Rayonier Mill Off-Property Soil Dioxin Study

Soil Sampling Plan

PUBLIC REVIEW DRAFT

Prepared for

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List of Acronyms and Abbreviations

CCHA	Clallam County Housing Authority
cm	centimeters
CSM	conceptual site model
E & E	Ecology and Environment, Inc.
EPA	U.S. Environmental Protection Agency
ESI	environmental site investigation
FALCON	[EPA's] *Fingerprint Analysis of Contaminant Data*
FAQ	frequently asked questions
FWEC	Foster Wheeler Environmental Corporation
HASP	health and safety plan
HLA	Harding Lawson Associates
HpCDD	heptachlorodibenzo-*p*-dioxin
HpCDF	heptachlorodibenzofuran
HxCDD	hexachlorodibenzo-*p*-dioxin
HxCDF	hexachlorodibenzofuran
ISC-ST3	Industrial Source Complex Short-Term
ITT	International Telephone and Telegraph [Corporation]
LEKT	Lower Elwha Klallam Tribe
MCDD	monochlorodibenzo-*p*-dioxins
MCDF	monochlorodibenzofurans
MPE	Malcolm Pirnie Engineers
MTCA	Model Toxics Control Act
ng/kg	nanograms per kilogram
NGVD	National Geodetic Vertical Datum
OCDD	octachlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
PA/SI	preliminary investigation / site inspection
PCA	principal components analysis
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PeCDD	pentachlorodibenzo-*p*-dioxin
PeCDF	pentachlorodibenzofuran
PGWG	Pacific Ground Water Group
PH-SKC	Public Health – Seattle-King County
RTAG	Rayonier Technical Advisory Group
SQAP	sampling and quality assurance plan
SSP	soil sampling plan
TCDD	tetrachlorodibenzo-p-dioxin
TEF	toxicity equivalency factor
TEQ	total toxic equivalent concentration
TOC	total organic carbon
TPCHD	Tacoma-Pierce County Health Department
WAC	Washington Administrative Code

WDOH	Washington Department of Health
WDOT	Washington Department of Transportation

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1.0 Introduction

The former Rayonier Pulp Mill (Mill) was located in Port Angeles, Washington (Figure 1-1). The Mill operated between 1930 and 1997 and used an ammonia-based acid sulfite process for pulp production. This sampling design report, the *Rayonier Mill Off-Property Soil Dioxin Study Soil Sampling Plan*, focuses on polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) in soils near the former mill. "Off-property" refers to areas outside the current Rayonier Inc. property boundary.

Dioxins/furans are known to have been associated with Mill processes and emissions. All of the mill structures have now been demolished and remedial investigations of both upland and marine areas are being conducted under an Agreed Order with the Washington State Department of Ecology (Ecology).

Since the Mill's closure in 1997, multiple investigations have been conducted on the facility property and in the off-shore marine environment. Limited sampling has been performed at off-site residential properties and at two landfills used to dispose of mill-related wastes, the 13th and M Street Landfill and the Mt. Pleasant Landfill. While most investigations have been within the facility property, Ecology is interested in understanding potential impacts of atmospheric releases of dioxins/furans from former Mill operations on off-property areas.

The study design outlined in this Soil Sampling Plan (SSP) was developed in consultation with Ecology to meet the study objectives. The SSP consists of the following sections:

- Section 2.0, Study Objectives
- Section 3.0, Overview of Study
- Section 4.0, Definition of Study Area
- Section 5.0, Selection of Sample Locations
- Section 6.0, Sample Analysis
- Section 7.0, Study Implementation
- Section 8.0, Data Evaluation
- Section 9.0, Data Reporting

Implementation of the study will begin upon finalization of the SSP.

1.1 Introduction to Dioxins/Furans

Dioxins and furans are two classes of similar chemicals that both contain two carbon benzene ring structures. All dioxins include two oxygen atoms, while all furans include one oxygen atom. There are 75 unique dioxin compounds, each called a "congener." Congeners differ from each other in the number and position of chlorine atoms on the benzene rings. There are 135 furan congeners.

Dioxin and furan congeners can contain one to eight chlorine atoms, so there are eight homologue groups for dioxins and furans, ranging from monochlorodibenzo-*p*-dioxins (MCDDs) and monochlorodibenzofurans (MCDFs) to octachlorodibenzo-*p*-dioxins (OCDDs) and

octachlorodibenzofurans (OCDFs). Figure 1-2 shows the basic structure of dioxins/furans. Chlorine atoms can be attached at one or more of the carbon atoms numbered 1-4 and 6-9.

Although there are 210 unique dioxin and furan congeners, only 17 of these, all of which have chlorine atoms attached in the 2, 3, 7, and 8 positions, are typically evaluated because the U.S. Environmental Protection Agency (EPA) and the World Health Organization consider them the most toxic. In this study, the terms “dioxins” and “furans” will be used to refer to the 17 congeners of primary interest, presented along with their homologue group names in Table 1-1. Concentrations of the 17 dioxins/furans are often expressed as a total toxic equivalent concentration (TEQ) to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), meaning that the concentrations of the congeners have been normalized to the most toxic congener, 2,3,7,8-TCDD. The concentrations are presented as mass of chemical per mass of soil (e.g., 1.5 nanograms of 2,3,7,8-TCDD TEQ per kilogram of soil, or 1.5 ng/kg 2,3,7,8-TCDD TEQ).

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 biodegradation, do not dissolve in water, and attach strongly to particles such as soil, dust, and sediment. This means that they are persistent and can bioaccumulate in people and animals. Because they are persistent, dioxins/furans can be measured in environmental media long after they have been released. Despite their persistence and ubiquitous presence, levels of dioxins/furans in the environment have been declining since the 1970’s due to improvements in air pollution control technologies for combustion and incineration facilities and cleanup of dioxin-contaminated areas (U.S. EPA 2003a).

Dioxins/furans make their way into the environment from a variety of sources. Except for small quantities used for research purposes, they are not created intentionally. Instead, dioxins/furans are unwanted by-products 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 also can 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
- Incineration of salt-laden materials
- Secondary copper smelting
- Forest fires
- Land application of sewage sludge
- Cement kilns
- Coal-fired power plants
- Residential wood burning
- Chlorine bleaching of wood pulp
- Backyard burning of household waste
- Combustion engines burning petroleum fuels
- Byproducts and derivatives of chemical production (e.g., pentachlorophenol, 2,4,5-T)

Dioxins/furans are present at some level throughout the environment in air, food, and water and in soils and sediments. Dioxins/furans tend to be found in higher concentrations near industrial areas but are present at various concentrations throughout urban and rural areas and even in remote wilderness regions as a result of long-range atmospheric transport.

1.2 Rayonier Mill

The Olympics Forest Products Company constructed a pulp mill along the waterfront in 1930. The mill later merged with two independent companies in 1937 to become Rayonier Inc. In 1968, International Telephone and Telegraph (ITT) Corporation purchased Rayonier Inc., renaming the mill ITT Rayonier. The mill operated under ITT Corporation until 1994, when the mill was spun off from ITT Corporation and resumed operating under the name Rayonier Inc. until its closure in 1997. Descriptions of Mill history and operations are provided by Foster Wheeler Environmental Company (FWEC; 1997) and Integral Consulting Inc. (2006).

The Rayonier property, which has been almost completely cleared of its mill facility and outbuildings, totals 80 acres. The property is located in Section 11 of Township 30 north, Range 6 west, at a latitude of 48° 07’ 00” north and longitude of 123° 24’ 25” west. Most of the property extends into the eastern portion of Port Angeles harbor. The northern portion of the property is generally flat, with relatively steep bluffs rising rapidly to approximately 75 feet above National Geodetic Vertical Datum (NGVD) immediately to the southeast and southwest (HLA 1993). The terrain continues to rise to approximately 200, 265, and 150 feet above NGVD within approximately one mile southeast, south, and southwest of the property, respectively.

Throughout the Mill’s operating history, air emissions were released from numerous sources on-site under normal operating conditions, including the recovery and hog fuel boiler stacks, the chlorine dioxide generator, and vents in the bleach plant, acid plant, and blowpits. The recovery boiler was constructed in 1974, in part to reduce sulfur dioxide emissions. At the same time, scrubbers and demisters were placed on the recovery boiler stack (U.S. EPA 1993). A scrubber and demisters also were installed on hog fuel boiler No. 6 in 1974 (FWEC 1997).

Rayonier used wood chips, including salt-laden wood, in the on-site hog fuel boiler (Integral 2006). Due to the location of the Mill on Port Angeles harbor and the abundance of wood as a source of fuel for on-site burners, the Mill burned wood chips and wood wastes coming from logs floated in Port Angeles harbor. Use of salt-laden wood in hog fuel burners can result in significantly higher emissions of dioxins/furans than 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). Combustion of salt-laden hog fuels in the hog fuel boilers is considered the primary source of dioxins/furans emitted from the former Mill.

Limited testing was performed in 1988 on samples collected from hog fuel boiler No. 6 at the former Rayonier Mill, including bag house ash (1,310 ng/kg 2,3,7,8-TCDD TEQ) and washed ash (170 ng/kg 2,3,7,8-TCDD TEQ; FWEC 1997). The presence of dioxins/furans has been confirmed in further sampling performed on samples from the hog fuel boiler. Samples from the hog fuel boiler were obtained in 1989, with analytical results documenting total dioxin and total furan concentrations of 2,700 ng/kg and 19,000 ng/kg in boiler ash and 22,000 ng/kg and 22,000

ng/kg in filter ash, respectively (FWEC 1997). In 1995, stack tests of air emissions from the hog fuel boiler confirmed the presence of dioxins/furans (FWEC 1997).

Additional samples of bag house fly ash (total TCDD 160,000 ng/kg; total TCDF 64,000 ng/kg) and filter ash (total TCDD 380,000 ng/kg and total TCDF 33,000 ng/kg) were collected in 1991 and 1993, respecitvely. In 1996, concentrations of 2,3,7,8-TCDD (110 ng/kg) and 2,3,7,8-TCDF (350 ng/kg) were detected in vacuum filter ash (FWEC 1997). Generally, dioxin/furan loading is associated with fly ash as opposed to grate or filter ash (Yake et al 1998). A complete description of these sample results is provided by FWEC (1997) and Integral Consulting Inc. (2006).

1.3 Review of Existing Dioxin/Furan Data

A review of analytical data for soil samples collected in Port Angeles is provided in Table 1-2. Table 1-3 summarizes measured dioxin/furan levels in other areas of Washington state.

Table 1-2 includes a summary of the types of samples collected, methods of collection, and analytical results from the following studies:

- *Rayonier Pulp Mill: Expanded Site Inspection (E & E 1998a).*
- *Final Combined Preliminary Assessment/Site Inspection Report, Rayonier Mt. Pleasant Landfill (E & E 1998b).*
- *Final Combined Preliminary Assessment/Site Inspection Report, Rayonier 13th & M Street Landfill (E & E 1998c).*
- *Remedial Investigation for the Uplands Environment of the Former Rayonier Mill Site (Integral 2006).*
- *Clallam County Housing Authority, Gale's Addition Site (CCHA 2008).*
- *Graving Dock Excavation Sampling (WDOT 2003).*

General observations gleaned from a review of these studies indicate that dioxins/furans in Port Angeles residential surface soils range from nondetect to 30 ng/kg 2,3,7,8-TCDD TEQ with an arithmetic mean of 8.0 ng/kg 2,3,7,8-TCDD TEQ[1]. Additional surface soil data summarized in *Evaluation of the Mt. Pleasant Landfill Closure Plan* (WDOH 2000) include samples collected from residential roof drip lines with dioxin/furan concentrations as high as 96 and 100 ng/kg 2,3,7,8-TCDD TEQ. These two soil samples were collected from a home near the Mt. Pleasant Landfill at which a house fire had been reported.

Many of the residential samples listed in Table 1-2 were collected from play areas, gardens, and other locations of disturbed or imported soils that may not be as representative of long-term deposition of Mill emissions as undisturbed soils (discussed further in Section 5.0). Dioxins/furans deposited on these garden and play area soils could have been mixed with soil from lower depths and thereby diluted, mixed with, or covered by fill or landscaping materials or otherwise disturbed. Sampling depth intervals also varied across studies.

[1] TEQ values presented as reported in referenced studies; values were not recalculated using most up-to-date toxic equivalency factors.

The ecological soil samples ranging from 0- to 4-inch depth intervals to 0- to 8-inch depth intervals below ground surface during the upland remedial investigation (Integral 2006) were taken from locations near the former Mill but may represent soils that have eroded or received eroded materials if collected on or at the base of steep slopes. Dioxins/furans in these samples ranged from less than 1 to 14 ng/kg 2,3,7,8-TCDD TEQ.

Additional dioxin/furan concentrations measured in soil were reported for the Gales Addition neighborhood; concentrations ranged from less than 1 to 12 ng/kg 2,3,7,8-TCDD TEQ (CCHA 2008). These samples were collected from soil following tree removal and other land clearing activities performed in preparation for housing construction. Collected from disturbed soils, the samples may or may not be representative of surface soils that could have received emissions from the former Mill.

The Washington State Department of Transportation (WDOT) collected samples from an industrialized area along the Port Angeles harbor to support a graving dock project (WDOT 2003). Dioxin/furan results for soil samples collected from an excavated area at the construction site ranged from less than 1 to 14 ng/kg 2,3,7,8-TCDD TEQ. An additional sample collected from a soil pile contained dioxins/furans at 229 ng/kg 2,3,7,8-TCDD TEQ (WDOT 2003). There was no available explanation for what contributed to the elevated levels.

The available data on soil dioxin/furan levels in Port Angeles soils provide some preliminary information, but are limited in spatial coverage and incorporate sampling protocols that are inconsistent with the objectives of this study. Locations for these samples are shown, to the extent possible, on Figure 1-3.

Table 1-3 presents results of soil samples collected in other areas in Washington state to provide a point of reference for samples collected in Port Angeles although direct comparison may not be possible for all samples due to differences in location types (for example, residences, parks, and agricultural or forested areas) and sampling methods.

Urban soil (public parks) samples were collected from 14 locations from 0 to 2 inches below ground surface in metropolitan Seattle, Tacoma, Tri Cities, and Spokane. Dioxins/furans in these samples ranged from less than 1 to 19 ng/kg 2,3,7,8-TCDD TEQ with an arithmetic mean of 4.1 ng/kg 2,3,7,8-TCDD TEQ (Rogowski et al. 1999). An additional 70 samples were collected from statewide agricultural, open field, and forested areas from a depth interval of 0 to 2 inches below ground surface (Rogowski et al. 1999). Concentrations in these samples were lower than dioxins/furans measured in urban areas (less than 1 to 5.2 ng/kg 2,3,7,8-TCDD TEQ). Dioxin/furan concentrations collected at Lake Ozette, arithmetic mean of 0.43 ng/kg 2,3,7,8-TCDD, were consistent with lower concentrations observed in agricultural field samples collected by Rogowski et al. (1999) (U.S. EPA 2007a). Rogowski et al. (1999) note that dioxins/furans measured in forested areas tended to be greater than in open field and agricultural areas. This difference in concentrations may be due in part to the trees “scrubbing” particulates from the air. The particulates then may be washed to underlying soils by rain or wind, or may fall to underlying soils with the leaves or needles.

Table 1-3 also summarizes results for urban surface soil samples collected in Bellingham, Washington, during a Superfund remedial investigation (E & E 2002). Ten urban soil (public

parks) samples were collected outside the influence of a wood-treating facility and other known, major sources from 0 to 2 inches below ground surface. Dioxins/furans in these "background" urban samples ranged from less than 1 to 2.8 ng/kg 2,3,7,8-TCDD TEQ with an average of 1.3 ng/kg 2,3,7,8-TCDD TEQ. Ten background residential soil samples collected from drip lines, walkways, and yards contained dioxins/furans ranging from less than 1 to 19 ng/kg 2,3,7,8-TCDD TEQ. Background surface soil samples collected in Bellingham were substantially lower than samples collected from 27 residential properties located within the influence of a wood-treating facility that used pentachlorophenol and creosote in its operations.

Dioxins/furans in samples collected from residences near the facility ranged from less than 1 to 47 ng/kg 2,3,7,8-TCDD TEQ, with an average of 8.6 ng/kg 2,3,7,8-TCDD TEQ (E & E 2002). An additional 34 samples collected from undeveloped open areas within the influence of the wood-treating facility contained dioxins/furans ranging from less than 1 to 435 ng/kg 2,3,7,8-TCDD TEQ. Dioxins/furan concentrations were greater in samples collected from the undeveloped, open areas near the facility than from the high-traffic and drip line areas of residential properties, suggesting that in residential properties near the facility, dioxins/furans may be diluted by soil disturbances.

Concentrations of dioxins/furans in samples collected from rural areas of Skagit County, Washington were greater than in other samples reported in Table 1-3 (Cobb et al. 1993). Arithmetic mean total dioxin/furan concentrations, not reported as 2,3,7,8-TCDD TEQ, ranged from 13.5 to 355 ng/kg among six sampling locations. The samples were collected prior to start-up of a rotary kiln municipal waste incinerator and were judged to be influenced by multiple industrial sources in the vicinity of the incinerator.

Additional sampling near the former Rayonier Mill will provide an expanded dataset, collected using consistent methods, of total dioxin/furan levels in area soils and will help Ecology understand the potential impacts of former Mill emissions on the surrounding community soils.

2.0 Study Objectives

The goal of the Rayonier Mill Off-Property Soil Dioxin Study is to increase understanding of dioxin/furan soil contamination in areas surrounding the former Rayonier Mill, including the magnitude and likely sources of contamination of surface soils. While a small number of soil sampling results for dioxins/furans in Port Angeles upland areas (reviewed in Section 1) are available, those data are too limited in number and inconsistent in sampling and analysis protocols to provide the desired information. Specific study objectives include:

- Determine the magnitude of dioxin/furan contamination in off-property surface soils potentially impacted by airborne emissions from the former Rayonier Mill, and
- Determine the relative contribution to measured soil dioxin/furan concentrations of former Rayonier Mill emissions compared to other potential sources.

While this study assesses the impacts from cumulative Mill emissions, it is recognized that there are other sources of dioxins/furans in soils. These include both diffuse “urban plume” sources and specific non-Mill facility emissions. The study design must take these other sources into account while meeting the objectives listed above. The patterns of soil contamination surrounding a single air emissions source in isolation are expected to demonstrate observable gradients over a relatively large spatial scale. However, these patterns may be largely obscured where multiple sources are present. Moreover, experience has shown that at small, local spatial scales the variability in soil contaminant concentrations among nearby sampling locations can be quite large, especially in more developed land use areas.

This study seeks to characterize the upper-range of soil dioxin/furan concentrations throughout the defined study area, wherever feasible, as a means of confirming whether Rayonier Mill emissions are found on local soils. Only the air emissions pathway associated with Mill operations is of interest for this study. Direct disposal of Mill-related materials (e.g., ash and wastes) is excluded from the scope of this study.

The study design must meet a resource constraint that will support collection and analysis of not more than 100 soil samples. It is notable that the scope for the study will produce one of the most detailed and extensive assessments of soil dioxin/furan contamination in an urban area completed to date within Washington state. Based on discussions with Ecology, time constraints also led to a decision to rely on a single mobilization for sample collection rather than a phased sample collection approach, in which study designs could be refined based on initial, early-phase results.

2.1 Magnitude of Contamination

The first objective of the study is to better define the magnitude of surface soil contamination resulting from airborne emissions from the former Rayonier Mill. The goals of the historical soil studies summarized in Section 1.0 varied. None of the studies aimed to define the extent of off-property contamination potentially resulting from Rayonier Mill emissions or the point of maximum impact of airborne emissions from the former Mill. As shown in Table 1-2, historical data are not comparable across studies due to low sample densities, different land uses across sample areas, and inconsistent sample collection and analysis methods. This study will provide a

much larger data set than previous off-property studies in Port Angeles and will be based on consistent sample collection, sample handling, and analytical protocols.

The current study aims to characterize the magnitude of dioxin/furan contamination in surface soil, including the upper-range concentrations of dioxins/furans throughout the study area. Existing soil studies demonstrate an inverse relationship between concentration and distance from the source; the trend is for dioxin/furan levels to be greatest near a specific emission source and to decrease as distance from the source increases (U.S. EPA 2003a), in spite of localized variability. Closer to the source, concentrations can vary substantially over relatively small distances, as depicted in Figure 2-1. Farther from the source and absent other dominant sources, concentrations may still vary over small distances but within a restricted range.

Even in the absence of a dominant source of dioxin/furan emissions, levels of dioxins/furans tend to be greater in urban settings and to decrease with distance from urban areas. This is referred to as the "urban plume" effect (U.S. EPA 2003a). In fact, dioxins/furans have been detected at measurable, albeit low, concentrations even at remote locations. Their ubiquitous distribution is the result of long-range atmospheric transport.

The variability of dioxin/furan concentrations observed within localized areas is due to a number of factors discussed in the *Rayonier Off-Property Soil Dioxin Study Conceptual Site Model Document* (E & E 2008). Briefly, concentrations in soil may be influenced by meteorological conditions during the operating or emission period; the presence or absence of ground cover that scrubs dioxins/furans from air; ground surface slope and erosion of soils containing dioxins/furans; soil disturbances such as landscaping, filling, or application of amendments; and the chemical characteristics of soil, such as organic carbon content.

To accomplish the objective of determining soil dioxin/furan concentrations in off-property upland soils, samples will be collected over a relatively large spatial area surrounding the former Mill. Consistent with the conceptual model of spatial patterns around a point source of air emissions, sampling densities will be greater in areas closer to the former Mill where both local variability and upper-range concentrations are expected to be higher. Sampling densities will be lower in more distant areas where the range in variability is expected to be less. Allocation of sample locations is discussed further in Section 5.2

Collection of a greater number of samples near the source will increase the probability of capturing the upper-range of dioxin/furan concentrations. Characterization of the upper-range of concentrations is particularly important because it will provide information on the maximum impact of former Mill emissions. In addition, this will provide the most useful information to distinguish between "urban plume" and Mill impacts, in terms of both dioxin/furan concentrations and congener profiles. These distinctions are crucial to meeting the second objective, source identification.

Although the number of locations to be sampled in this study is large compared to most other studies of dioxins/furans in soil, the inherent variability of dioxin/furan concentrations in highly developed urban area soils makes it difficult to delineate the complete spatial pattern of dioxin/furan levels. The focus on the upper-range of dioxin/furan levels in this study design reflects this problem and supports the first identified study objective – determining if there are

impacts that can be associated with former Mill emissions, but not necessarily the full spatial pattern of such impacts.

2.2 Source Identification

The second objective of this study is to evaluate the dioxin/furan results with respect to source identification. The former Rayonier Mill, a source of dioxin/furans emissions, was located near other recognized dioxin/furan sources, which are discussed in Section 4.2. It will be important for Ecology to support its determination of potentially liable persons under MTCA (WAC 173-340-500), if any, based on credible evidence of the comparative contributions of different sources to the measured dioxins/furans in surface soil.

Consideration was given to identifying additional, unique chemical analytes that could be used as tracers, or indicators, of Mill impacts. However, no such additional tracer chemical(s) were identified. To meet the source identification and source allocation objective of the study, analyses will be performed for the seventeen 2,3,7,8-substituted dioxin/furan congeners and all ten homologue groups for collected soil samples. The chemical patterns within this data set will be evaluated using one or several statistical techniques, as described below in Section 8.0. In addition, the reasonableness and consistency of interpretations will be evaluated using statistical analyses. The selection of one or more multivariate statistical data evaluation approaches will be made based on a preliminary data review.

Existing studies from published literature illustrate the application of several approaches to source identification and allocation, including source profile matching and multivariate statistical techniques. Profile matching and multivariate analyses may be examined for this study, although several factors may limit the utility of source profile matching analyses. Based on a review of the literature and discussions with the project chemometrics expert (Ramos 2008), collecting samples from an area within which the chemical profiles for dioxins/furans are expected vary as a result of contributions from various sources may help identify different sources and support source allocation evaluations. This factor was considered in selecting the study area boundaries.

Emissions from different dioxin/furan sources have been characterized by the chemical profile or chemical “fingerprint” of the 2,3,7,8-substituted congeners (U.S. EPA 2003a; Cleverly et al. 1997; Pandompatam et al. 1997). As discussed in Section 1.1 above, dioxins/furans consist of 210 structurally similar but unique chlorinated compounds called “congeners.” Of these congeners, 17 having chlorine atoms at the 2,3,7, and 8 positions are considered the most toxic (U.S. EPA 2003a). The amount of each dioxin/furan congener formed varies depending on the source, resulting in a distinguishable pattern, or chemical “fingerprint,” characteristic of the source. Biogeochemical processes such as weathering may alter these patterns, so the statistical significance of differences found between source materials may decrease with increasing time since deposition.

Comparing the source emission profiles to profiles observed in soil samples—“fingerprint analysis”—is one approach used in source identification. EPA’s *Fingerprint Analysis of Contaminant Data* (FALCON) guidance recommends using normalized profile data and regression analysis to compare source and soil chemical profiles (Plumb 2004). This approach relies on several assumptions: that profiles for candidate sources are adequately characterized;

that these profiles will be sufficiently distinct and discernable within the soils dataset; and that following emission from the source and deposition onto soils, transformation and fate processes do not significantly alter the chemical profile.

The FALCON approach to fingerprint analysis has been attempted for the former Mill (Ridolfi 2005; MPE 2006). Rayonier concluded that there was no distinctive pattern for on-site sources that could be used to evaluate dioxin/furan congener patterns in off-property soil samples. Available source data and off-property soil data were limited, and use of the FALCON method was further complicated by the influence of other dioxin/furan sources in Port Angeles.

The Rayonier Mill Off-Property Soil Dioxin Study area is a developed urban landscape so it will be influenced by general "urban plume" impacts as well as other sources in Port Angeles (U.S. EPA 2003a; E & E 2008). Therefore, the approach to source identification will address co-mingling of dioxins/furans from potentially different sources. Multivariate statistical techniques will be used to partition sample results and provide source allocation estimates.

Because the mechanisms for air transport and deposition and other factors mentioned in Section 2.1 influence variability in soil concentrations of dioxins/furans, the relative contributions from various sources are expected to change as a function of sampling location. Therefore, source allocation analyses will be performed for individual sample results.

2.3 Issues Outside the Scope of This Study

The objectives of this study are to evaluate concentrations and spatial patterns in dioxin/furan contamination in soil. The objectives do not include the following:

- Delineation of the entire extent, or boundary, of contamination resulting from emissions from the former Mill;
- Complete characterization of contamination at sampled properties to support exposure and risk assessments or cleanup actions;
- Definition of background soil dioxin/furan levels; or
- Interpolation of results from sampled to not-sampled properties.

This study is focused on identifying the upper-range of dioxin/furan concentrations within the predominant impact area of former Mill emissions. Delineation of the full extent of emissions is outside the scope of the study, requiring in-depth investigation to determine appropriate background levels of dioxins/furans in addition to the full horizontal and vertical extent of contamination. Characterization of natural or anthropogenic background values for dioxins/furans in soil would require a different study design than what is proposed here.

Due to local variability, the dioxin/furan concentrations measured in this study may underestimate the true maximum concentration present on an individual property or in any local subarea. Also, the sampling performed at each sample location will be limited to one portion of the property and will not include a full characterization of the horizontal extent of the entire property. This study also will not include characterization of chemicals at multiple soil depths to determine the vertical extent of contamination. For these reasons, the data generated for this study will not be appropriate for characterizing properties to support cleanup actions.

The localized variability also prevents effective interpolation of dioxin/furan concentrations from sampled to unsampled properties. While it may be possible to generalize about dioxin/furan concentration ranges in soils for various locations across the study area, it is not reasonable to attempt to predict soil concentrations on a property-specific basis. Factors affecting soil concentrations at the individual sample location or property-specific level are discussed in the *Rayonier Off-Property Soil Dioxin Study Conceptual Site Model Document* (E & E 2008).

In addition, undisturbed areas are ideal soil sampling locations for this study, as they will be most likely to represent historical emissions deposition from the former Mill that have not been diluted due to earth-moving or erosion. Samples will not be collected from locations considered ideal for risk assessment, areas where people are most likely to contact soil. Areas most suited for assessing risk include soils contacted by people while working and recreating outdoors, soils used for gardening, and erodable soils that may be tracked indoors or blown in by the wind.

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3.0 Overview of Study Design

This section introduces the major components of the study design discussed in this plan. As with other area-wide sampling programs developed in Washington state (TPCHD and Glass 2002; PH-SKC and Glass 2000; PGWG and TerraStat 2005), hierarchic steps define the approach for this study.

Once the study objectives are defined, the study design requires a series of decisions on where samples will be collected. The principal sampling decisions include:

- Defining a study area;
- Identifying candidate sampling areas within the study area;
- Defining sampling zones, within which variations in sampling protocols may be considered;
- Determining sample allocations by sampling zone;
- Selecting properties for sampling, including consideration of land use/land cover type(s);
- Selecting locations within selected properties for sample collection; and
- Determining the depth interval(s) to be sampled.

A relatively large study area was defined for this study. The factors considered in establishing the study area boundaries are discussed in Section 4.0.

Multiple exclusion and/or preference criteria were applied at various stages of the development of the sampling design to identify sampling locations deemed most appropriate to meet the study objectives. These criteria are discussed for relevant levels of the design hierarchy within Section 5.0.

To meet the objective of sampling at locations reflecting the upper-range of concentrations in soil concentrations, Section 5 discusses the preference for sampling in wooded areas not otherwise excluded (e.g., by steep slopes). Previous studies and models for air particulate contaminants support a conclusion that soil dioxin/furan concentrations are generally higher in forested areas than in open areas. Since available wooded areas are limited within the study area, many samples will be collected from developed properties.

Section 5 also describes a set of sampling zones defined primarily as a means to apply a sample allocation scheme in which sampling densities are varied across the study area. The sampling zones also reflect some differences in available land use and land cover types across the study area; however, all other aspects of sample collection (compositing and sampled depth interval) are identical across all sampling zones. The defined sampling zone boundaries follow topographic contours or transportation routes as a matter of convenience and are not assumed to precisely define areas of varying dioxin/furan concentration. Because very limited information was available to use as a basis for defining the spatial patterns of soil dioxin/furan contamination, more detailed and complex approaches to providing a sample allocation with varying densities across the study area were deemed unnecessary.

All samples will be collected from a single, uppermost depth interval of 0 to 4 inches (see Section 5.5) and will be composites of a small number of subsamples.

The selection of analytes and importance of obtaining low limits of detection are discussed in Section 6.0. The process for putting the sampling plan into action, including the development of field implementation plans, the approach for gaining site access, and the schedule, are presented in Section 7.0.

Section 8.0 summarizes the proposed approach for data evaluation, including an overview of source identification and source allocation methods that may be employed. The first step in data evaluation is to explore the dataset using summary and descriptive statistics to determine the most appropriate steps for further data analysis. Evaluation of chemical data for pattern recognition, modeling, and statistics is referred to as "chemometrics." An expert in chemometrics, Dr. Scott Ramos of Infometrix, Inc., has been retained to perform the data evaluation and source identification analyses described in Section 8.0.

Once the analytical results have been reported to study participants and the data evaluation process is complete, a draft final report will be developed and presented for public review. The data reporting and results communication phases of the study are presented in Section 9.0.

4.0 Definition of Study Area

The first step in selecting sample locations is to define the study area. The study area boundary is selected using the following factors, discussed further in subsequent sections:

- Review of historic studies conducted in Port Angeles, including odor and air modeling studies.
- Inclusion of areas near other potential sources.
- Inclusion of preferred land cover areas.
- Maintenance of adequate sampling density.

The proposed study area surrounds the former Mill, extending to Tumwater Creek on the west, to Buchanan Drive on the east, and to Lauridsen Boulevard on the west side of the southern border (Figure 4-1). The east side of the southern border extends approximately one mile inland from the bluff to include the Drennan-Ford Funeral Home and Crematory. The study area encompasses approximately 4.2 square miles.

The study area extends farther to the east than to the west, consistent with the annual wind rose pattern in which westerly wind directions dominate. The eastern extension of the study area also encounters less-developed lands that should reflect the anticipated urban-to-rural gradient for "urban plume" impacts. Suitable forested properties also are most frequently available for sampling within the extended eastern portion of the study area.

Based on the judgment of field sampling personnel, some samples may be collected slightly beyond the mapped boundary of the study area if sampling locations are better, such as those in mature and relatively undisturbed forest. Several such areas were identified during a preliminary field survey in April 2008, for example, near Peninsula College and Peninsula Golf Club.

A small number of targeted samples will also be collected outside of the primary mapped study area. Additional samples will be collected along three north-south transects south of the study area. This is discussed further in Section 5.2. These inland samples are at higher elevations and are more distant from the urbanized Port Angeles area and most local sources of dioxin/furan emissions.

4.1 Historic Studies in Port Angeles

To define the study area boundary, information reviewed included historical soil studies, an odor complaint study, area topographic maps, air deposition and dispersion modeling, and the conceptual site model (CSM; E & E 2008). As shown in Section 1, soil samples were collected for the ESI (E & E 1998a) from various off-property locations. The results range in magnitude, up to tens of parts per trillion TEQ, with moderate spatial variability. The historic soil sampling results do not strongly support a study area definition.

4.1.1 Odor Study

In 1992, ITT Rayonier retained TRC Environmental Corporation to investigate odors in the vicinity of the former Mill after prolonged complaints from community residents (TRC 1992). The goals of the study included measuring odors in the community to determine the severity of impact, determining locations where odors occurred, identifying meteorological conditions most conducive to transporting odors to surrounding residential areas, determining the frequency of odor impacts, and evaluating the relative contribution of individual sources of odor at the Mill.

During summer 1992, Port Angeles residents lodged 400 odor complaints with two trained interns via a local phone "hot line." The interns then verified 103 of the complaints at the odor's location. Odors were typically characteristic of compounds smelling of sulfur or chlorine and the interns were trained to associate a specific odor with a specific source at the Rayonier Mill. Odor maps based on the resident complaints indicate most complaints were received from the Gales Addition neighborhood located within one mile east of the former Mill and from nearby areas south and west of the Mill. Based on odor identification and classification by source, the interns found that the hog fuel boiler and chlorine dioxide generator induced the greatest number of odor complaints (47 percent), followed by the recovery boiler (34 percent) and the Purayonier[2] system (19 percent; TRC 1992).

The odor complaint maps were used to focus further odor investigation by interns, who made an additional 822 routine and opportunistic odor measurements at various locations within the vicinity of the Mill (Figure 4-2). Odors were rated using an 8-point scale based on severity of odor, with a score of 8 representing the strongest odor. Odors were noticed as far as three miles from the Mill but most were noticed closer to the Mill in the Gales Addition neighborhood. The Gales Addition neighborhood odors were ranked as most severe (score of 4 or greater).

The 1992 TRC study found that complaint locations were consistent with the predominant wind direction at the time of the complaint. In addition, average wind speeds were lower on days when residents issued complaints (5 miles per hour) than on other days during the study period (7 miles per hour).

Almost no information exists to scale the mapped incidence, frequency, or severity of odors associated with the former Rayonier Mill against soil dioxin/furan concentrations. The verified odor maps do indicate a pathway for airborne substances to travel from the Mill to relatively widespread locations within several miles of the Mill at varying frequencies and magnitudes. The maps showing resident-reported odors very likely reflect population density, with lower density areas probably translating to fewer complaints. Additional anecdotal information from contacts with local air agency staff and long-time area residents is consistent with this spatial scale of perceived impacts.

The proposed study area includes most, but not all, locations mapped in the TRC odor study. Note in Figure 4-2 that odors were registered as far west as Tumwater Creek, as far east as Mt. Pleasant Road/N. Larch Avenue, and as far south as Park Avenue. The sample allocation scheme

[2] The Purayonier system removes impurities from processed cellulose using chemicals and heat to create a pure product (TRC 1992).

proposed in Section 5.2, with denser sampling in areas close to the Mill, is consistent with the greater severity of odors reported in areas close to the Mill.

4.1.2 Air Dispersion and Deposition Modeling

The ambient air dispersion and deposition modeling study conducted by Rayonier Inc. for the Port Angeles Mill was reviewed to provide an independent assessment of the model adequacy and to assess its usefulness in defining the soil study area and sample allocation. Modeling was performed by Rayonier Inc. to define an area and approximate boundary within which soil sampling could be conducted, based on estimates of particulate deposition from mill emissions. The area shown in Figure 4-3 would likely have the highest deposition from historical operations of the facility. Other non-Mill-related sources of dioxins/furans were not included in the modeling effort.

A detailed review of the Rayonier air model, described in a technical memorandum submitted to Ecology separately, included a discussion of the meteorological data, surface air data, upper air data, and dispersion model inputs (terrain, receptors, emission data, building downwash, and deposition). The following air modeling-related documents were reviewed:

- *Aerial Deposition of Particulates from Stack Emissions* prepared for Rayonier Inc. by Kennedy Jenks Consulting and Integral Consulting, dated August 2004. This report was reproduced as Appendix H in *Remedial Investigation for the Uplands Environment of the Former Rayonier Mill Site* (Integral 2006).

- Comments from the Rayonier Technical Advisory Group (RTAG) on the August 2004 report. These comments were included as Appendix I in Integral (2006).

- *Validation of ISC Model*, presented in the *Remedial Investigation for the Uplands Environment of the Former Rayonier Mill Site* (Integral 2006). This study was conducted by Malcolm Pirnie Engineers for Rayonier in response to RTAG comments. Meteorological data and ISC-ST3 model input and output files used in the modeling study also were reviewed.

The input and output files from the modeling study were examined in detail. The model input files were imported into a commercial software vendor's version of the Industrial Source Complex Short Term (ISC-ST3) / AERMOD model (Bee-Line Software) to evaluate the layout of the receptor grids, confirm that elevation values were assigned to receptor locations, and evaluate the positioning of the stacks and buildings in context with the receptor grids. Output files from the Rayonier modeling study also were examined; graphical output files were pulled into the model and displayed to examine the deposition pattern contours compared to those shown in the modeling report. No discrepancies were found.

In addition, confirmatory model runs were performed for some of the original model runs using the meteorological data from the Olympic Region Clean Air Agency site provided by Rayonier and the imported input files. The version of the ISC-ST3 and ISC-PRIME models used for the Rayonier study, while current at the time of the study, were subsequently updated by EPA. Since the ISC-ST3 model is no longer an EPA-preferred model, information on the update history of

the model is no longer available from the EPA modeling web site. Thus, any difference in confirmatory model results from the original model results may be due to the update of the model. Nevertheless, confirmatory model results were used to reproduce the deposition pattern shown in the Rayonier modeling report. The confirmatory modeling showed lower maximum deposition rates than the original modeling, but in general, the results were spatially similar.

Both the initial and the independent review air deposition modeling results suggest very limited areas for major impacts from Mill emissions of dioxins/furans. The proposed study area is quite large compared to the limited areas of higher deposition suggested by the model. It is not assumed that considerable soil contamination associated with Rayonier emissions will be found throughout the larger study area; any impacts associated with Mill emissions might be restricted to only a small portion of the study area. However, the larger study area will provide an opportunity for compiling "confirming negative evidence" without pre-judging the spatial scale of impacts.

However, the soils data could be inconsistent with the deposition modeling results, showing more widespread impacts and suggesting inadequacies in the model. Inconsistencies between the model and observed impact areas could be due to upset operating conditions, turbulent boundary layer fumigation events, or other factors related to operations and meteorology unaccounted for in the air model. The sample allocation scheme provides for much greater sampling density in areas where deposition modeling indicates the greatest impacts should have occurred, and is in that respect consistent with the modeling results.

4.2 Potential Dioxin/Furan Sources

Potential and known sources of dioxins/furans in Port Angeles are discussed in the *Final Rayonier Off-Property Dioxin Soil Study Conceptual Site Model Document* (E & E 2008). Fixed sources include:

- Current and historical pulp and paper and related industries (Fibreboard Company, Nippon Paper Industries, Rayonier Inc., K-Ply);
- Medical waste incinerator at the Olympic Memorial Hospital;
- Miscellaneous boilers (court house, public schools);
- Crematories;
- Vehicle emissions;
- House and other structural fires; and
- Home oil/wood stove heating and waste incineration (for example, burn barrels).

The locations of fixed sources such as pulp and paper facilities, boilers, crematories, and incinerators, shown in Figure 4-4, and other non-fixed or diffuse sources such as automobiles and burn barrels were considered during delineation of the study boundary. The proposed study area boundary is intended to be large enough to include other non-Mill sources (although not necessarily all such sources in the greater Port Angeles area) and to provide a reasonable likelihood of including disparate congener profiles, which may enhance the source identification and source allocation evaluations.

4.3 Preferred Land Cover/Land Use Areas

As previously mentioned, sampling soils in relatively undisturbed areas, especially those with mature forest cover, is preferred to determine the magnitude of maximum deposition of emissions from the former Mill. Previous studies have found that undisturbed soils better represent upper-range contaminant concentrations because development and other forms of soil disturbance dilute or remove contaminants (TPCHD and Glass 2002; PH-SKC and Glass 2000; PGWG and TerraStat 2005).

Undisturbed areas in the vicinity of the former Mill are limited and typically occur on steep slopes along the shoreline or in creek ravines. Because steep slopes and ravine bottoms are subject to erosion or additional soil deposition, they have been excluded from the study area. Elevated soil dioxin/furan levels are possible in such areas, but it is less certain that those areas represent regional uplands impacts. However, it may be appropriate to sample these areas in later phases of the investigation.

The proposed study area boundary encompasses a few suitable wooded areas within the urbanized areas, as well as more extensive wooded areas east of the city. The study area provides an opportunity to sample at wooded properties in the primary downwind direction from the former Mill. The available wooded areas appear adequate to allow for a downwind transect extending several miles from the Mill and passing through an area with decreasing development, which may offer optimal information on gradients in dioxins/furans deposited from Mill emissions.

4.4 Sample Density

Resource constraints limit the number of soil samples that can be collected and analyzed in this study to no more than 100. The study area size allows for adequate density of sampling to meet study objectives given the expected variability in soil dioxin/furan concentrations. The relatively large proposed study area combined with a variable density sample allocation approach is intended to provide broad spatial coverage while allowing for intensive sampling of higher-impact areas. A non-uniform sample allocation approach is deemed critical for designating a relatively large study area under the stated resource constraint.

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5.0 Selection of Sample Locations

This section provides the rationale for selection of sample locations following the hierarchical approach introduced in Section 3.0. The first step in selecting locations was to define the study area. This section will discuss the following five steps leading to selection of sample locations:

- Delineation of sampling zones
- Allocation of samples
- Selection of within-grid sample locations
- Selection of within-property sample locations
- Selection of sampling depth interval

As mentioned in Section 4.0, properties sampled in the study will include undeveloped (wooded) properties and developed (residential) properties. Specific locations at either property type may be undisturbed or disturbed. The terms undisturbed and disturbed are used to reflect patterns of soil disturbance relevant to sampling decisions, representativeness, and data interpretation. Properties may include both undisturbed and disturbed areas, such as forested acreage and cleared fields and lawns, although many typical, smaller urban residential properties will have only disturbed areas. Forested properties may be largely undisturbed, but with some degree of disturbed surfaces from animal and human pathways, uprooted trees, animal foraging, or other causes. To the extent they are available, undisturbed areas will be sampled preferentially to provide the best estimates for upper-range soil concentrations. Aerial photographs and initial field surveys reviewed during preparation of the sampling design indicate that much of the study area is developed; therefore, most of the samples will be from developed properties.

Developed sampling areas include a variety of land use types. Residential properties, vacant (cleared) lots, meadows and grazing lands, parks and playgrounds, schools, and commercial properties are all considered developed properties offering mostly disturbed sampling sites compared to wooded lands. The development and soil disturbance history of each property affects its current pattern of soil contamination from the cumulative deposition and retention of dioxins/furans. Within highly developed urban areas, older residential properties are generally preferred to characterize the magnitude of contamination where wooded land cover is absent. Though not true in every case, the greatest soil disturbance is often associated with initial construction of a home. Older homes may therefore represent a longer period post-construction for accumulation of soil contaminants from former Mill emissions. For this reason, both construction date and date(s) of earth-moving activities (as indicated, for example, by grading permits or information obtained during interviews) will be considered when selecting a sample location.

5.1 Delineation of Sampling Zones

The study area encompasses approximately 4.2 square miles. This area was divided into seven distinct sampling zones, shown in Figure 5-1. As noted in section 3.0, the primary purposes for delineating sampling zones are (1) to distinguish areas of different land use and land cover, and (2) to allow variable sampling densities in different portions of the study area.

The proposed zones are designated as west (W1, W2, W3) or east (E1, E2, E3, E4) with reference to the former Rayonier Mill site and Ennis Creek. Zones W1, W2, and W3 represent more densely developed, urban properties. Zones W1 and W2 are separated by Highway 101 and are delineated from Zone W3 by Peabody Street. Referring to Figure 4-2, Zones W1 and W2 encompass areas with a large number of odor complaint locations (TRC 1992). Zone W1 and the Highway 101 corridor are dominated by commercial properties, whereas Zones W2 and W3 include primarily residential properties.

Zones E1, E2, E3, and E4 represent less-developed areas, although with mostly disturbed soils. Of these four sampling zones, Zone E1 (Gales Addition) has the most residential land use. Zones E2, E3, and E4 are dominated by open fields, agricultural areas, and wooded lots.

Zones E1 and E2 are generally separated from Zones E3 and E4 by Highway 101 and Zones E1 and E3 are generally separated from Zones E2 and E4 by Lees Creek. The southern boundary of Zone E2 cuts off the S-curve of Highway 101. The eastern edge of Zone E2 is separated from Zone E4 by Morse Creek. The eastern edge of Zone W2 meets Zone E3 along South Golf Course Road. Zones E1 and E3 had a larger number of odor complaint locations than Zones E2 and E4.

In delineating sampling zones within the defined study area, a number of exclusion criteria were considered. At this stage of the process, exclusion criteria are applied only for relatively larger areas; additional exclusion criteria applicable to smaller areas are considered in subsequent stages. Creeks and the steep side slopes along creek ravines were excluded, as previously noted, because of the potential for erosion and flooding to affect the representativeness and interpretation of surficial soil measurements. The topography of the creek ravines and their orientation with respect to the former Mill and air transport pathways also might shelter the areas from deposition of Mill emissions. Sampling zone boundaries generally follow the top of the slope along the creek ravines and follow the bluff along the shoreline.

Other potential exclusion criteria were considered but only one additional excluded area was included at the scale of sampling zones. No large areas with land ownership considered likely to deny access for sampling were identified. Areas where exposed soils are not likely to be available, such as developed, paved commercial properties, are localized and too small to be identified for exclusion at this stage. Preliminary review of a city database with building construction dates indicated that only one small neighborhood within Zone W2 has numerous houses constructed fewer than 30 years before Mill closure in 1997. Therefore, no substantial areas were excluded because they lacked properties that had been undisturbed long enough to accumulate dioxins/furans from Mill emissions. However, the relatively large Peninsula Golf Course within Zone E3 was developed fairly recently and is subject to fairly intensive maintenance, so that property was excluded.

5.2 Allocation of Samples

After delineating the study area and sampling zones, the next step in sample design is to allocate the limited number of samples. Considering the study objectives, the characteristics of the study area, and the type of information likely to enhance the chemometrics analyses for source identification, three types of targeted or preferred sample locations were identified. A total of 21

samples were assigned to these targeted locations, as discussed below, leaving 79 samples from the total of 100 to be allocated for broad coverage across all seven sampling zones.

Professional judgment was used to allocate samples to the seven sampling zones with the objective of obtaining information relevant to the study objectives using the maximum allowable number of samples. Several principles were identified and used to guide the allocation decisions. Since the dominant annual wind directions based on available wind roses are westerly, more samples are allocated to zones east versus west of the former Mill site. Relatively more samples (greater sampling densities) are allocated to areas closer to the former Mill site. The conceptual model for an air emissions source, as well as information from the odor and deposition modeling studies, indicate that the magnitude of impacts from Mill emissions should decrease with greater distance downwind.

The variability in dioxin/furan concentrations is likely to be greater in developed areas near the Mill because of the wide range of soil-disturbance histories among properties. Developed properties dominate areas close to the former Mill site. A study objective is to document whether Mill emissions are present in local soils, but not to determine the total extent of such impacts. Allocating more samples to closer, down-wind properties increases the probability of detecting potential Mill-related impacts. The proportional contribution from Mill emissions compared to other sources will very likely be greatest at properties closest to and down-wind from the Mill, so more samples should be taken there.

Allocating fewer samples to more distant sampling zones will likely lead to underestimating the upper-range of dioxin/furan concentrations in those zones. Since delineating the full extent of Mill impacts is not a study objective, such uncertainty in zones where Mill impacts are likely to be of lesser magnitude are tolerable. Sample allocations for more distant zones are anticipated to be sufficient to reveal other potential sources for soil dioxins/furans and for initial evaluation of spatial gradients in concentrations at the scale of the study area.

The proposed number of spatial coverage samples within each zone, plus additional targeted location sample counts, is summarized in Table 5-1. The actual number of collected samples by category may be affected somewhat by property owner participation and the availability of suitable sampling locations within each zone.

The size of each sampling zone and the allocated number of samples for that zone can be used to calculate an approximate grid spacing that provides coverage of the zone. This calculation is approximate because the irregular shapes of the sampling zones and “edge effects” along zone boundaries must be considered to achieve the allocated sample counts. Using this approach, the approximate grid spacing for each zone is shown in Table 5-2.

These approximate grid spacings are illustrated visually in Figure 5-2. The sampling densities reflected by this sample allocation scheme vary by about a factor of 10 over the entire study area.

In addition to the “spatial coverage” samples for the seven sampling zones, 21 samples will be collected from targeted or preferred locations to provide additional information and meet three purposes. The reasoning for this allocation is described below:

- Ten samples will be collected from forested areas in Zones E2 and E4. Those zones include most of the not otherwise excluded undisturbed forested properties available for sampling within the entire study area and can be used to investigate the dioxin/furan gradient along the primary downwind direction from the Mill.

- Nine samples from three transects (three samples each) will be collected in upslope areas south of the main study area, as shown in Figure 5-3. The transects will be aligned north-south and will reflect a gradient away from urban land use to more rural areas, in a non-prominent wind direction according to the area wind rose. Other dioxin/furan sources may be dominant in these upslope areas, including local burning activities and deposition from long-range transport. These samples will allow examination of a regional-scale pattern in magnitude and congener pattern for dioxins/furans.

- Two additional samples will be collected from high traffic areas along Highway 101 to characterize the potential source pattern and contribution of dioxins/furans from transportation sources.

5.3 Selection of Within-Grid Sampling Locations

Selecting candidate properties distributed according to the approximate sampling zone grid layout is the next step in study design. Four important considerations are involved: (1) forested (undisturbed) locations are preferred, (2) spatial coverage across sampling zones must be achieved, (3) no more than 100 samples may be collected, and (4) access agreements must be completed before sampling.

Where multiple candidate forested areas can be identified within a sampling zone, access agreements may be requested for all of them. However, those ultimately selected for sampling will be spaced such that the grid size for that zone is maintained to the extent practical. Once forested properties have been selected, developed properties with what are expected to be disturbed sampling locations will be selected to complete spatial coverage within each sampling zone. In urbanized zones these will mostly be residential properties. In less-developed zones open areas may dominate.

The grid sizes derived from allocated sample counts and sampling zone areas are relatively small in some cases, and the number of properties within many grid cells may be correspondingly small. Rather than attempting to find suitable (non-excluded) properties at or near grid nodes to produce a regularly spaced grid of sampled properties, a process for selecting one property for sampling within each grid cell will be used. This may result in a less-evenly spaced distribution of selected properties but will provide for spatial coverage throughout each sampling zone. The application of sampling grids thus provides a means for assuring spatial coverage.

Access agreements may not be obtained for some properties. For efficiency, access agreements will be sought for a small number of unexcluded properties in each grid cell. Ultimately only one property will be selected for sampling per grid cell. If no properties meeting exclusion criteria are available, or no access agreements can be obtained within a grid cell, another sampling location will be chosen from within the same sampling zone as a second property from another grid cell.

As previously noted, the shape of sampling zones and "edge effects" mean that the grid sizes applied to the sampling zones may produce actual sample counts varying somewhat from the allocated sample counts. To meet the constraint of taking no more than 100 samples, nominal grid sizes may be adjusted before starting to select properties to be sampled, and judgment will be used to combine small partial grid cells with adjacent cells so that the allocated sample counts are maintained.

Exclusion and preference criteria will be used to select properties for sampling. These will be discussed in more detail in the Sampling and Quality Assurance Plan (SQAP). At this stage of the design process, these criteria reflect the spatial scale of properties and are thus intermediate in scale between sampling zones and detailed sampling locations within properties.

Criteria for the selection of undisturbed forested properties include the following:

- A minimal size of at least several contiguous forested acres.
- A preference for more mature forested areas to reflect at least 30 years of accumulation before Mill closure in 1997. Tree height and girth are useful indicators of age. Recently replanted forest areas, and areas subject to recent fires, are excluded.
- Exclusion of wetland forest areas.
- Exclusion of steeply sloped areas and areas potentially shielded topographically from deposition of Mill emissions.

Criteria for the selection of developed properties include the following:

- Exclusion of homes built after 1977, and a preference for older homes among non-excluded homes.
- Exclusion/setback from heavily traveled transportation routes and rail lines.
- The availability of surface of adequate size allow for sampling.
- Exclusion of steeply sloped areas and areas potentially shielded topographically from deposition of Mill emissions.

As discussed in Section 7.0, the ultimate selection of the targeted property for sampling will be contingent on written consent from the property owner.

5.4 Selection of Within-Property Sample Locations

Once the candidate properties for sampling have been selected and the property owner has provided access, the precise location for sample collection on the property must be selected.

Exclusion and preference criteria also will be applied at the most detailed level to identify specific locations within properties for collecting soil samples. These criteria will be developed more extensively in the SQAP. The field sampling personnel will make the final decisions on where to collect samples using the criteria and applying field observations and information obtained from property owners/occupants. The general principle is to try to collect soils from the least disturbed, most representative locations within properties.

Sampling at undisturbed forested properties can consider factors such as the following:

- Ground-level vegetative cover as an indication of disturbance or a lack of disturbance.
- Exclusion of obvious animal or human pathways.
- "Hummocky" appearance of the ground surface, which often indicates disturbance (for example, treefall or animal digging).
- Exclusion of erosion channels.
- Exclusion of areas near the transition from forest to open/developed land cover, where incidental intrusion or disposal activities may have been more common.

Sampling at developed properties can consider factors such as the following:

- Exclusion of ornamental planting beds, garden areas, dog runs, or developed play areas where soil importation, amendment, or substantial disturbance are very likely.
- Exclusion of fire pits or areas where ashes have been admixed with soils.
- Exclusion of areas where regrading is known or suspected to have occurred after 1977, with a preference for areas with the least regrading since original property development.
- Exclusion/setback from driveways, downspouts, drip lines, areas where treated wood is present, or other activities potentially affecting representativeness of airborne deposition can be identified.

The concentration of air-deposited contaminants in surface soils can vary greatly over very short distances. This was demonstrated in the Tacoma Smelter Plume and Everett Smelter studies for arsenic and other inorganic contaminants emitted by the smelters. This phenomenon is believed to be a result of small-scale differences in deposition and soil characteristics, and, most importantly, of natural and anthropogenic soil-disturbing actions, which typically occur in a patchy fashion. The resources available for this study preclude collecting and independently testing multiple samples from individual properties. A single sample might not represent concentrations throughout a property. A decision was reached to collect small-scale composite samples in this study, which will better represent typical values at the compositing spatial scale. The compositing approach is consistent with the protocols in other studies of soil dioxin/furan contamination (U.S. EPA 2007a; Rogowski et al. 1999), although details of the compositing strategy have differed across studies.

Five subsamples will be collected at each target property and combined to form one composite sample for analysis. The size and shape of areas available for sampling will differ from one property to another, especially at residential properties. Undisturbed forested areas will typically have more local relief, variable ground conditions, and obstacles to sampling (e.g., trees) than residential lawns. Therefore, a default design for composite sampling will be used as a point of departure for modification (within bounds) by field personnel using their best judgment on collecting representative materials.

The default design will be to collect subsamples from the four corners and the center of a 10-foot-by-10-foot template. Most residential yards will accommodate this template size. Within larger yards, the standard template can be used at any representative subarea as determined by the field personnel. At residential or other developed properties, this layout may be modified as long as subsamples are separated by at least 5 feet. If this is not possible, an alternate property should be considered for sampling.

Wherever possible, all subsamples will be collected within one portion of the property, such as a back yard or a front yard, whichever portion is considered most likely to be least disturbed based on visual observation or interviews with property owners. Absent any information about a particular yard, a back yard or a side yard should be sampled rather than a front yard, based on the assumption that front yards are often more landscaped. For sampling at forested locations, the size of the sampling template may be modified upward from a minimum 10-foot by 10-foot square so that samples are collected up to 50 feet apart, and slightly off of the corners of a square template if obstacles or excluded ground surfaces occur.

Additional definition of sample collection protocols will be provided in the SQAP.

5.5 Sample Depth

Determining the depth of soil to collect is the final step in sample collection design. EPA's guidance on preparation of soil sampling protocols indicates that the upper-most 6 inches of soil reflect deposition of airborne contaminants (U.S. EPA 1992). This is particularly relevant for hydrophobic chemicals such as dioxins/furans that do not appreciably leach downward into soils with precipitation (U.S. EPA 2003a; 2007a). Brzuzy and Hites (1995) confirm the low mobility of dioxins/furans in studies showing that 80 percent of total dioxins/furans were found in the upper 15 centimeters (cm; 6 inches) of soil.

Although previous dioxin/furan sampling in Washington state soils focused on the upper 5 centimeters (2 inches) of soil (Rogowski et al. 1999), EPA adopted a target surface soil sampling depth of 0 to 10 cm (4 inches) for its pilot survey of dioxins/furans in rural U.S. soils (U.S. EPA 2007a). This depth was selected because handling a 0-to-5-cm soil interval can be challenging in the field and because other field studies have not shown significant differences in dioxin/furan concentrations measured from 0 to 5 cm and 5 to 10 cm (U.S. EPA 2007a). For consistency with EPA methodology and to facilitate proper sample handling in the field, a sample depth of 0 to 10 cm (0 to 4 inches) will be used for this study. The SQAP will provide further details on where the top of the depth interval being sampled occurs (protocol for removal of grass, forest duff, etc.).

Uppermost soil intervals are most representative of potential human contact with and exposure to soil contaminants, and, absent physical disturbance of the soils, these intervals typically contain the highest concentrations of dioxins/furans (if present) at a sampling location. Available information indicates that the uppermost sampling interval should be limited in depth to avoid dilution of higher near-surface concentrations with the lower concentrations that are present at greater depths.

While downward movement in the soil column due to leaching is very limited, the soil depth profile for dioxins/furans can be greatly affected by physical disturbances of soils. Disturbance can occur even in relatively undisturbed forest soils, but is much more likely at developed (for example, residential) sampling locations. Where unrecognized disturbance of a soil profile results in higher concentrations of dioxins/furans at depths greater than the uppermost sampled interval, the results from only that depth interval would underestimate impacts at that location and bias overall results toward lower concentrations. Previous soil contamination studies such as

the Tacoma Smelter Plume studies that included multiple depth intervals have demonstrated such "inverted" depth profiles for developed properties.

For this study, including multiple depth intervals could only be accomplished by sampling fewer properties, given the constraint on the total number of samples to be analyzed. This tradeoff was judged to be less favorable than providing better spatial coverage using only a single uppermost depth interval and accepting the potential for some bias toward low concentrations in the results, especially at developed properties. Data evaluations and interpretations will recognize limitations of the study design.

6.0 Sample Analysis

Analysis of all soil samples will include dioxin/furan congeners by EPA Method 1613B and total organic carbon (TOC). An attempt was made to identify unique tracer chemical(s) that may have been co-emitted with dioxins/furans from the former Mill, but none were identified.

6.1 Dioxin/Furan Analyses

The study will focus on dioxins/furans present in soils in the vicinity of the former Rayonier Mill because (1) pulp and paper mills are known to release these chemicals during operations, (2) hog fuel boiler ash testing and stack testing confirmed the presence of dioxins/furans, and (3) dioxins/furans have been found at elevated concentrations in soils on the Rayonier property. As discussed in the *Rayonier Off-Property Soil Dioxin Study Conceptual Site Model Document* (E & E 2008), dioxins/furans are persistent in the environment, with a half-life ranging from 10 to 12 years, and are toxic to humans and wildlife (U.S. EPA 2003a). Their persistence and toxicity further support their appropriateness as the primary analytes for this study. Based on available information, dioxins/furans are the most toxic chemicals that were emitted from the Mill and are the primary contaminants of interest for areas beyond the Mill property.

Dioxin/furan analyses will include quantification for the ten homologue groups and 17 congeners with chlorine substitution in the 2, 3, 7, and 8 positions using EPA Method 1613B. Based on results from the small number of samples previously collected in Port Angeles soils (Table 1-2), the results for this study can be expected to yield a substantial range of congener concentrations in off-property residential and forest surface soils.

If all samples yield concentrations well above nominal method detection limits for each congener, then the lower achievable detection limits are not necessary. However, the existing off-property sample data do not indicate that this is likely for individual congener concentrations. In fact, analytical results for some congeners may be dominated by nondetected concentrations if lower achievable detection limits are not obtained. Because a wide range in values is expected and congener and homologue profiles must be distinguished, it will be highly advantageous to obtain lower practicably achievable detection limits and minimize the frequency of nondetect concentrations. Obtaining results at the lowest concentration practicable will increase the probability of revealing subtle differences in congener patterns between samples. For these reasons, the contract laboratory will provide modified reporting limits that are lower than the minimum level defined by EPA Method 1613B, shown in Table 6-1.

6.2 Total Organic Carbon

Organic carbon in soils comes from decaying natural organic matter (humic acid, fulvic acid, amines, urea, and so forth) as well as from synthetic sources such as detergents, fertilizers, and pesticides. TOC is a potentially useful measure in soil because dioxins/furans adsorb to organic matter in soils. Thus, the greater the TOC content in soil, the greater the capacity of the soil to retain dioxins/furans.

However, researchers have reported mixed results for correlations of TOC and dioxins/furans (U.S. EPA 2007a). EPA's analysis of recently collected data for rural soils across the United States revealed a number of positive correlations of TOC to dioxin/furan homologues and dioxins/furans, measured as a TEQ. However, the correlations are not particularly strong, indicating that other factors such as grain size may also contribute (U.S. EPA 2007a). TOC will be measured in off-property soils to gain understanding of area soil capacity to bind dioxins/furans. TOC also may be used to normalize dioxin/furan data and allow for direct comparison of results between samples of different soil composition.

6.3 Grain Size

Organic carbon is sometimes correlated with grain size and dioxin/furan concentration, and grain size may correlate with dioxin/furan concentration (U.S. EPA 2003a; 2003b). However, grain size analysis will not be performed for this study nor will soil samples be sieved for analysis of specific size fractions. EPA's *Standard Operating Procedure for Surface Soil Sampling for Dioxins* (2003b) suggests use of a sieve with a 19 millimeter opening or a gloved hand to remove rocks, pebbles, vegetation, or debris from the soil sample. For this study, a gloved hand will be used to remove large debris.

Adequate sieving to collect a specific size fraction of soil requires air drying, which can take several weeks for wetter soils unless accelerated with heat. Dry sieving is not recommended for dioxin/furan analysis and may invalidate results because analyte loss could occur. Either air drying or use of heat could lead to analyte losses to the air. Once dried, the material to be sieved would be ground, which leads to further losses to the mortar, pestle, and sieve. If sieving is performed on a sample, reuse of a sieve also may transfer contaminants between samples. Wet sieving also is problematic due to difficulties in adequately screening the proper size fraction when clays and larger soil components are present. Again, wet sieving may also result in loss of sample to the sieve, as well as potential cross contamination between samples. These physical constraints on sieving create problems with data comparability and accuracy.

Submission of hand-screened, composite field samples to the laboratory for analysis is not consistent with the MTCA regulation stating that soils should be screened to retain only the fraction with particles less than 2 millimeters in diameter for analysis. Analysis of even smaller-size fractions, particles less than 0.25 or 0.15 millimeters in diameter or even smaller size fractions, is more relevant for risk assessment, which is not a focus of this study.

The proposal not to sieve samples to these smaller-size fractions is based on sample handling and analytical chemistry concerns, as discussed with the selected analytical laboratory staff. This also appears to be consistent with EPA's standard protocol mentioned earlier in this section (U.S. EPA 2003b). If dioxin/furan soil concentrations are enriched in smaller-size soil fractions compared to unsieved fractions, the data produced in this study could be biased low from the perspective of MTCA regulatory requirements, exposure and risk assessments, and cleanup levels.

6.4 Tracer Chemicals

Because the soils data set will likely be complex, it would be useful to supplement the analysis with an evaluation of other "tracer" chemicals that may have been co-emitted from the former Mill with the dioxins/furans. Identifying one or more tracer chemicals other than dioxins/furans could help differentiate deposition from the former Rayonier Mill from other potential sources, such as boilers and incinerators, vehicle emissions, and incidental burning (urban plume impacts from fireplaces, burn barrels, and other diffuse sources).

Tracer analyses have proven valuable for source allocation determinations at other sites. Useful tracer chemicals do not have to reflect primary contaminants of concern for exposure and risk evaluations or cleanup decisions; the important point is that they can be used to identify and track effects from a particular source. To discriminate one source from other potential sources and from background conditions, a tracer chemical should have a relatively high signal-to-noise ratio. Multiple inorganic tracer elements were effective in identifying downwind impacts on soils from Tacoma Smelter emissions (Glass 2003). These tracer elements were constituents of the ores and concentrates processed at the smelter. However, each facility must be evaluated individually to determine whether tracer chemicals may warrant allocation of resources for additional laboratory analyses.

The pulping process used at the former Mill was examined to identify material inputs, chemicals produced, and waste products. For a chemical to function as a tracer in hog fuel boiler emissions, it would have had to (1) withstand the high temperatures of the hog fuel or recovery boiler, (2) remain relatively unchanged during dispersion from the stack(s), and (3) undergone little weathering once deposited on soil. No chemicals other than dioxins/furans were identified that could meet these criteria. Furthermore, a review of on-site data did not reveal metals in soil, sediment, or groundwater that were sufficiently elevated or unique to allow their use as a tracer chemical. Manganese was suggested as a possible tracer chemical due to elevated detection in effluent but it is not likely suitable as a tracer chemical due to its relatively high natural occurrence in soils.

Sample materials submitted to the analytical laboratory will be archived for at least one year after completion of planned analyses. If further evaluations identify any candidate tracer chemicals, it may be possible to perform additional analyses on selected archived samples. For example, additional dioxin/furan congeners, other than the 2,3,7,8-substituted congeners targeted in this study, could be considered among possible tracer chemicals, although there is little precedent in the literature for their effective use.

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7.0 Implementation of Soil Sampling Plan

Implementation of the SSP will occur in three phases: (1) sample collection planning, (2) sample collection, and (3) sample analysis and data validation. These activities will begin in sequence upon finalization of the SSP.

7.1 Sample Collection Planning

Collecting 100 soil samples throughout the proposed study area will require substantial effort to obtain consent from owners of candidate properties and to outline methods for property-specific sample collection. The SQAP will include (1) detailed sample location maps; (2) field protocols for interviewing property owners, selecting the property-specific sample location, and collecting the samples; (3) quality assurance and quality control criteria; (4) a field health and safety plan (HASP); and (5) a completed cultural resource review for the study area. The SQAP will be developed following finalization of the SSP.

Properties selected for sampling will be identified prior to initiating the field sampling event. Planning will begin as soon as practical to allow for mobilization to the field in September 2008. As discussed in Section 5.3, properties will be selected to provide spatial coverage within zones throughout the study area, as well as to meet criteria for targeted sampling. Access agreements will be requested from property owners according to the process shown in Figure 7-1.

The first step in obtaining access is sending letters to candidate property owners. The letters will explain the nature of the study, the proposed sampling and results reporting schedule, methods used to collect the sample, and will include contact information for E & E staff and a “frequently asked questions” (FAQ) sheet. An example letter and access agreement will be provided in the SQAP. Property owners will be contacted via telephone within approximately seven days of mailing access agreement letters to request participation in the study. Five attempts will be made to contact property owners via telephone over a 10-day period, at different times of the day. If contact is made, owners who want to participate in the study may submit the signed access agreement to E & E; owners who do not want to participate will be removed from the candidate property list.

If candidate property owners cannot be contacted via telephone, recruitment staff will travel to Port Angeles and visit properties in person to request participation in the study. Three attempts will be made to contact each candidate property owner at different times of the day, on different days of the week. Owners wanting to participate in the study may submit the signed access agreement to the recruitment staff at this time. Owners who do not want to participate will be removed from the candidate property list. Multiple candidate property owners per cell will be contacted, but only one property per cell will be sampled. If after one week of recruiting, access is not granted to any properties meeting sample location selection criteria within a grid cell or target sample location, Ecology staff will be contacted to request assistance with obtaining access from an alternate property.

All property owners who submit a signed access agreement will be contacted via telephone or in person to complete a pre-sampling interview. The interview will include questions relating to

exclusion and preference criteria listed in Section 5.3 and described in more detail in the SQAP. If one or more properties meeting sample location selection criteria are accessible for sampling, one property will be selected for sampling. Properties not selected but considered appropriate for sampling will be retained on the candidate property list in case the primary selection becomes unavailable. Owners of selected properties will be notified and a sampling date will be scheduled.

An attempt to contact each participating property owner will be made one week and again two days prior to their scheduled sampling date.

7.2 Sample Collection

Sample collection will be performed in accordance with the SQAP. The sampling team will consist of two pairs of qualified environmental scientists who, along with the site safety officer, will be identified in the HASP. Every effort will be made to collect all samples during one field mobilization, requiring approximately 12 days of sampling by the two field pairs.

In areas where cultural resources may be present, a certified archaeologist and representative of the Lower Elwha Klallam Tribe (LEKT) will oversee the field sampling team. Cultural resource review and sampling oversight will be completed in accordance with state and federal laws, the Deferral Agreement for the Rayonier Mill Site between EPA, Ecology, and the LEKT, the Preliminary Intergovernmental Agreement between Ecology and the LEKT, and Executive Order 05-05 regarding cultural resources in Washington state, as well as protocols specific to the Lower Elwha Klallam Tribe.

Field team leaders will determine specific sample locations in the field based on field observations, best professional judgment, and interview information obtained from property owner(s) and/or tenants. Sample locations will be recorded using global positioning systems described in the SQAP.

7.3 Sample Analysis and Data Validation

Samples will be analyzed and data validated in accordance with the SQAP. Samples will be submitted to the contracted laboratory daily. Analysis turn-around will be approximately 45 days. Electronic data packages will be provided to the third-party data validation contractor for a 30-day data validation period. Data will be validated following the guidelines outlined by EPA's Analytical Operations/Data Quality Center, *National Functional Guidelines for Chlorinated Dioxin/Furan Data Review* (2005), *National Functional Guidelines for Superfund Organic Methods Data Review* (2007b), and *EPA Region 10 SOP for the Validation of Polychlorinated Dibenzodioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data* (1996). When validation is complete, the data will be entered into Ecology's Environmental Information Management system.

8.0 Data Evaluation

Multiple approaches to data evaluation will be combined in this study to support conclusions regarding potential source identification. Weight of evidence and consistency criteria will be used in combining the various lines of evidence. Primary evaluation approaches will address the spatial patterns, chemical patterns, and numerical magnitude and statistical distribution of values as measured for individual congeners and homologue groups and as a 2,3,7,8-TCDD TEQ. Additional evaluations will consider the relationship of dioxin/furan concentrations to soil TOC and land use and land cover types.

Throughout data evaluation, potentially anomalous results will be identified and carefully reviewed for possible contributing factors such as details of the characteristics of the sampling locations. Beyond descriptive data summaries and simple correlation and regression analyses, an objective for data evaluations will be attribution of contributions from the former Rayonier Mill and other sources to the observed dioxin/furan results in soil samples.

Different dioxin/furan sources have been characterized by their chemical profiles for the seventeen 2,3,7,8-substituted congeners (Cleverly et al. 1997 and Pandompatam et al. 1997). The FALCON profile-matching or fingerprint approach discussed in Section 2.2 compares source (emission) profiles to sampled soil profiles, using various statistical approaches. FALCON relies on the initial finding that source profiles for different candidate sources are sufficiently distinct to be classified and discriminated in evaluating the soils data set. If source-specific congener profiles are not available (for example, for the former Mill), a general profile for the source category must be used. This is a potential source of uncertainty for the analysis. Moreover, transformation and fate processes during air transport and after deposition can alter the congener profile or fingerprint, affecting the effectiveness and representativeness of a “profile matching” analysis. For this study, the soils data may be initially evaluated using a profile-matching approach, although there will likely be limitations to this approach.

Traditional univariate methods (those that consider only one variable or factor at a time) will not allow for adequate evaluation of the data. Multivariate methods, including chemometrics, allow the statistician to characterize information while looking at all of the measurements as a block of data. Algorithms have been developed for specific purposes of data exploration, pattern recognition, property prediction, and mixture analysis.

Soil data set can be analyzed using a variety of multivariate statistical methods. A general overview of such multivariate methods can be found in environmental forensics texts (Murphy and Morrison 2001; Morrison and Murphy 2005). These statistical analysis approaches can work “backward” from the soils data set to identify the number of potential major sources of dioxins/furans and their contributions to individual samples. Using this method, source profiles are not required.

Mixture analysis methods are typically used in studies of source apportionment to identify the possible origin(s) of pollutants. A variety of algorithms are available to solve source identification problems. The most commonly applied methods include polytopic vector analysis,

positive matrix factorization, and alternating least squares. They are similar in approach, but determining which to use depends on the characteristics of the data set.

Before any mixture analysis method is used in a study, it is highly recommended to visualize the data using an exploratory tool. Two of the most commonly used tools include hierarchical cluster analysis and principal components analysis (PCA). PCA is commonly used because it does not distort sample relationships and it allows the statistician to focus on characteristics of the data that are most important, such as the variability in the dataset. PCA offers insight into trends and relationships among samples, while also allowing an interpretation of which variables are most important in describing those relationships.

Any interpretations of the data with respect to potential source(s) based on profile matching, spatial evaluations, or chemometric evaluations also will be evaluated for reasonableness on the basis of source-pathway relationships. Information such as the likely magnitude of dioxin/furan emissions, wind rose data, deposition modeling results, validated odor complaint mapping, and other relevant information can be considered as part of the plausibility analysis.

9.0 Data Reporting

A preliminary technical memorandum will be prepared and submitted to Ecology and will be followed by a public review draft project report. The final project report is expected to be completed by June 2009.

9.1 Technical Memorandum

Once data validation is completed, a technical memorandum will be prepared compiling all the results and providing descriptive and exploratory data evaluations. This memorandum will provide a point of departure for more detailed chemometric data evaluations to investigate source contributions to soil dioxin/furan concentrations throughout the study area. The technical memorandum will focus on the sampling results, introduced only by a brief summary of the study purpose and design.

The technical memorandum will provide complete data tables with relevant data qualifiers assigned by the validation subcontractor. The data set will be graphically summarized using approaches such as concentration histograms, cumulative frequency plots, and/or probability plots. The magnitude and overall spatial pattern of dioxin/furan contamination will be illustrated by mapping the results using color coding for each sampling location to show the range in chemical concentration. In addition, scatter plots will be developed to demonstrate the relationship(s) among distance, direction, and concentration, including overall trends and local variability in concentration. These plots will facilitate review of the data with respect to magnitude and spatial pattern.

Other evaluations will include assessments of the correlation between TOC and dioxin/furan concentration, comparisons of results for residential (disturbed) and wooded (undisturbed) land use types, and preliminary analyses of variability in dioxin/furan profiles using normalized multi-congener values and plots.

After completion of the technical memorandum and submittal to Ecology for review, an appropriate strategy for chemometric evaluation of the data will be assessed and discussed with Ecology. During this period, Ecology will send individual dioxin/furan results to study participants along with a letter describing the significance of the results. Data also will be uploaded to Ecology's Environmental Information Management system.

9.2 Final Project Report

A project report will be developed that will document the study objectives, protocols, and results. That report will include validated data and calculated TEQ values, summary and descriptive statistics and data visualizations, georeferenced concentration maps, any deviations from the SSP and SQAP, and a discussion of the chemometric data evaluation process including source identification analysis results.

Details of the chemometric evaluations will be provided as an appendix to the final project report. The public review draft report will be submitted to Ecology and then finalized following a public comment period.

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Tables

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Table 1-1. Dioxin/furan homologue groups and the 17 congeners of greatest concern.

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

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Table 1-2. Summary of dioxin/furan data collected in Port Angeles.

Investigation	Sample Location	Year of Sample Collec-tion	Number of Samples	Distance & Direction from Rayonier	Sample Location Type (lawn, garden, planting strip, etc.)	Sample Depth (inches)	Seive (Y/N)	Composite or Discrete	Soil Type	Arith-metic Mean TEQ (ng/kg)	Range TEQ (ng/kg)	TEF Source	Detection Limit Treatment	Congener Data (Y/N)	Homo-logue Data (Y/N)	Analytical Method
Studies Conducted in Port Angeles, Washington																
Expanded Site Investigation, Former Rayonier Mill (E & E 1998a)			20			0-3	N	Discrete			0.05 - 29.72	a				
OMH-01	Olympic Memorial Hospital	1998	1	< 0.5 mile southwest	Hospital grounds	0-3	N	Discrete	Brown loamy topsoil with organic content		2.99	a	RL = 0	Y	Y	EPA Method 8290
OMH-02	Olympic Memorial Hospital	1998	1	< 0.5 mile southwest	Hospital grounds	0-3	N	Discrete	Brown loamy topsoil with organic content	2.69	2.39	a	RL = 0	Y	Y	EPA Method 8290
CTR-01	1800 Block, Harborcrest Drive	1998	1	< 0.5 mile southeast	Residential yard	0-3	N	Discrete	Brown sandy topsoil with low organic content	8.66	8.66	a	RL = 0	Y	Y	EPA Method 8290
JWR-01	1300 Block, East Third Street	1998	1	< 1 mile south	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content		0.49	a	RL = 0	Y	Y	EPA Method 8290
JWR-02	1301 Block, East Third Street	1998	1	< 1 mile south	Residential yard	0-3	N	Discrete	Brown sandy topsoil with low organic content	11.1	21.71	a	RL = 0	Y	Y	EPA Method 8290
GLR-01	2100 Block, East Third Avenue	1998	1	< 1 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content	3.98	3.98	a	RL = 0	Y	Y	EPA Method 8290
BDC-01	Caroline Street and South Eunice Street	1998	1	< 1 mile southwest	Commercial property grounds	0-3	N	Discrete	Brown sandy topsoil with low organic content	0.48	0.48	a	RL = 0	Y	Y	EPA Method 8290
JNR-01	2200 Block, East Third Avenue	1998	1	< 0.5 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content		28.98	a	RL = 0	Y	Y	EPA Method 8290
JNR-02	2200 Block, East Third Avenue	1998	1	< 0.5 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content	19.845	10.71	a	RL = 0	Y	Y	EPA Method 8290
ECP-01	Erickson Playfield	1998	1	< 1 mile southwest	City park	0-3	N	Discrete	Brown loamy topsoil with organic content	0.05	0.05	a	RL = 0	Y	Y	EPA Method 8290
VMP-01	County Courthouse	1998	1	< 1.5 mile southwest	City park	0-3	N	Discrete	Brown loamy topsoil with organic content	4.48	4.48	a	RL = 0	Y	Y	EPA Method 8290
ZMR-01	1900 Block, East Third Avenue	1998	1	< 0.5 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content		10.26	a	RL = 0	Y	Y	EPA Method 8290
ZMR-02	1900 Block, East Third Avenue	1998	1	< 0.5 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content	10.57	10.88	a	RL = 0	Y	Y	EPA Method 8290
MSR-01	2000 Block, East Fifth Avenue	1998	1	< 1 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content		7.25	a	RL = 0	Y	Y	EPA Method 8290
MSR-02	2000 Block, East Fifth Avenue	1998	1	< 1 mile southeast	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content	4.63	2.01	a	RL = 0	Y	Y	EPA Method 8290
ENR-01	1200 Block, East Third Street	1998	1	< 1 mile south	Residential yard	0-3	N	Discrete	Brown sandy topsoil with low organic content		6.89	a	RL = 0	Y	Y	EPA Method 8290
ENR-02	1200 Block, East Third Street	1998	1	< 1 mile south	Residential yard	0-3	N	Discrete	Brown sandy topsoil with low organic content	8.995	11.1	a	RL = 0	Y	Y	EPA Method 8290
AGD-01	1300 Block, East Fourth Street	1998	1	< 1 mile south	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content	5.63	5.63	a	RL = 0	Y	Y	EPA Method 8290
WPI-01	1300 Block, East Fourth Street	1998	1	< 1 mile south	Residential yard	0-3	N	Discrete	with organic content	1.23	1.23	a	RL = 0	Y	Y	8290
TBS-01	1000 Block, Columbia Street	1998	1	< 0.5 mile southwest	Residential yard	0-3	N	Discrete	Brown loamy topsoil with organic content	29.72	29.72	a	RL = 0	Y	Y	EPA Method 8290
	Background		3					Discrete			ND - 0.42	a	RL = 0	Y	Y	EPA Method 8290
ONP-01	Olympic National Park	1998	1	5 miles south	area	0-3	N	Discrete	with organic content	0.42	0.42	a	RL = 0	Y	Y	8290
ONP-02	Olympic National Park	1998	1	5 miles south	Wooded/Undeveloped area	0-3	N	Discrete	Brown loamy topsoil with organic content	ND	ND	a	RL = 0	Y	Y	EPA Method 8290
SCP-01	Salt Creek County Park	1998	1	10 miles west	Wooded+F49/Undeveloped area	0-3	N	Discrete	Brown loamy topsoil with organic content	0.19	0.19	a	RL = 0	Y	Y	EPA Method 8290

(Table 1-2 page 1 back side)

Table 1-2. Summary of dioxin/furan data collected in Port Angeles.

Investigation	Sample Location	Year of Sample Collec-tion	Number of Samples	Distance & Direction from Rayonier	Sample Location Type (lawn, garden, planting strip, etc.)	Sample Depth (inches)	Seive (Y/N)	Composite or Discrete	Soil Type	Arith-metic Mean TEQ (ng/kg)	Range TEQ (ng/kg)	TEF Source	Detection Limit Treatment	Congener Data (Y/N)	Homo-logue Data (Y/N)	Analytical Method
PA/SI Rayonier 13th & "M" Street Landfill (E & E 1998c)			4								0.92 - 3.5	a	RL = 0			EPA Method 8290
RS-02-SS	Stephen residence	1997	1	3.5 miles west (< 0.5 mile from landfill)	Gardens, play areas, exposed soil	0-6	N	Discrete	NR	1.5	1.5	a	RL = 0	Y	Y	EPA Method 8290
RS-03-SS	Hoe residence	1997	1	3.5 miles west (< 0.5 mile from landfill)	Gardens, play areas, exposed soil	0-6	N	Discrete	NR	3.5	3.5	a	RL = 0	Y	Y	EPA Method 8290
RS-25-SS	Perry residence	1997	1	3.5 miles west (< 0.5 mile from landfill)	Gardens, play areas, exposed soil	0-6	N	Discrete	NR	2.7	2.7	a	RL = 0	Y	Y	EPA Method 8290
RS-26-SS	Dekreon-Dorcy residence	1997	1	3.5 miles west (< 0.5 mile from landfill)	Gardens, play areas, exposed soil	0-6	N	Discrete	NR	0.92	0.92	a	RL = 0	Y	Y	EPA Method 8290
	Background residence		1													EPA Method 8290
RS-07-SS	Fuson residence	1997	1	3 miles west	Gardens, play areas, exposed soil	0-6	N	Discrete	NR	0.41	0.41	a	RL = 0	Y	Y	EPA Method 8290
PA / SI Rayonier Mt. Pleasant Landfill (E & E 1998b)			6								2.3 - 17	a	RL = 0			EPA Method 8290
RS-01-SS	Owens residence	1997	1	NR	Gardens, play areas, exposed soil	0-7	N	Discrete	NR	2.3	2.3	a	RL = 0	Y	Y	EPA Method 8290
RS-04-SS	R. Johnson residence	1997	1	NR	Gardens, play areas, exposed soil	0-8	N	Discrete	NR	6.7	6.7	a	RL = 0	Y	Y	EPA Method 8290
RS-09-SS	T. Johnson residence	1997	1	NR	Gardens, play areas, exposed soil	0-9	N	Discrete	NR	4.3	4.3	a	RL = 0	Y	Y	EPA Method 8290
RS-12-SS	Schmuck residence	1997	1	NR	Gardens, play areas, exposed soil	0-10	N	Discrete	NR	3.6	3.6	a	RL = 0	Y	Y	EPA Method 8290
RS-18-SS	Brown residence	1997	1	NR	Gardens, play areas, exposed soil	0-11	N	Discrete	NR	8.5	8.5	a	RL = 0	Y	Y	EPA Method 8290
RS-19-SSBK	Gorss residence	1997	1	NR	Gardens, play areas, exposed soil	0-12	N	Discrete	NR	17	17	a	RL = 0	Y	Y	EPA Method 8290
	Background residence		1													EPA Method 8290
RS-13-SS	Nichols residence	1997	1	NR	Gardens, play areas, exposed soil	0-6	N	Discrete	NR	2.3	2.3	a	RL = 0	Y	Y	EPA Method 8290
Rayonier Uplands Environment RI (Integral 2006)			12			Biologically active zone[c]	N	Composite (5 subsamples)	NR		0.6 - 14.2 0.9 - 14.2	a	RL = 0 RL = 1/2	Y	Y	EPA Method 1613B
ECO-20	Southwest border of Rayonier property	2004	1	Adjacent bluffs	Undeveloped, vegetated	0-8	N	Composite (5 subsamples)	NR	3.9	3.9	a	RL = 0	Y	Y	EPA Method 1613B
ECO-21	Southwest border of Rayonier property	2004	1	Adjacent bluffs	Undeveloped, vegetated	0-8	N	Composite (5 subsamples)	NR	2.8	2.8	a	RL = 0	Y	Y	EPA Method 1613B
ECO-22	South border of Rayonier property	2004	1	Adjacent bluffs	Undeveloped, vegetated	0-8	N	Composite (5 subsamples)	NR	13.0	13.0	a	RL = 0	Y	Y	EPA Method 1613B
ECO-23	West border of secondary treatment area/West of Ennis Creek ravine	2004	1	< 0.25 mile south	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	3.8	3.8	a	RL = 0	Y	Y	EPA Method 1613B
ECO-25	West border of secondary treatment area/East side of Ennis Creek ravine	2004	1	< 0.25 mile south	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	0.6	0.6	a	RL = 0	Y	Y	EPA Method 1613B
ECO-26	West border of secondary treatment area/East side of Ennis Creek ravine	2004	1	< 0.5 mile south	Undeveloped, vegetated	0-4	N	Composite (5 subsamples)	NR	4.3	4.3	a	RL = 0	Y	Y	EPA Method 1613B
ECO-27	West border of secondary treatment area/East side of Ennis Creek ravine	2004	1	< 0.5 mile south	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	12.6	12.6	a	RL = 0	Y	Y	EPA Method 1613B
ECO-28	West border of secondary treatment area/East side of Ennis Creek ravine	2004	1	< 0.5 mile south	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	10.3	10.3	a	RL = 0	Y	Y	EPA Method 1613B
ECO-29	South of secondary treatment area/West side of Ennis Creek ravine	2004	1	< 0.5 mile south	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	3.9	3.9	a	RL = 0	Y	Y	EPA Method 1613B

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Table 1-2. Summary of dioxin/furan data collected in Port Angeles.

Investigation	Sample Location	Year of Sample Collec-tion	Number of Samples	Distance & Direction from Rayonier	Sample Location Type (lawn, garden, planting strip, etc.)	Sample Depth (inches)	Seive (Y/N)	Composite or Discrete	Soil Type	Arith-metic Mean TEQ (ng/kg)	Range TEQ (ng/kg)	TEF Source	Detection Limit Treatment	Congener Data (Y/N)	Homo-logue Data (Y/N)	Analytical Method
ECO-30	East border secondary treatment area/bluffs	2004	1	< 0.25 mile southeast	Undeveloped, vegetated	0-4	N	Composite (5 subsamples)	NR	13.0	13.0	a	RL = 0	Y	Y	EPA Method 1613B
ECO-31	East border secondary treatment area/bluffs	2004	1	Adjacent bluffs	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	2.7	2.7	a	RL = 0	Y	Y	EPA Method 1613B
ECO-32	Southeast border of Rayonier property/bluffs	2004	1	Adjacent bluffs	Undeveloped, vegetated	0-6	N	Composite (5 subsamples)	NR	14.2	14.2	a	RL = 0	Y	Y	EPA Method 1613B
Gale's Addition Housing Development (CCHA 2008)			8								0 - 12.0 5.7 - 13.8	b	RL = 0 RL = 1/2			
G1-NE	Gale's Addition	2007	1	< 1 mile east	Disturbed wooded	0-3	N	Discrete	NR	12.0	12.0	b	RL = 0	Y	N	NR
G2-NW	Gale's Addition	2007	1	< 1 mile east	Disturbed wooded	0-3	N	Discrete	NR	2.2	2.2	b	RL = 0	Y	N	NR
G3-SES	Gale's Addition	2007	1	< 1 mile east	Disturbed wooded	0-3	N	Discrete	NR	0.8	0.8	b	RL = 0	Y	N	NR
G4-SED	Gale's Addition	2007	1	< 1 mile east	Disturbed wooded	12-18	N	Discrete	NR	0	0	b	RL = 0	Y	N	NR
G5-SWS	Gale's Addition	2007	1	< 1 mile east	Disturbed wooded	0-3	N	Discrete	NR	2.9	2.9	b	RL = 0	Y	N	NR
G6-SWD	Gale's Addition	2007	1	< 1 mile east	Disturbed wooded	12-18	N	Discrete	NR	0	0	b	RL = 0	Y	N	NR
G7-Stockpile	Gale's Addition	2007	1	< 1 mile east	Stockpile	NA	N	Composite	NR	3.2	3.2	b	RL = 0	Y	N	NR
G8-Stockpile	Gale's Addition	2007	1	< 1 mile east	Stockpile	NA	N	Composite	NR	0.9	0.9	b	RL = 0	Y	N	NR
Graving Dock Excavation Composite Samples (WDOT 2003)			11							5.13	0.371 - 228.9					
WSDOT-GDSP	Soil pile	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite	NR	228.90	228.9	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX-1/2	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	8.12	8.12	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 3/7	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	14.44	14.44	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 4/8	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	10.73	10.73	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 5/9	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	0.982	0.982	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 6/10	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	0.854	0.854	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 11/14	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	0.567	0.567	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 12/15	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	0.371	0.371	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 13/16	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	0.844	0.844	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 17/20	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (6 subsamples)	NR	5.13	5.13	a	RL =0	Y	N	EPA Method 8290
WSDOT-GDEX- 18/19	Excavation area	2003	1	< 2 miles west	Developed, industrial area	NR	N	Composite (7 subsamples)	NR	9.29	9.29	a	RL =0	Y	N	EPA Method 8290

Notes:

a = Van den Berg et al. 1998.

b = Ecology 2007.

c = Biologically active zone - Defined as depth to which roots and earthworms extended. Depths were typically 0 - 15 cm or 0 - 20 cm.

Key:

N = No.
NA = Not applicable.
NR = Not repored.
RL = Reporting limit.
TEF = Toxicity equivalency factor.
TEQ = Total toxic equivalent concentration.
Y = Yes.

(Table 1-2 page 3 back side)

Table 1-3. Summary of dioxin/furan data collected in Washington state.

Sample Location	Year of Sample Collection	Number of Samples	Sample Location Type (lawn, garden, planting strip, etc.)	Sample Depth (inches)	Seive (Y/N)	Composite/ Discrete	Arithmetic Mean TEQ (ng/kg)	Range TEQ (ng/kg)	TEF Source	Detection Limit Treatment	Congener Data (Y/N)	Homologue Data (Y/N)	Analytical Method
Studies Conducted in Washington State													
Oeser Company Superfund Site, Bellingham (E & E 2002)													
Off-facility, Open Areas	1999	28	Undeveloped open areas	0-2	N	Discrete	47.6	0.28 - 434.9	a	RL = 0	Y	Y	EPA Method 8290
Off-facility, Residences	1999	27	Drip lines, walkways, yards	0-2	N	Composite (2 - 5 subsamples)	8.61	0.57 - 47.36	a	RL = 0	Y	Y	EPA Method 8290
Off-facility, Biased Areas	1999	6	Mixed use, near high-traffic road and known run-off/drainage area from Site	0-2	N	Composite (2 - 5 subsamples)	55.8	9.61 - 192	a	RL = 0	Y	Y	EPA Method 8290
Background Residences - away from site influence but within city	1999	10	Drip lines, walkways, yards	0-2	N	Composite (2 - 5 subsamples)	5.46	0.78 - 18.8	a	RL = 0	Y	Y	EPA Method 8290
Background Open Areas - away from site influence but within city	1999	10	Undeveloped open areas, mostly parks	0-2	N	Discrete	1.29	0.12 - 2.81	a	RL = 0	Y	Y	EPA Method 8290
Dioxins in Washington State Soils (Rogowski et al. 1999)													
Agricultural soils, state-wide	1999	54	Active agricultural fields	0-2	N	Composite (10 subsamples)	0.14	0.0078 - 1.2	b	RL = 0	Y	Y	EPA Method 8290, 1613 B
Open areas	1997 - 1998	8	Undeveloped, non-urban, non-forested, non-agricultural	0-2	N	Composite (10 subsamples)	1.0	0.04 - 4.6	b	RL = 0	Y	Y	EPA Method 8290, 1613 B
Forested areas	1997 - 1998	8	Commercial and public forested lands	0-2	N	Composite (10 subsamples)	2.3	0.03 - 5.2	b	RL = 0	Y	Y	EPA Method 8290, 1613 B
Urban areas	1997 - 1998	14	Parks	0-2	N	Composite (10 subsamples)	4.1	0.13 - 19	b	RL = 0	Y	Y	EPA Method 8290, 1613 B
Skagit County Municipal Waste Incinerator (Cobb et al. 1993)[d]													
Site 1	1988	3	Open field	NR	NR	Discrete	43.3	33.0 - 57.9	NA	RL = 0	Y	Y	NR
Site 2	1988	3	Open field	NR	NR	Discrete	13.5	ND - 20.6	NA	RL = 0	Y	Y	NR
Site 3	1988	3	Open field	NR	NR	Discrete	24.3	19.9 - 29.1	NA	RL = 0	Y	Y	NR
Site 4	1988	3	Open field	NR	NR	Discrete	354.6	233.8 - 590.2	NA	RL = 0	Y	Y	NR
Site 5	1988	3	Open field	NR	NR	Discrete	30.5	20.4 - 40.5	NA	RL = 0	Y	Y	NR
Site 6	1988	3	Open field	NR	NR	Discrete	84.8	57.6 - 98.5	NA	RL = 0	Y	Y	NR
Dioxin Pilot Study (EPA 2007a)													
Lake Ozette, WA	2003	1	Forested land	0-4	N	Composite (5 subsamples)	0.43	NA	c	RL = 0	Y	Y	EPA Method 1613B

Notes:
a = Van den Berg et al. 1998
b = EPA 1989
c = Van den Berg et al. 2006
d = Values reported are for total dioxin/furan concentration, not a TEQ

Key:
N = No.
NA = Not applicable.
ND = Not detected.
NR = Not reported.
RL = Reporting limit.
TEF = Toxicity equivalency factor.

(Table 1-3 back side)

Table 5-1. Proposed sample allocation scheme.

Sampling Zone/Target	Zone Area (square miles)	Number of Samples
W1	0.25	12
W2	0.93	16
W3	0.80	6
E1	0.32	24
E2	0.86	9
E3	0.25	6
E4	0.76	6
Targeted forested areas within Zones E2 and E4		10
North-south transects (Upslope)		9
Roadside locations		2
Total	*4.2*	*100*

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Table 5-2. Proposed grid spacing within each zone.

Zone	Spacing (square feet)	Total Area (square miles)
W1	750	0.25
W2	1,250	0.93
W3	1,900	0.80
E1	600	0.32
E2	1,600	0.86
E3	1,100	0.25
E4	1,900	0.76

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Table 6-1. Dioxin/furan analytes and reporting limits for EPA Method 1613B.

Dioxins/Furans	Method Detection Limit Defined by EPA Method 1613B for 10 g dry sample size (ng/kg)	Lower Method Detection Limit prorated for 20 g dry sample size (ng/kg)
Total TCDD	0.1	0.025
2,3,7,8-TCDD	0.1	0.025
Total PeCDD	0.5	0.065
1,2,3,7,8-PeCDD	0.5	0.065
Total HxCDD	0.5	0.095
1,2,3,4,7,8-HxCDD	0.5	0.095
1,2,3,6,7,8-HxCDD	0.5	0.09
1,2,3,7,8,9-HxCDD	0.5	0.085
Total HpCDD	0.5	0.085
1,2,3,4,6,7,8-HpCDD	0.5	0.085
OCDD	1.0	0.42
Total TCDF	0.1	0.025
2,3,7,8-TCDF	0.1	0.025
Total PeCDF	0.5	0.048
1,2,3,7,8-PeCDF	0.5	0.048
2,3,4,7,8-PeCDF	0.5	0.048
Total HxCDF	0.5	0.06
1,2,3,4,7,8-HxCDF	0.5	0.046
1,2,3,6,7,8-HxCDF	0.5	0.06
1,2,3,7,8,9-HxCDF	0.5	0.047
2,3,4,6,7,8-HxCDF	0.5	0.06
Total HpCDF	0.5	0.05
1,2,3,4,6,7,8-HpCDF	0.5	0.05
1,2,3,4,7,8,9-HpCDF	0.5	0.044
OCDF	1.0	0.14

g = gram
kg = kilogram
ng = nanogram

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Figures

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