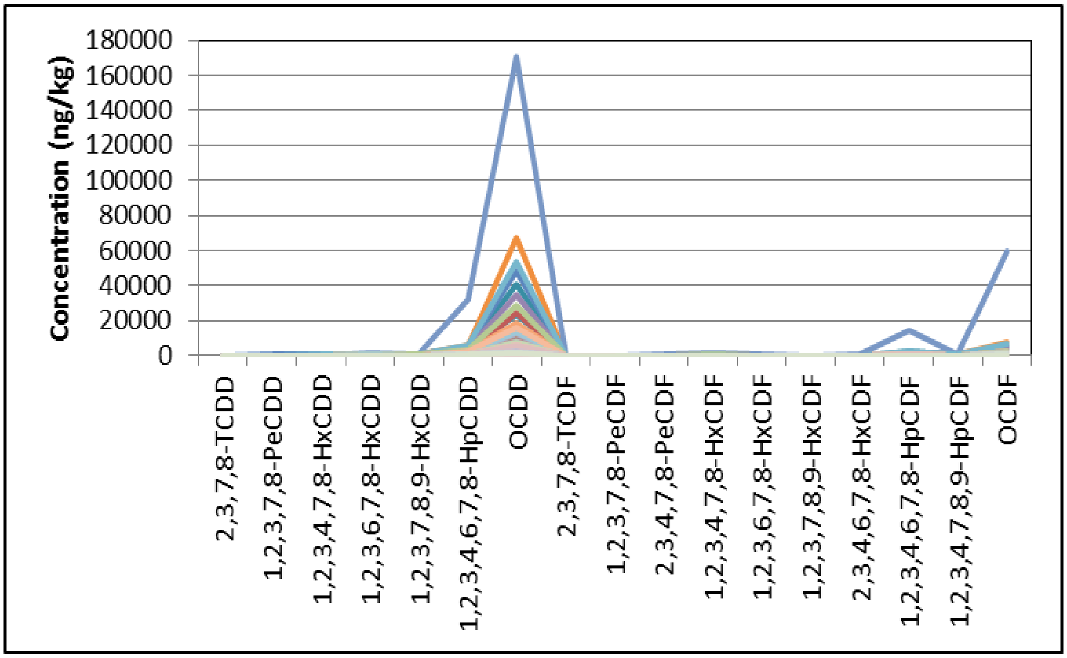
This screening resulted in a reduction from 81 to 77 samples. Of the 4 samples excluded in this manner, none had a TEQ value greater than 2 ng/kg.

3.0 Data Scaling

Dioxin/furan sample results were reported from the lab as bulk congener concentrations, in nanograms per kilogram (ng/kg) dry weight. It was typical for certain congeners, such as the octa-chloro dioxin congener (OCDD), to be present at concentrations many of orders of magnitude greater than other congeners. If multivariate analysis were to be performed on this raw concentration data in which the measurements vary by such large amounts, those compounds with the greatest concentration would drive the analysis. To allow interpretation of the differences in congener fingerprints, it is customary to scale the variables such that they are all roughly in the same order of magnitude.

For example, the bulk congener data can be shown as a line plot (Figure 3). This figure shows the dioxin/furan data of the 77 samples retained in the Unmixing Data Set without any scaling of the congener concentrations. Each trace in this figure presents one sample plotted as a function of congener. Plotted in this way, it is clear that the overwhelming contribution to overall intensity comes from OCDD, while the lesser-chlorinated dioxins and furans contribute relatively little intensity. For this reason, concentrations for many of the congeners are not even apparent in Figure 3.

Figure 3. Bulk Congener Profiles of Unmixing Data Set



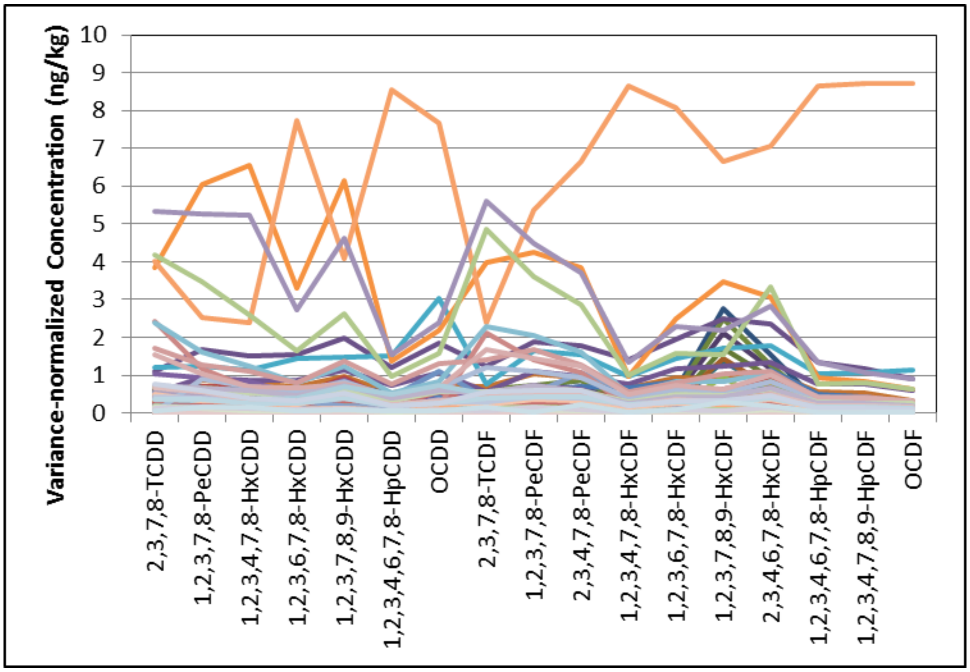
There are different approaches to accomplish variable scaling; however different methods may not produce equivalent results. Two methods of variable scaling were explored:

1. *Variance-Scaling* – each congener concentration is scaled by the standard deviation of the measure across all samples.
2. *TEF-Scaling* – congener concentrations are scaled to congener-specific toxicity equivalency factor (TEF) values.

3.1 Variance-Scaling

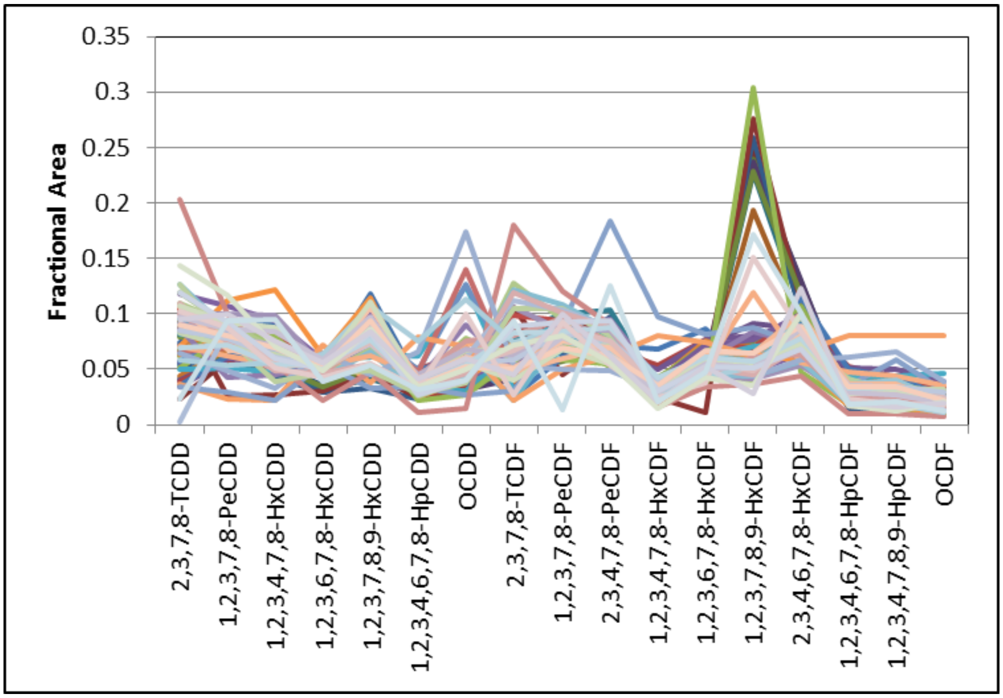
In Figure 4, the data from Figure 3 have been scaled by the standard deviations of the individual congeners across the set of samples (Wold et al. 1987; Kramer 1998; Craig et al. 2006). The result is that each scaled congener has a variance of 1. There remains variation in magnitude for the different congeners but patterns become more discernible.

Figure 4. Variance-scaled profiles of the Unmixing Data Set



It is customary to further normalize the data to account for different sample sizes such that variation in absolute concentration is minimized. Although various methods of normalization are used in the multivariate field, area percent normalization is typical for chromatography data and was used in this study. Area percent normalization is applied on a sample-by-sample basis after the entire data set has undergone variance normalization. For example, Figure 5 shows area percent normalized data from Figure 4. All individual sample profiles in Figure 5 have an area of 1. Data in this form is what is used as input for multivariate analyses; the sample profiles shown in Figure 5 are those that the chemometric model will unmix.

Figure 5. Area-normalized variance-scaled profiles of the Unmixing Data Set



In Figure 5 it can be seen that two of the congeners with the most variability among sample profiles are 2,3,7,8-TCDD and 1,2,3,7,8,9-HxCDF. These also happen to be the congeners most frequently not detected for the data set (Figure 1). Such a result suggest that it may be prudent to remove the congeners 2,3,7,8-TCDD and 1,2,3,7,8,9-HxCDF from further analysis using variance-scaling methods. This also highlights the first of three major drawbacks of variance-scaling:

1. There is a risk that a variable of little importance and of intensities in the noise level will be magnified to the same importance as variables with real, diagnostic signals.
2. The scaling factor is a function of the samples that are included in the calculation and would therefore change if different samples were processed.
3. Because the scaling factors are specific to the data set being scaled, the resulting congener profiles cannot be directly compared to profiles outside of the data set, such as a profile library.

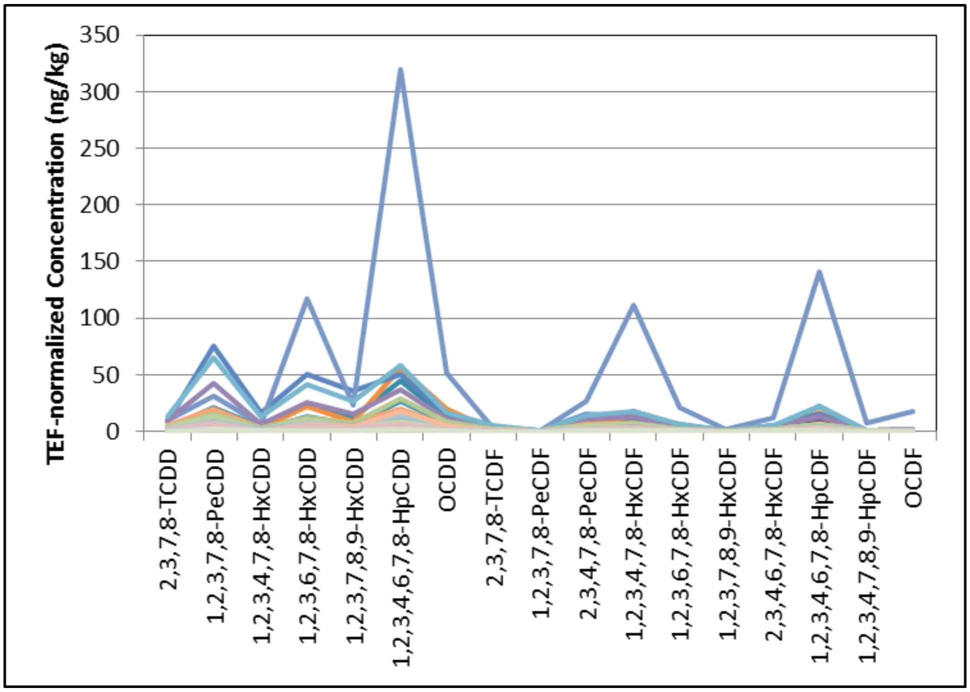
3.2 TEF-Scaling

Because of the above variance-scaling shortcomings, the alternative method of TEF-scaling for dioxin/furan congener data has frequently been applied (Lohmann and Jones 1998; Alcock et al. 2002; Hilscherova et al. 2003; E & E and Glass 2011; NewFields 2013). This method of scaling based on congener toxicity relative to 2,3,7,8-TCDD has three distinct advantages over variance-scaling:

1. Scaling factors (congener-specific TEFs) are independent of the samples in the data set being processed.
2. Because the scaling factors can be applied universally to dioxin/furan congener data, analysis results can be compared profile libraries scaled by the same means.
3. Chemometric analysis of TEF-scaled data identifies dioxin/furan profiles that contribute to a significant portion of sample TEQ. This useful for decision making, as human health risk, ecological risk, and cleanup criteria are all based on TEQ.

In Figure 6, the data from Figure 3 have been scaled by the TEFs (Table 1). As with variance-scaling, this initial scaling of the raw concentration data reveals pattern among the different congeners, however there is considerable variation in magnitude.

Figure 6. TEF-scaled profiles of the Unmixing Data Set

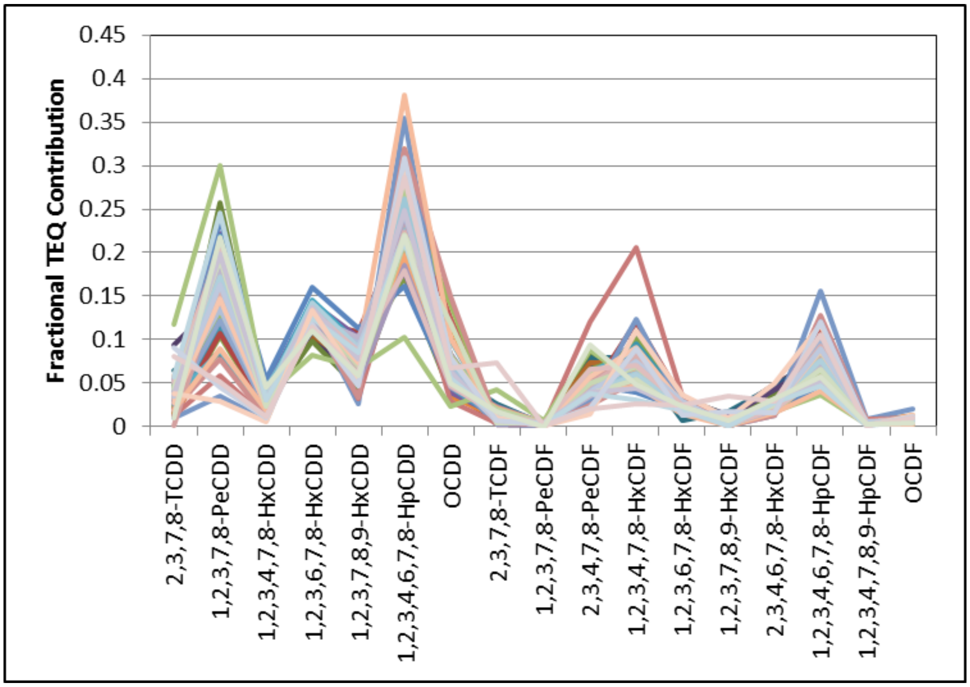


As with the variance-scaled results, further normalization by percent area is performed such that each sample profile has a congener sum of 1 (Figure 7). Because the results in Figure 7 were first TEF-normalized, the values for each congener in a sample's profile is the congener's fractional contribution the sample's total dioxin/furan TEQ.

Table 1. Dioxin/Furan Homologue Groups and 17 Congeners of Greatest Concern

Homologue Group	Congener	Abbreviation	TEF
Dioxins			
Tetrachlorodibenzo-p-dioxins		TCDD	--
	2,3,7,8-tetrachlorodibenzo-p-dioxin	2,3,7,8-TCDD	1
Pentachlorodibenzo-p-dioxins		PeCDD	--
	1,2,3,7,8-pentachlorodibenzo-p-dioxin	1,2,3,7,8-PeCDD	1
Hexachlorodibenzo-p-dioxins		HxCDD	--
	1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	1,2,3,4,7,8-HxCDD	0.1
	1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	1,2,3,6,7,8-HxCDD	0.1
	1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	1,2,3,7,8,9-HxCDD	0.1
Heptachlorodibenzo-p-dioxins		HpCDD	--
	1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	1,2,3,4,6,7,8-HpCDD	0.01
Octachlorodibenzo-p-dioxin	Octachlorodibenzo-p-dioxin	OCDD	0.0003
Furans			
Tetrachlorodibenzofurans		TCDF	--
	2,3,7,8-tetrachlorodibenzofuran	2,3,7,8-TCDF	0.1
Pentachlorodibenzofurans		PeCDF	--
	1,2,3,7,8-pentachlorodibenzofuran	1,2,3,7,8-PeCDF	0.03
	2,3,4,7,8-pentachlorodibenzofuran	2,3,4,7,8-PeCDF	0.3
Hexachlorodibenzofurans		HxCDF	--
	1,2,3,4,7,8-hexachlorodibenzofuran	1,2,3,4,7,8-HxCDF	0.1
	1,2,3,6,7,8-hexachlorodibenzofuran	1,2,3,6,7,8-HxCDF	0.1
	1,2,3,7,8,9-hexachlorodibenzofuran	1,2,3,7,8,9-HxCDF	0.1
	2,3,4,6,7,8-hexachlorodibenzofuran	2,3,4,6,7,8-HxCDF	0.1
Heptachlorodibenzofurans		HpCDF	--
	1,2,3,4,6,7,8-heptachlorodibenzofuran	1,2,3,4,6,7,8-HpCDF	0.01
	1,2,3,4,7,8,9-heptachlorodibenzofuran	1,2,3,4,7,8,9-HpCDF	0.01
Octachlorodibenzofuran	Octachlorodibenzofuran	OCDF	0.0003

Figure 7. Area-normalized TEF-scaled profiles of the Unmixing Data Set



Unlike Figure 5, where sample profile variation was most apparent for frequently non-detected congeners, profile variation in Figure 7 is dominated by frequently detected congeners. Also in Figure 7, a single sample (SH-10-SS) stands out as having unusually high proportions of the furan 1,2,3,4,7,8-HxCDF compared to the remaining data set. This sample was treated as a potential outlier during further evaluation, and was confirmed as an outlier during multivariate analysis.

4.0 Unmixing Model

The software Pirouette (Infometrix, Bothell, WA) was used for the application of chemometric modeling. The mathematical model of the *Unmixing Data Set* produces the following component results:

- The number of significant factors contributing to the sample measurements;
- The chemical patterns of model factors (dioxin/furan TEQ profiles);
- The fractional contribution of each model factor to each sample total TEQ; and
- A characterization of the model's goodness-of-fit through residuals (congener-by-congener differences between modeled and measured values for every sample) and deviations of summed factor fractional contributions from 1 (non-closure deviations; see below).

Chemometric analyses are a form of receptor-oriented modeling. Starting from the receptor (sediment) measurements, and without any prior assumptions about the number or patterns of potential factors, the analyses mathematically derive a model of the factors – conceptually "working backwards" from receptors to sources. There are several similar mathematical approaches used for unmixing evaluations. In this study, a combination of Principal Component Analysis (PCA) and Alternating Least Squares (ALS) methods was used.

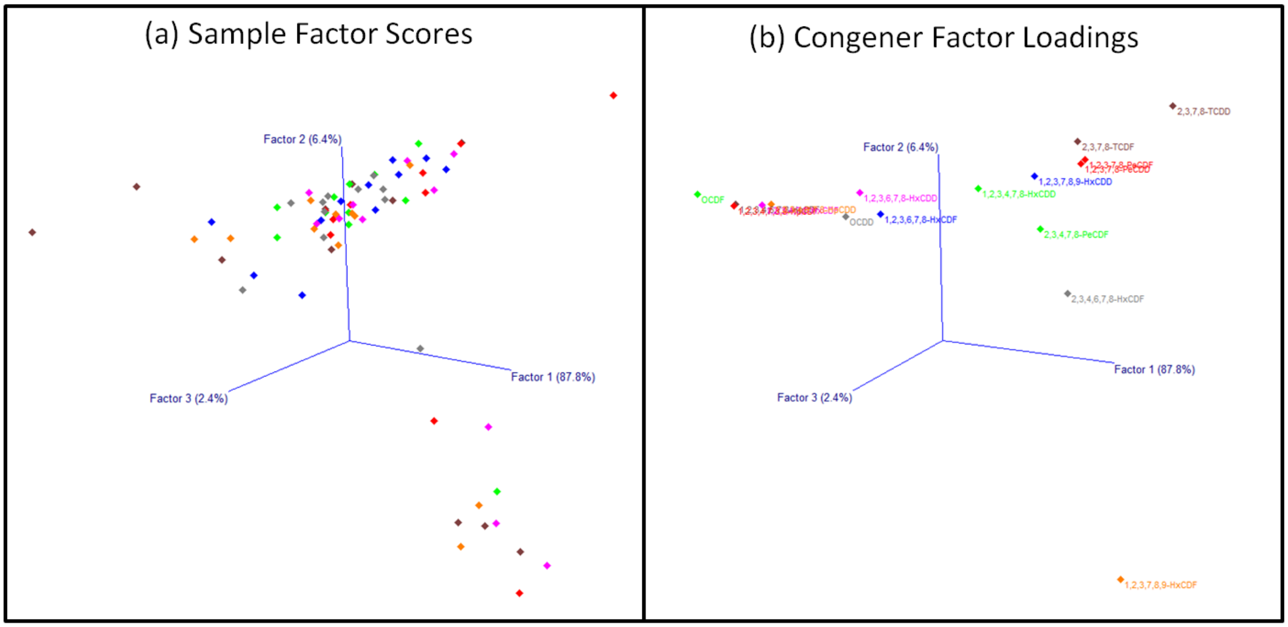
4.1 Principal Component Analysis

With 17 TEF-scaled dioxin/furan congeners defining the chemical patterns in the sample profiles, each sample can be visualized or mapped as a point in a 17-dimensional space. Samples with similar TEQ profiles would be located near one another in that 17-dimensional space. PCA attempts to reduce the number of dimensions required to map the data, while accounting for almost all of the variability in the data set. PCA factors, each representing some combination of the congeners, are determined with each added factor accounting for successively less of the overall variance.

4.1.1 Variance-Scaled PCA

Figure 8 is a 3-dimensional representation of PCA results for the variance-scaled data from Figure 5. In Figure 8a, samples are concentrated in two separate clusters, with considerable spread within each cluster. The vast majority of data set variability is explained by Factor 1 (87.8 percent). While these results appear informative, Figure 8b shows that Factor 1 has the highest congener loadings for 2,3,7,8-TCDD and 1,2,3,7,8,9-HxCDF, the two congeners previously identified as being the most frequent non-detected and generally having low measured concentrations. For these reasons, variance-scaling of the data was no longer considered a valid means of understanding dioxin/furan patterns of the *Unmixing Data Set*.

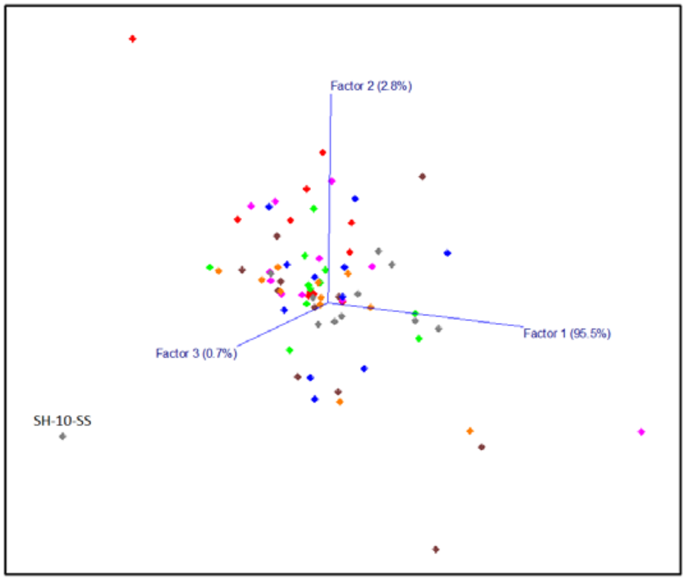
Figure 8. PCA Factor Scores (a) and Loadings (b) of Variance-scaled Unmixing Data Set



4.1.2 TEF-Scaled PCA

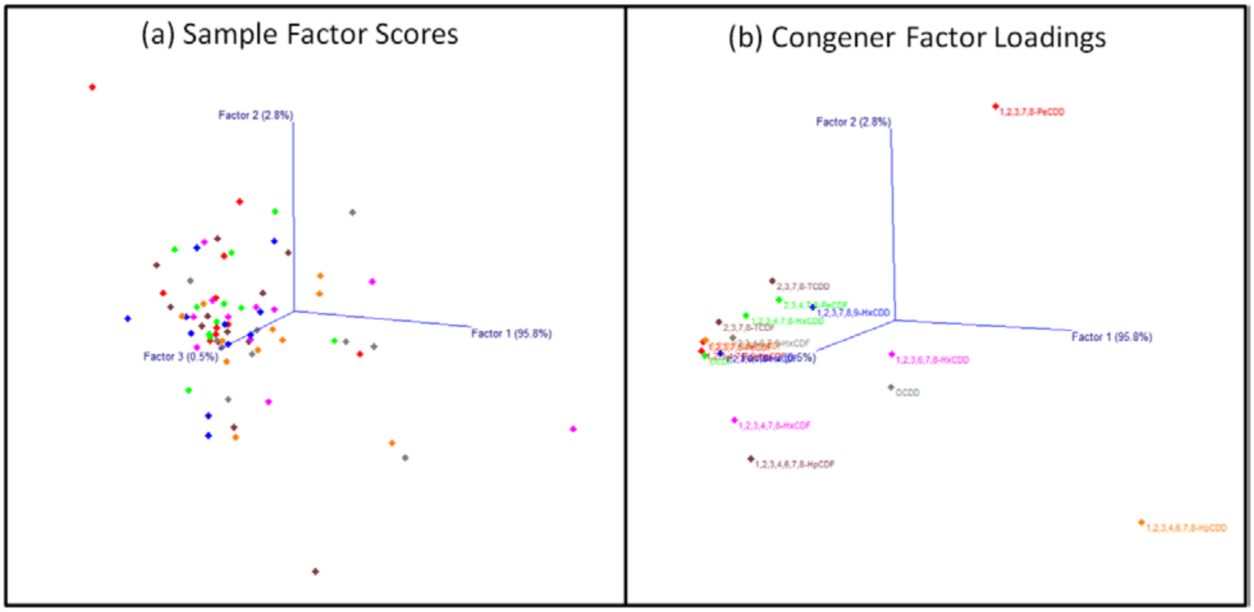
Figure 9 is a 3-dimensional representation of PCA results of the TEF-scaled data from Figure 7. Visualization of the data in this manner often allows identification of unusual or aberrant samples that should be excluded from processing, as retaining outlier samples can influence subsequent interpretation. Sample SH-10-SS is such an outlier, separate from the majority of clustered samples and responsible for most of the small amount of total data set variability (0.7 percent) represented by Factor 3 (Figure 9). For this reason, further discussion of the data does not include sample SH-10-SS, resulting in an *Unmixing Data Set* of 76 sediment samples.

Figure 9. PCA Factor Scores of TEF-scaled Unmixing Data Set



After removal of sample SH-10-SS, the PCA data cloud changes little (Figure 10). The vast majority of data set variability (95.8 percent) is explained by Factor 1, with this variability primarily driven by the dioxin congeners 1,2,3,7,8-PeCDD and 1,2,3,4,6,7,8-HpCDD (Figure 10b). The first two factors together account for more than 98 percent of the total data set variability.

Figure 10. PCA Factor Scores (a) and Loadings (b) of TEF-scaled Unmixing Data Set



4.2 Alternating Least Squares

Mixture analysis algorithms are designed to extract the patterns from which sample mixtures are composed. For this study an ALS method was used for the unmixing analysis. The ALS method assumes the data set reflects the variable contributions from a fixed number of factors. Therefore, the measured values are assumed to be the product of the chemical patterns for the factors and the fraction contributed from each factor to each sample. This product is calculated iteratively using matrix algebra, with one matrix of factor profiles and a second matrix of factor contributions to samples. Starting values are assigned to both matrices to begin the calculations. As the iteration proceeds, constraints are applied; for example, one constraint is that no negative contributions from factors are allowed, because negative contributions lack physical meaning. When the iterative calculations converge, the unmixing model is complete. The solution provided consists of the chemical profiles of factors and their contributions to each sample (i.e., sample composition). The residuals of the resulting model illustrate the goodness-of-fit.

The number of PCA factors required to account for nearly all of the data set variance is an indication of the number of factors to be included in the ALS unmixing model. As noted in Section 4.1.2, two factors account for more than 98 percent of the total data set profile variability, with three factors accounting for 99 percent of the variability. Therefore, both a 3-factor and a 2-factor ALS model were explored and compared.

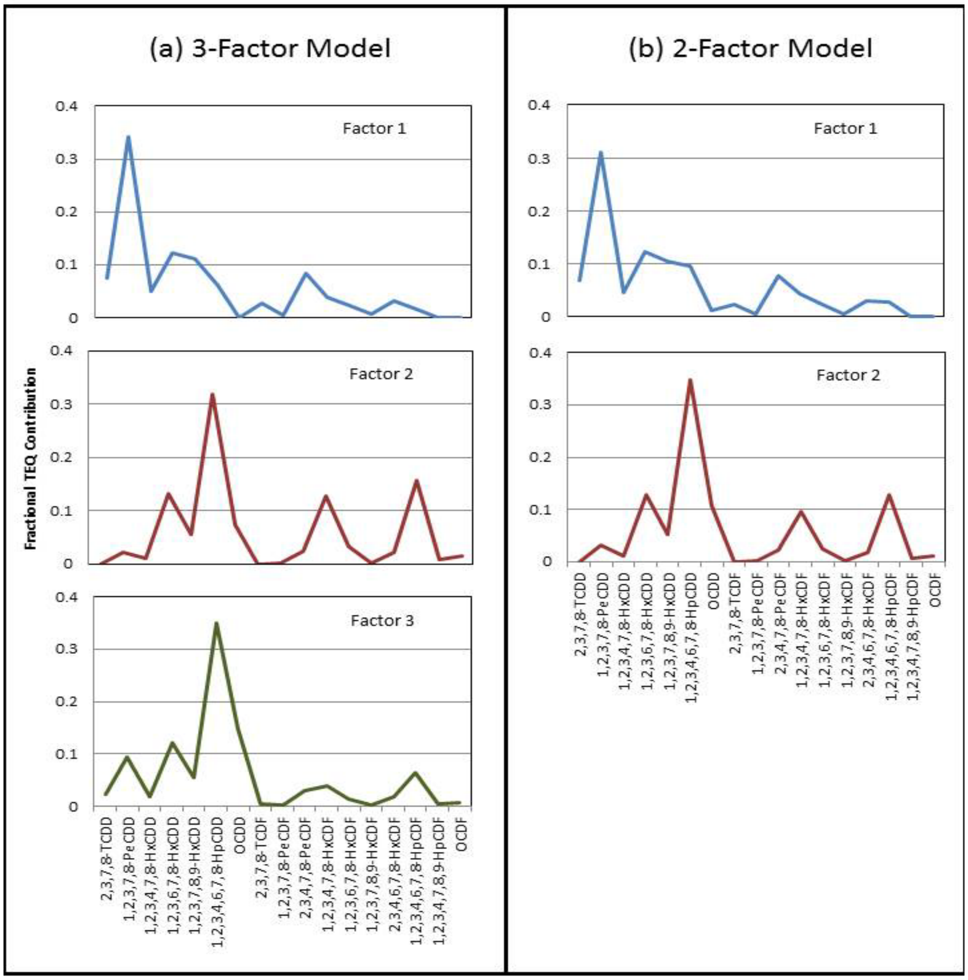
4.2.1 3-Factor Model

The normalized TEQ profiles for 3 factors are shown as line plots, with separate panels for each factor profile, in Figure 11a. Numerical values for these factor profiles are provided in Table 2. For all of the 3 profiles, the dioxin congeners are dominant, accounting for between 61 and 81 percent of the TEQ. Factor 2 has the greatest furan contribution to TEQ (39 percent).

Table 2. Factor Profiles derived from the 3-Factor Model

Congener	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-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	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
Factor 1	0.08	0.34	0.05	0.12	0.11	0.06	0.00	0.03	0.01	0.08	0.04	0.02	0.01	0.03	0.02	0.00	0.00
Factor 2	0.00	0.02	0.01	0.13	0.06	0.32	0.07	0.00	0.00	0.02	0.13	0.03	0.00	0.02	0.16	0.01	0.01
Factor 3	0.02	0.09	0.02	0.12	0.06	0.35	0.15	0.00	0.00	0.03	0.04	0.01	0.00	0.02	0.06	0.00	0.01

Figure 11. Dioxin/Furan Profiles derived from the 3-Factor Model (a) and 2-Factor Model (b)



Although the 3 factor profiles are unique, Factor 2 and Factor 3 have distinct similarities and differ greatly from Factor 1 (Figure 11a). The TEQ profiles of both Factors 2 and 3 are dominated by 1,2,3,4,6,7,8-HpCDD, constituting 32 and 35 percent of the profiles, respectively. The Factor 1 profile is composed of 6 percent of this dioxin congener, instead being dominated by 34 percent 1,2,3,7,8-PeCDD. The profile of Factor 1 is composed of lower molecular weight dioxins/furan, consisting of 92 percent tetra-, penta-, and hexa-substituted congeners. In contrast, profiles of both Factors 2 and 3 consist of 57 and 58 percent, respectively, of the heavier hepta- and octa-substituted congeners.

The fractional contributions of each factor to each of the 76 samples included after data screening, are listed as numerical values in Appendix C1. Some of the factor fractional contributions are zero, as not every model factor is found to contribute to every sample. Samples are shown, however, to be composed of varying contributions from multiple factors. The sum of the fractional contributions is not equal to 1 because the unmixing model was run without a closure constraint. Only 4 of the 76 samples (5.3 percent) have summed factor fractions differing from 1 by more than 5 percent. This result, as well as examination of the residuals for sample profiles, indicates good model fit to the original data set.

The factor TEQ increments calculated from the factor fractions and sample measured TEQs are listed in Appendix C1. The sum of factor TEQ increments does not equal the sample measured TEQ because the model was run without a closure constraint on factor fractions. Note that where the sample TEQ is relatively small, even the higher deviations from 1 for the sum of factor fractions may result in only small differences between measured and modeled sample TEQs. Conversely, relatively small differences for factor fractions may result in larger differences in sample TEQs when total TEQs are higher. Of the 76 samples included in the model, only 4 have differences in TEQ of more than 2 ng TEQ/kg. Thus, the 3-factor model produces total TEQ values within 2 ng TEQ/kg for more than 94 percent of the 76 sediment samples.

4.2.2 2-Factor Model

A detailed review of the results of the 3-factor model shows that two of the factor profiles have a substantial degree of commonality, even though there are some differences in the ranking of congener contributions. The ALS unmixing model was therefore repeated for a 2-factor model. The normalized TEQ profiles for the 2 factors are shown as line plots in Figure 11b. Numerical values for the two factor profiles are provided in Table 3. As was the case for the 3-factor model, the 2-factor profiles are dominated by dioxin congeners, accounting for between 76 and 68 percent of the TEQ for Factor 1 and Factor 2, respectively.

The factor fractions for the 2-factor model are listed as numerical values in Appendix C2. Unlike the 3-factor model, only a single sample has a factor fraction of zero; sample SH-10-SC_2-3ft (the sample with the greatest TEQ of the data set) is composed entirely of Factor 2. Five of the 76 samples (6.6 percent) have summed factor fractions differing from 1 by more than 5 percent, only one sample more than the 3-factor model. With fewer factors, this model has somewhat higher residuals than the 3-factor model, but overall model fit is still judged to be good.

The factor TEQ increments calculated from the factor fractions and sample measured TEQs are listed in Appendix C2. Of the 76 samples included in the model, eight have differences in TEQ of more than 2 ng TEQ/kg. Thus, the 2-factor model still produces total TEQ values within 2 ng TEQ/kg for almost 90 percent of the 76 sediment samples.

Table 3. Factor Profiles derived from the 2-Factor Model

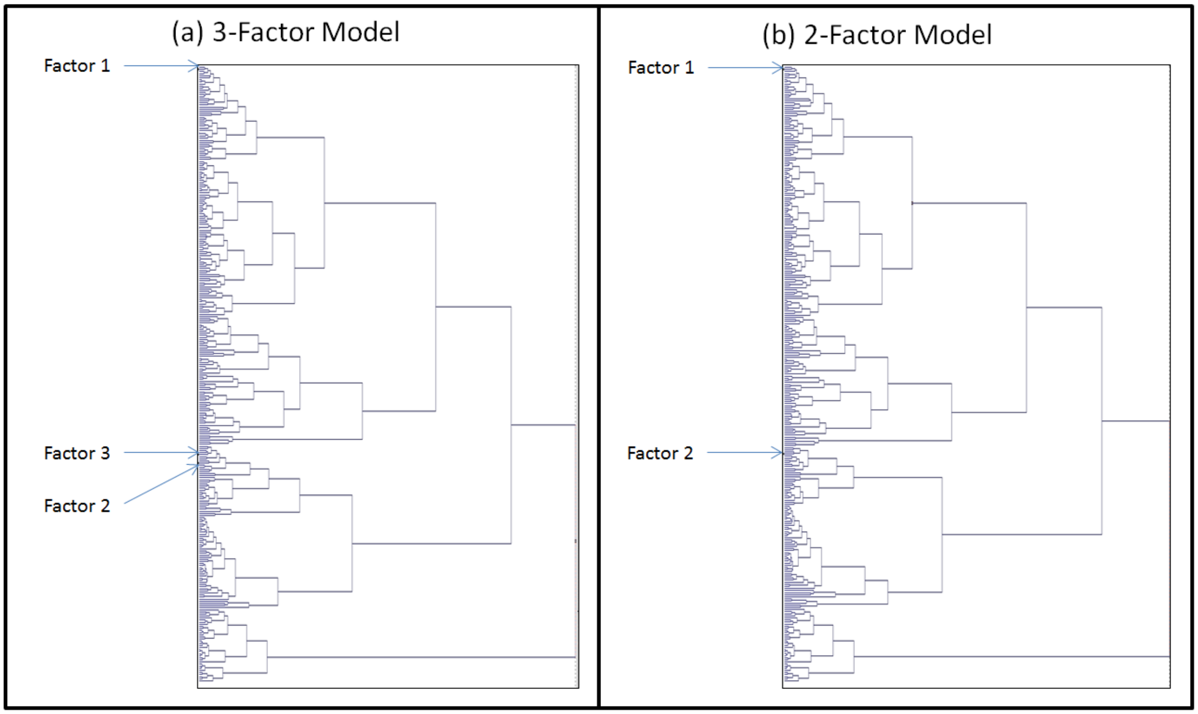
Congener	2,3,7,8-TCDD	1,2,3,7,8-PeCDD	1,2,3,4,7,8-HxCDD	1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD	1,2,3,4,6,7,8-HpCDD	OCDD	2,3,7,8-TCDF	1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDF	2,3,4,6,7,8-HxCDF	1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF	OCDF
Factor 1	0.07	0.31	0.05	0.12	0.10	0.09	0.01	0.02	0.00	0.08	0.04	0.02	0.01	0.03	0.03	0.00	0.00
Factor 2	0.00	0.03	0.01	0.13	0.05	0.35	0.11	0.00	0.00	0.02	0.10	0.03	0.00	0.02	0.13	0.01	0.01

4.2.3 Comparison of 3 and 2-Factor Models

While some differences in factor profiles and factor fractions can be identified between the two unmixing models, a comparative evaluation indicates that these differences are relatively small. The two unmixing models lead to factor profiles that are not markedly different.

As discussed above, both Factors 2 and 3 of the 3-factor model had the largest contribution from 1,2,3,4,6,7,8-HpCDD, with moderately elevated contributions from the same dioxin congeners (Figure 11a). Factors 2 and 3 of the 3-factor model differed mostly in relative contributions from furan congeners. While Factor 2 has a more substantial contribution from furans, the specific furan congeners most prevalent in Factors 2 and 3 are the same. The similarity of these two profiles is apparent when analyzed by hierarchical cluster analysis (HCA [further discussed in Section 5.0]), with Factors 2 and 3 clustering closely and having a similarity of almost 95 percent (Figure 12a). Removal of Factor 3 does not change the interpretation of Factor 2, as it remains in the same HCA cluster when using the 2-factor model (Figure 12b).

Figure 12. HCA Dendrograms for the 3-Factor Model (a) and 2-Factor Model (b)



The Factor 1 profiles of both the 2-factor and 3-factor models are essentially identical (Figure 11a,b). The interpretation of Factor 1 also doesn’t change between the 3 and 2-factor models as Factor 1 remains in the same HCA cluster (Figure 12).

These findings support the use of the 2-factor model as being most appropriate for the data set, with interpretation of a third dioxin/furan factor unnecessary and not supported by the variability of dioxin/furan patterns observed in Oakland Bay sediments. Therefore only the 2-factor model was used as the basis for all further evaluations.

5.0 Source Library Comparison

A library of comparison dioxin/furan profiles was compiled to support interpretations of the factor profiles obtained through chemometric modeling. The “source library” included over 300 candidate profiles compiled from published literature, regional environmental samples, and site-specific studies. Examples of source types present in the source library include air emissions, effluent discharges, ash, and various chemicals known to include dioxins/furans from their manufacture. Also part of the source library was the *Comparison Data Set*, composed of samples relevant to the study area, but not included in the *Unmixing Data Set* (see Section 2.1).

Comparisons of factor profiles from the ALS model to those in the compiled source library were made by two means:

3. Hierarchical Cluster Analysis (HCA); and
4. Tabulation of correlation coefficients.

As the name implies, HCA is a method of evaluating similarity by organizing data into a hierarchy of clusters. The results of HCA are best represented graphically by a dendrogram, or similarity tree. This manner of representation displays highly similar sample pairs with relatively small separation distances. As applied to this study, HCA was used to identify library profiles with high similarity to the ALS-derived factor profiles.

A correlation coefficient (r-value) can be calculated for sample pairs as a measure of the strength and direction of their relationship. Correlation between two samples can be either positive or negative, with perfect positive correlation having a value of +1. Correlation analyses were performed for ALS-derived profiles against the entire source library.

The HCA dendrogram for the 2-factor model is presented in Figure 12b. Factors 1 and 2 cluster with very different source types. Profiles from the 2-factor model were considered to significantly “match” that of a source library profile when either the HCA similarity metric or correlation coefficient were greater than or equal to 0.95.

5.1 Factor 1 Comparison

Dioxin/furan profiles of the source library that best match Factor 1 are all related to hog fuel boiler (HFB) sources, both emissions and ash. The best-matched library samples and associated references are provided in Table 4. These matches include:

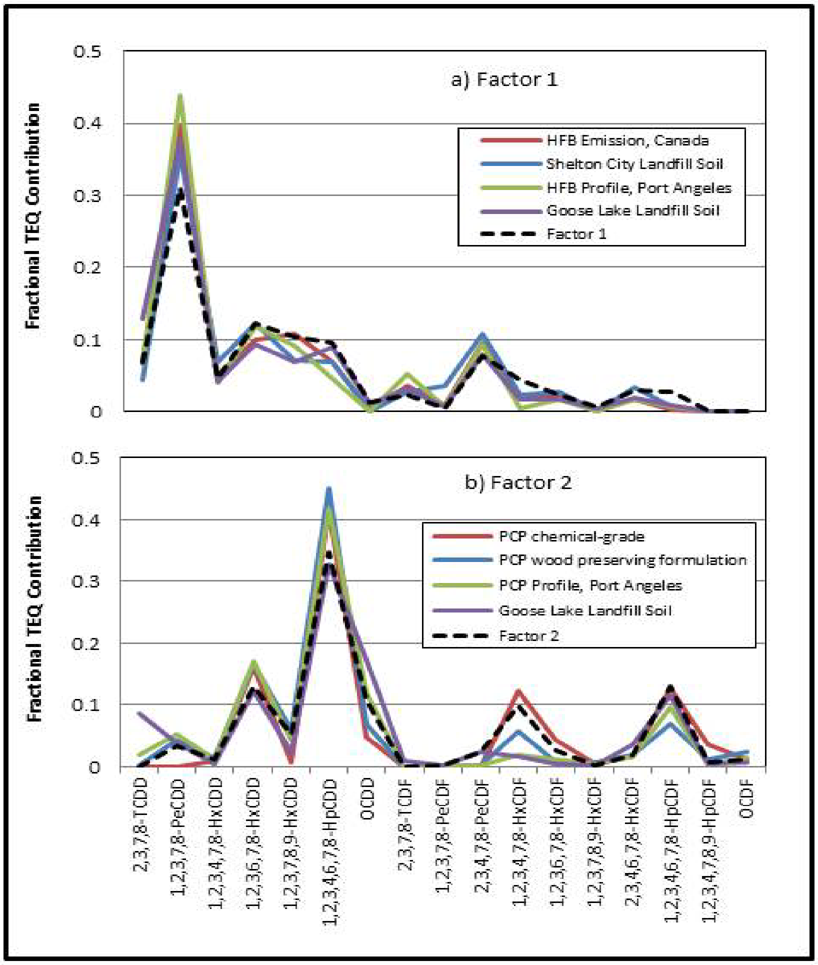
- A soil sample from Shelton's City Landfill, likely containing HFB ash;
- Port Angeles Harbor's dioxin/furan Factor 4, derived from HFB sources;
- Emissions from Canadian HFBs;
- Ash from Rayonier's Port Angeles HFB; and
- Multiple samples from the Goose Lake site.

Figure 13a presents a selection of these library profiles along with that of Factor 1. All profiles in this figure share the same most prominent congeners, including 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF as the dioxin and furan congeners that contribute most to TEQ.

Table 4. Factor Profile Matches to Source Library

Oakland Bay Sediment Profile	Source Library Match		HCA Similarity (fractional %)	Correlation Coefficient (r-value)
	Description	Reference		
Factor 1	Shelton City Landfill Soil	CH2M Hill (1987)	0.99	0.97
	Port Angeles HFB Source 4	NewFields (2013)	0.98	0.97
	HFB Stack Emission (CANST58)	DeAbreu (2009)	0.98	0.98
	Goose Lake Sediment (SED-09, 0-0.4 ft)	GeoEngineers (2012)	0.96	0.94
	Goose Lake Landfill Soil (MW-17, 3-4 ft)	GeoEngineers (2012)	0.95	0.97
	Rayonier HFB Ash (Port Angeles)	FWEC (1997)	0.94	0.95
Factor 2	PCP chemical-grade	Masunaga et al. (2001)	0.98	0.97
	Goose Lake Landfill Soil (TP-35, 15 ft)	GeoEngineers (2012)	0.96	0.91
	Port Angeles PCP Source 3	NewFields (2013)	0.94	0.96
	PCP treated utility pole	Lorber et al. (2002)	0.94	0.96
	PCP wood preservative	Christmann et al. (1989)	0.94	0.95

Figure 13. Source Library Profile Matches to Factor 1 (a) and Factor 2 (b)



5.2 Factor 2 Comparison

Dioxin/furan profiles of the source library that best match Factor 2 are all related to pentachlorophenol (PCP) sources. The best-matched library samples and associated references are provided in Table 4. These matches include:

- Chemical-grade PCP;
- Port Angeles Harbor’s dioxin/furan Factor 3, derived from PCP sources;
- PCP used as a wood preservative; and
- Multiple samples from the Goose Lake site.

Figure 13b presents a selection of these library profiles along with that of Factor 2. All profiles in this figure share the 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,7,8-HxCDD same most prominent dioxin congeners, with little contribution from other dioxins. The Goose Lake landfill soil sample shown in Figure 13b has a greater relative TEQ contribution from 2,3,7,8-TCDD and OCDD than the others, possibly suggesting that the sample contains other sources. Two furans are prevalent in the Factor 2 profile, 1,2,3,4,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF. While the latter is a consistently moderate component to the library profiles displayed, the former is quite variable among the library profiles.

6.0 Summary

Over 80 sediment samples from Oakland Bay were analyzed for polychlorinated dioxins and furans. Data from these analyses were collectively processed with several chemometrics algorithms to look for underlying patterns that might explain their distribution in bay sediments.

Following principal component analysis to understand the complexity in the data set, mixture analysis was performed using an alternating least squares method. Based on diagnostics from the two methods, it appears justified to describe 2 different dioxin/furan source types contributing to sediments of Oakland Bay.

The 2 source patterns that were discovered in this process appear to be correlated to materials commonly found in harbors of this type, particularly where wood processing occurs. These include the following:

1. A source that has a pattern similar to those found in stack emissions and ash from HFBs which utilize salt-laden wood, and

2. A source that strongly resembles that from pentachlorophenol.

7.0 References

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Appendix C1

3-Factor Model Results

Appendix C1. Factor Fractions and TEQ Increments derived from the 3-Factor Model

Location ID	Fractional Contribution			TEQ Increment (ng/kg)			Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3			
Surface Samples									
G1_0-1ft	0.51	0.15	0.35	4.7	1.4	3.3	9.4	9.3	-0.18
Gold-1_0-2cm	0.38	0.04	0.57	0.24	0.03	0.36	0.62	0.63	0.01
HI-02-SS_0-10cm	0.44	0.38	0.23	1.4	1.2	0.73	3.3	3.2	-0.07
HI-03-SS_0-10cm	0.57	0.33	0.10	7.4	4.3	1.3	13	13	-0.03
HI-04-SS_0-10cm	0.43	0.41	0.19	0.77	0.73	0.34	1.8	1.8	-0.01
HI-05-SS_0-10cm	0.38	0.41	0.19	0.83	0.91	0.42	2.2	2.2	0.00
HI-06-SS_0-10cm	0.53	0.41	0.08	5.1	4.0	0.79	9.9	9.7	-0.13
HI-07-SS_0-10cm	0.33	0.48	0.17	0.90	1.3	0.47	2.7	2.7	0.01
OB-01-SS_0-10cm	0.43	0.43	0.16	1.9	1.9	0.72	4.5	4.4	-0.05
OB-02-SS_0-10cm	0.44	0.46	0.08	7.4	7.9	1.3	17	17	0.03
OB-03-SS_0-10cm	0.38	0.45	0.18	11	13	5.1	29	29	-0.09
OB-04-SS_0-10cm	0.56	0.41	0.03	15	11	0.69	27	27	-0.11
OB-05-SS_0-10cm	0.36	0.50	0.14	10	14	3.9	28	28	-0.19
OB-06-SS_0-10cm	0.40	0.49	0.13	17	21	5.6	44	43	-0.33
OB-07-SS_0-10cm	0.47	0.41	0.14	4.1	3.6	1.2	8.9	8.7	-0.18
OB-08-SS_0-10cm	0.46	0.38	0.20	17	14	7.3	39	37	-1.6
OB-09-SS_0-10cm	0.39	0.47	0.14	15	18	5.2	39	38	-0.25
OB-10S_0-2cm	0.36	0.38	0.22	20	21	12	54	55	1.5
OB-10S_2-10cm	0.39	0.39	0.19	4.3	4.3	2.1	11	11	0.31
OB-10-SS_0-10cm	0.37	0.43	0.20	20	23	11	54	54	-0.65
OB-11-SS_0-10cm	0.39	0.50	0.12	17	22	5.3	44	44	-0.63
OB-12.5S_0-2cm	0.41	0.34	0.22	13	11	6.9	31	32	0.84
OB-12.5S_2-10cm	0.43	0.38	0.17	17	15	6.6	39	40	1.3
OB-12-SS_0-10cm	0.39	0.50	0.12	21	27	6.6	55	54	-0.25
OB-13-SS_0-10cm	0.42	0.52	0.08	20	25	4.0	49	48	-0.79
OB-14-SS_0-10cm	0.42	0.45	0.14	9.3	9.8	3.1	22	22	-0.31
OB-17-WS_0-10cm	0.51	0.44	0.11	6.6	5.7	1.4	14	13	-0.30
OB-18-WS_0-10cm	0.36	0.45	0.19	12	15	6.4	33	33	-0.48
OB-19-WS_0-10cm	0.38	0.42	0.21	17	19	9.6	46	45	-0.61
OB-227S_0-2cm	0.36	0.24	0.32	3.2	2.1	2.8	8.0	8.8	0.71
OB-227S_2-10cm	0.58	0.09	0.35	2.5	0.40	1.5	4.4	4.3	-0.10
OB-232S_2-10cm	0.39	0.35	0.24	19	17	12	48	49	1.2
OB-636S_0-2cm	0.34	0.32	0.29	9.3	8.6	7.8	26	27	0.97
OB-636S_2-10cm	0.39	0.33	0.24	14	12	8.6	35	36	0.95
SH-01-SS_0-10cm	0.43	0.34	0.21	9.8	7.8	4.9	22	23	0.28
SH-02-SS_0-10cm	0.57	0.21	0.28	30	11	15	55	53	-1.8
SH-03-SS_0-10cm	0.06	0.35	0.56	11	63	100	180	180	0.06
SH-04-SS_0-10cm	0.21	0.11	0.66	12	6.2	38	57	58	0.89
SH-05-SS_0-10cm	0.18	0.10	0.67	4.8	2.7	18	26	27	0.92
SH-07-SS_0-10cm	0.38	0.15	0.46	2.5	1.0	3.0	6.5	6.5	-0.04
SH-09-SS_0-10cm	0.36	0.35	0.27	4.0	3.8	3.0	11	11	-0.13
SH-11-SS_0-10cm	0.82	0.00	0.14	40	0.00	7.0	47	49	1.4
SH-12-SS_0-10cm	0.50	0.22	0.27	50	22	27	100	100	0.81
SH-13-SS_0-10cm	0.27	0.22	0.48	30	24	53	110	110	-0.68
SH-14-SS_0-10cm	0.37	0.37	0.25	13	13	8.7	35	35	-0.27

Appendix C1 (continued). Factor Fractions and TEQ Increments derived from the 3-Factor Model

Location ID	Fractional Contribution			TEQ Increment (ng/kg)			Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3			
Surface Samples									
SH-15-SS_0-10cm	0.38	0.46	0.14	0.73	0.88	0.27	1.9	1.9	0.00
SH-16-SS_0-10cm	0.41	0.49	0.13	0.41	0.49	0.13	1.0	1.0	0.01
SH-18-WS_0-10cm	0.37	0.40	0.25	25	27	17	69	67	-1.8
SH-19-WS_0-10cm	0.42	0.42	0.15	33	33	12	78	79	1.00
SH-20-WS_0-10cm	0.31	0.41	0.27	16	21	14	50	51	0.34
SH-21-WS_0-10cm	0.31	0.30	0.43	17	16	23	55	54	-1.2
SH-22-WS_0-10cm	0.03	0.09	0.94	1.3	4.3	44	50	47	-2.4
SH-23-WS_0-10cm	0.32	0.38	0.28	9.3	11	8.2	29	29	0.15
SH-24-WS_0-10cm	0.38	0.47	0.14	12	15	4.6	32	32	-0.10
SH-25-WS_0-10cm	0.42	0.37	0.21	16	14	7.8	38	38	-0.47
SH-26-WS_0-10cm	0.44	0.29	0.27	2.3	1.5	1.4	5.3	5.2	-0.08
SH-27-WS_0-10cm	0.42	0.34	0.25	1.6	1.3	0.96	3.9	3.8	-0.05
SH-28-WS_0-10cm	0.37	0.50	0.10	11	15	3.1	30	30	0.11
SH-29-WS_0-10cm	0.40	0.44	0.15	0.85	0.92	0.32	2.1	2.1	-0.01
SH-30-WS_0-10cm	0.56	0.28	0.17	20	10	6.1	36	36	-0.01
Shelton-1_0-2cm	0.43	0.11	0.49	3.7	1.0	4.3	9.0	8.7	-0.37
Shelton-2_0-2cm	0.55	0.00	0.48	3.2	0.00	2.8	6.1	5.8	-0.27
Subsurface Samples									
OB-03-SC_1-2ft	0.32	0.66	0.02	26	54	2.0	82	82	-0.21
OB-06-SC_1-2ft	0.27	0.67	0.06	48	120	11	180	180	-0.32
OB-09-SC_1-2ft	0.23	0.71	0.09	12	37	4.5	53	52	-0.63
OB-10-SC_1-2ft	0.24	0.69	0.11	24	69	11	100	100	-0.82
OB-12-SC_1-2ft	0.25	0.76	0.00	18	54	0.00	73	71	-1.7
SH-02-SC_2-3ft	0.61	0.28	0.16	8.5	3.9	2.3	15	14	-0.34
SH-04-SC_2-3ft	0.65	0.15	0.25	200	46	76	320	310	-8.8
SH-09-SC_2-3ft	0.18	0.44	0.33	0.48	1.2	0.90	2.5	2.7	0.15
SH-10-SC_2-3ft	0.00	0.98	0.08	0.00	880	73	950	900	-50
SH-12-SC_1-2ft	0.55	0.24	0.22	110	48	43	200	200	1.10
SH-12-SC_2-3ft	0.55	0.26	0.22	170	80	67	310	310	-4.5
SH-13-SC_1-2ft	0.23	0.51	0.23	3.0	6.6	3.0	13	13	-0.04
SH-13-SC_2-3ft	0.00	0.32	0.69	0.00	5.1	11	16	16	0.25
SH-14-SC_2-3ft	0.48	0.58	0.00	3.8	4.6	0.00	8.4	8.0	-0.34

Notes:

Δ TEQ = (Measured TEQ) - (Sum of TEQ Increments)

Appendix C2

2-Factor Model Results

Appendix C2. Factor Fractions and TEQ Increments derived from the 2-Factor Model

Location ID	Fractional Contribution		TEQ Increment (ng/kg)		Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2	Factor 1	Factor 2			
Surface Samples							
G1_0-1ft	0.62	0.41	5.8	3.8	9.6	9.3	-0.31
Gold-1_0-2cm	0.52	0.49	0.33	0.31	0.64	0.63	-0.01
HI-02-SS_0-10cm	0.53	0.50	1.7	1.6	3.3	3.2	-0.06
HI-03-SS_0-10cm	0.65	0.34	8.5	4.4	13	13	0.11
HI-04-SS_0-10cm	0.51	0.51	0.91	0.91	1.8	1.8	0.00
HI-05-SS_0-10cm	0.45	0.50	1.0	1.1	2.1	2.2	0.02
HI-06-SS_0-10cm	0.60	0.40	5.8	3.9	9.7	9.7	0.01
HI-07-SS_0-10cm	0.41	0.59	1.1	1.6	2.7	2.7	0.04
OB-01-SS_0-10cm	0.50	0.52	2.2	2.3	4.4	4.4	-0.01
OB-02-SS_0-10cm	0.50	0.46	8.5	7.9	16	17	0.31
OB-03-SS_0-10cm	0.45	0.55	13	16	29	29	0.19
OB-04-SS_0-10cm	0.63	0.36	17	9.7	27	27	0.40
OB-05-SS_0-10cm	0.43	0.54	12	15	27	28	0.17
OB-06-SS_0-10cm	0.47	0.53	20	23	43	43	0.27
OB-07-SS_0-10cm	0.55	0.46	4.8	4.0	8.8	8.7	-0.08
OB-08-SS_0-10cm	0.54	0.49	20	18	38	37	-1.3
OB-09-SS_0-10cm	0.47	0.53	18	20	38	38	0.24
OB-10S_0-2cm	0.45	0.53	25	29	54	55	1.7
OB-10S_2-10cm	0.47	0.49	5.2	5.4	11	11	0.38
OB-10-SS_0-10cm	0.44	0.56	24	30	54	54	-0.33
OB-11-SS_0-10cm	0.45	0.52	20	23	44	44	0.01
OB-12.5S_0-2cm	0.50	0.47	16	15	31	32	0.94
OB-12.5S_2-10cm	0.50	0.48	20	19	38	40	1.6
OB-12-SS_0-10cm	0.46	0.54	25	29	54	54	0.53
OB-13-SS_0-10cm	0.48	0.52	23	25	48	48	0.07
OB-14-SS_0-10cm	0.50	0.50	11	11	22	22	-0.06
OB-17-WS_0-10cm	0.58	0.46	7.6	6.0	14	13	-0.12
OB-18-WS_0-10cm	0.45	0.55	15	18	33	33	-0.23
OB-19-WS_0-10cm	0.47	0.56	21	25	46	45	-0.35
OB-227S_0-2cm	0.45	0.47	4.0	4.1	8.1	8.8	0.65
OB-227S_2-10cm	0.72	0.33	3.1	1.4	4.4	4.3	-0.16
OB-232S_2-10cm	0.47	0.51	23	25	48	49	1.3
OB-636S_0-2cm	0.44	0.52	12	14	26	27	0.89
OB-636S_2-10cm	0.50	0.47	18	17	35	36	0.96
SH-01-SS_0-10cm	0.52	0.48	12	11	22	23	0.35
SH-02-SS_0-10cm	0.68	0.38	36	20	55	53	-2.2
SH-03-SS_0-10cm	0.17	0.83	30	150	180	180	-3.6
SH-04-SS_0-10cm	0.36	0.66	21	38	59	58	-1.1
SH-05-SS_0-10cm	0.32	0.67	8.6	18	27	27	-0.06
SH-07-SS_0-10cm	0.51	0.51	3.3	3.3	6.6	6.5	-0.17
SH-09-SS_0-10cm	0.45	0.53	4.9	5.8	11	11	-0.14
SH-11-SS_0-10cm	0.94	0.01	46	0.52	47	49	1.9
SH-12-SS_0-10cm	0.61	0.39	61	39	100	100	0.34
SH-13-SS_0-10cm	0.39	0.60	43	66	110	110	-2.8
SH-14-SS_0-10cm	0.46	0.54	16	19	35	35	-0.19

Appendix C2 (continued). Factor Fractions and TEQ Increments derived from the 2-Factor Model

Location ID	Fractional Contribution		TEQ Increment (ng/kg)		Sum of TEQ Increments (ng/kg)	Measured TEQ (ng/kg)	Δ TEQ[1] (ng/kg)
	Factor 1	Factor 2	Factor 1	Factor 2			
Surface Samples							
SH-15-SS_0-10cm	0.45	0.53	0.86	1.0	1.9	1.9	0.03
SH-16-SS_0-10cm	0.48	0.53	0.48	0.53	1.0	1.0	0.03
SH-18-WS_0-10cm	0.46	0.57	31	38	68	67	-1.6
SH-19-WS_0-10cm	0.48	0.48	38	38	77	79	1.8
SH-20-WS_0-10cm	0.39	0.59	20	30	50	51	0.43
SH-21-WS_0-10cm	0.43	0.61	23	33	56	54	-1.8
SH-22-WS_0-10cm	0.20	0.91	9.3	43	52	47	-5.0
SH-23-WS_0-10cm	0.41	0.59	12	17	29	29	0.15
SH-24-WS_0-10cm	0.44	0.53	14	17	32	32	0.30
SH-25-WS_0-10cm	0.53	0.47	20	18	38	38	-0.28
SH-26-WS_0-10cm	0.54	0.46	2.8	2.4	5.3	5.2	-0.09
SH-27-WS_0-10cm	0.53	0.50	2.0	1.9	3.9	3.8	-0.05
SH-28-WS_0-10cm	0.43	0.53	13	16	29	30	0.60
SH-29-WS_0-10cm	0.48	0.52	1.0	1.1	2.1	2.1	0.02
SH-30-WS_0-10cm	0.64	0.36	23	13	36	36	0.14
Shelton-1_0-2cm	0.56	0.51	4.9	4.4	9.3	8.7	-0.58
Shelton-2_0-2cm	0.71	0.36	4.1	2.1	6.2	5.8	-0.42
Subsurface Samples							
OB-03-SC_1-2ft	0.37	0.61	30	50	80	82	2.0
OB-06-SC_1-2ft	0.31	0.67	55	120	180	180	4.1
OB-09-SC_1-2ft	0.27	0.73	14	38	52	52	0.64
OB-10-SC_1-2ft	0.29	0.74	29	74	100	100	1.4
OB-12-SC_1-2ft	0.28	0.70	20	50	70	71	1.1
SH-02-SC_2-3ft	0.70	0.34	9.8	4.8	15	14	-0.28
SH-04-SC_2-3ft	0.77	0.28	240	87	330	310	-11
SH-09-SC_2-3ft	0.26	0.70	0.69	1.9	2.5	2.7	0.14
SH-10-SC_2-3ft	0.00	1.01	0.00	910	910	900	-11
SH-12-SC_1-2ft	0.65	0.36	130	71	200	200	0.98
SH-12-SC_2-3ft	0.65	0.39	200	120	310	310	-4.5
SH-13-SC_1-2ft	0.30	0.67	3.9	8.7	13	13	0.05
SH-13-SC_2-3ft	0.11	0.88	1.8	14	16	16	-0.14
SH-14-SC_2-3ft	0.51	0.45	4.1	3.6	7.7	8.0	0.32

Notes:
Δ TEQ = (Measured TEQ) - (Sum of TEQ Increments)