

# Reading Guide: Soil Dioxin Study

## Rayonier Mill Off-Property Soil Dioxin Study

Reading Guide July 2011

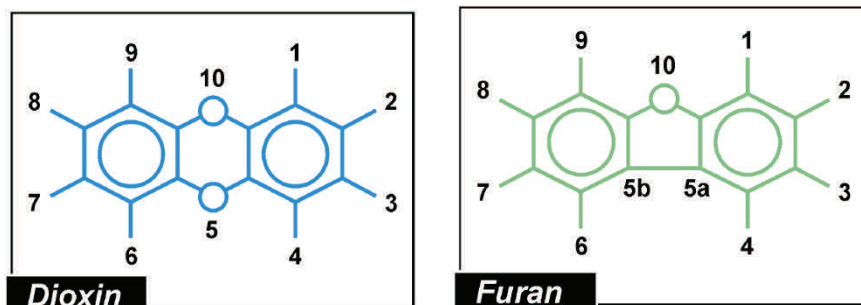
This reading guide summarizes the 2011 Soil Dioxin Study Report. It breaks down technical sections of the analysis and highlights helpful figures. Special terms are in **bold** and defined on page 2. Graphics from the report have a figure number listed.

### Introduction

This study looks at dioxins and furans, chemicals which have similar structures. Dioxins and furans come in 210 unique forms called **congeners**. The congener depends on the number and position of chlorine atoms (fig 1). **2,3,7,8-TCDD** is the most toxic congener.

The report focuses on 17 congeners. In a sample, **bulk** refers to the total mass of each congener. Bulk concentrations are multiplied by **TEFs** and summed to get a total toxicity or **TEQ**. TEFs are factors that scale bulk concentrations in terms of 2,3,7,8-TCDD's toxicity.

Ecology focused on the former Rayonier Mill as a potential source of dioxins in the Port Angeles area. Rayonier used salt-laden wood in its **hog fuel boiler**, to provide power for the mill. Burning salt-laden wood is known to produce more dioxins and furans than salt-free wood.



**Figure 1.** Dioxin and furan chemical structures (report fig 1-1) Both have two carbon rings with one to eight chlorine atoms. Dioxins have two oxygen molecules (noted by an "O"), while furans have one oxygen.

### Study Objectives

Ecology designed this study to determine the **magnitude** or levels of soil dioxins, and the former Rayonier Mill's contribution. The study targeted less disturbed soils to better represent the accumulation of dioxins over time. The goal was not to find exact boundaries of contamination, or a "background" level of dioxins.

### Report Contents

#### Executive Summary

**1.0 Introduction** - What dioxins and furans are and why the study focuses on the Rayonier Mill.

**2.0 Study Objectives** - What Ecology was trying to find and limitations of the study.

**3.0 Study Design** - Study boundary, how sample locations were chosen, and how volunteers were recruited.

**4.0 Soil Sampling Summary** - How samples were collected.

**5.0 Sample Analysis and Data Validation** - Checking the quality of the data and preparing it for analysis.

**6.0 Data Summary** - Ranges of dioxin levels and their overall toxicity.

**7.0 Data Evaluation: Overview** - Explanation of how data was evaluated.

**8.0 Data Evaluation: Results** - The magnitude of dioxins, chemical patterns, spatial patterns, and mass balance estimates.

**9.0 Summary** - Four "lines of evidence" that the former Rayonier Mill contributed to soil dioxin contamination in Port Angeles.

### Where is the report?

#### Ecology's website:

[http://www.ecy.wa.gov/programs/tcp/sites\\_brochure/rayonierOffProp/rayonierOffPr\\_hp.htm](http://www.ecy.wa.gov/programs/tcp/sites_brochure/rayonierOffProp/rayonierOffPr_hp.htm)

- Port Angeles Public Library
- Peninsula College Library
- WA Department of Ecology Southwest Region (Lacey, WA)

## Study Design, Sampling, & Analysis

**Boundary:** The study boundary includes areas near and downwind of the former Rayonier Mill, and other possible sources. It also covers many of the areas where odor complaints were made while the mill was in use.

**Sample locations:** Ecology chose sample locations to cover as much of the area investigated as possible, with denser sampling nearer to the former Rayonier Mill. The study excluded creeks and steep slopes, and heavily maintained areas like golf courses.

To increase the chance of finding higher dioxin levels, the study looked at the least disturbed areas within a property. The sample depth was 0-3 inches below the soil surface, also where higher dioxin levels should be.

**Sampling summary:** Ecology collected 85 samples:

- Sixty samples spread throughout the city in a grid.
- Fourteen samples from targeted forested areas, likely to have higher dioxin levels because soils were less disturbed.
- Nine samples from upslope areas, which should be less impacted from typical urban sources like wood burning.
- Two samples along high traffic areas of Highway 101, which should show a pattern typical of traffic emissions, as a comparison.

**Analysis and validation:** After the lab analysis, an independent firm checked the quality of the data. The validation found the data to be acceptable.

## Data Summary

The report mainly uses TEQ, which accounts for toxicity. Measured TEQs range from 0.8 to 76.3 parts per trillion (ppt). In 47% of samples, they are above the 11.1 ppt “Method B” **direct contact value** for protection of human health (Fig 2).

The nine upslope samples have the lowest average TEQ. The urban areas on the west side of the area investigated, and the forested areas on the east have the highest average TEQ.

## Terminology

**2,3,7,8-TCDD:** Tetrachlorodibenzo-p-dioxin—the most toxic type of dioxin.

**Bulk congeners:** Mass of each dioxin and furan congener in a sample.

**Chemometrics:** The use of math and statistics to get information from many variables of a chemical dataset.

**Congener:** A unique form of a chemical. Dioxins have 75 congeners and furans have 135, depending on the number of chlorine atoms and where they are.

**Direct contact value:** Soil dioxin level at which human health is protected if someone is exposed through ingestion.

**Increment:** The portion of each sample that is from a different source type.

**Hog fuel boiler:** A boiler that burns wood wastes to produce energy.

**Magnitude:** Amount or size

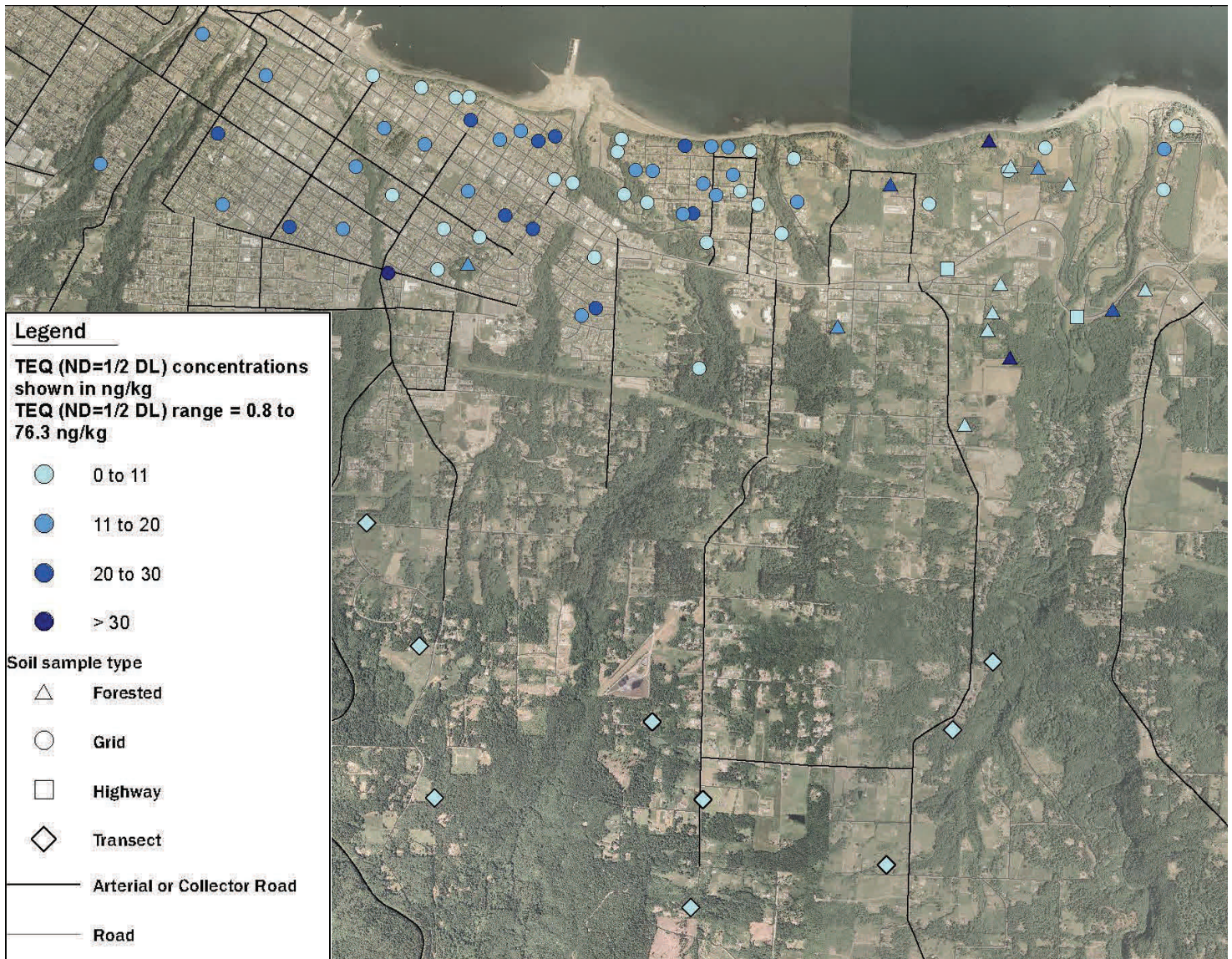
**Parts per trillion (ppt):** Compare to nanograms per kilogram, or one drop of ink in a 12 million gallon reservoir.

**Profile:** The chemical pattern of multiple congeners for any dioxin sample. Profiles can be in terms of bulk or TEQ.

**Toxic Equivalency Factor (TEF):** How toxic a congener is compared to 2,3,7,8-TCDD. The reference TEF for 2,3,7,8-TCDD is 1.

**Toxic Equivalency (TEQ):** The total toxicity of a sample in terms of 2,3,7,8-TCDD. Each bulk congener is multiplied by its TEF and the results are added together.

**Validation:** Checking the quality of the original lab results.



**Figure 2.** Sample results from the Rayonier Mill Off-Property Soil Dioxin Study

## Data Evaluation

Ecology has four key pieces of evidence that the Rayonier hog fuel boiler was a source of dioxin contamination:

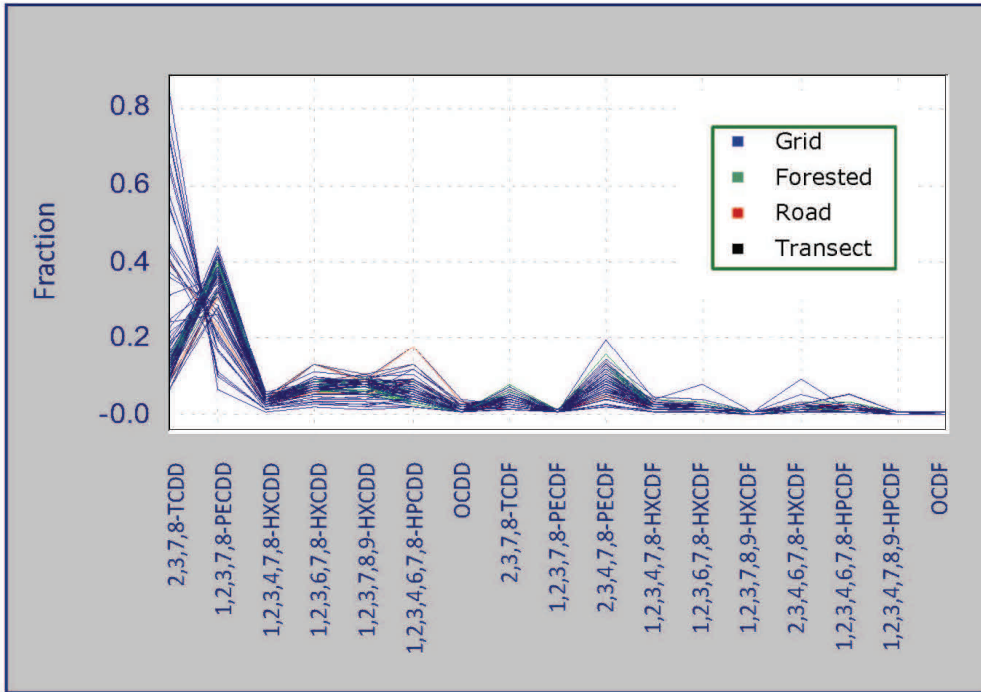
1. Magnitude (amount) of contamination: dioxins are present above 11.1 ppt.
2. Chemical patterns: one chemical pattern, or “**profile**”, found matches hog fuel boiler emissions.
3. Spatial patterns: Contributions from this profile have a spatial relationship to the Rayonier hog fuel boiler.

4. Mass balance: Rayonier’s hog fuel boiler likely produced enough dioxins to account for source three levels found in soils from the area investigated.

**Overview:** Each soil sample provides a great deal of information in its 17 congeners. This also makes analysis more complex. Many different sources may impact soil dioxin levels in Port Angeles, so any sample could be affected by several source profiles. Ecology’s consultant used **chemometrics** to “unmix” the different profiles using math and statistics.

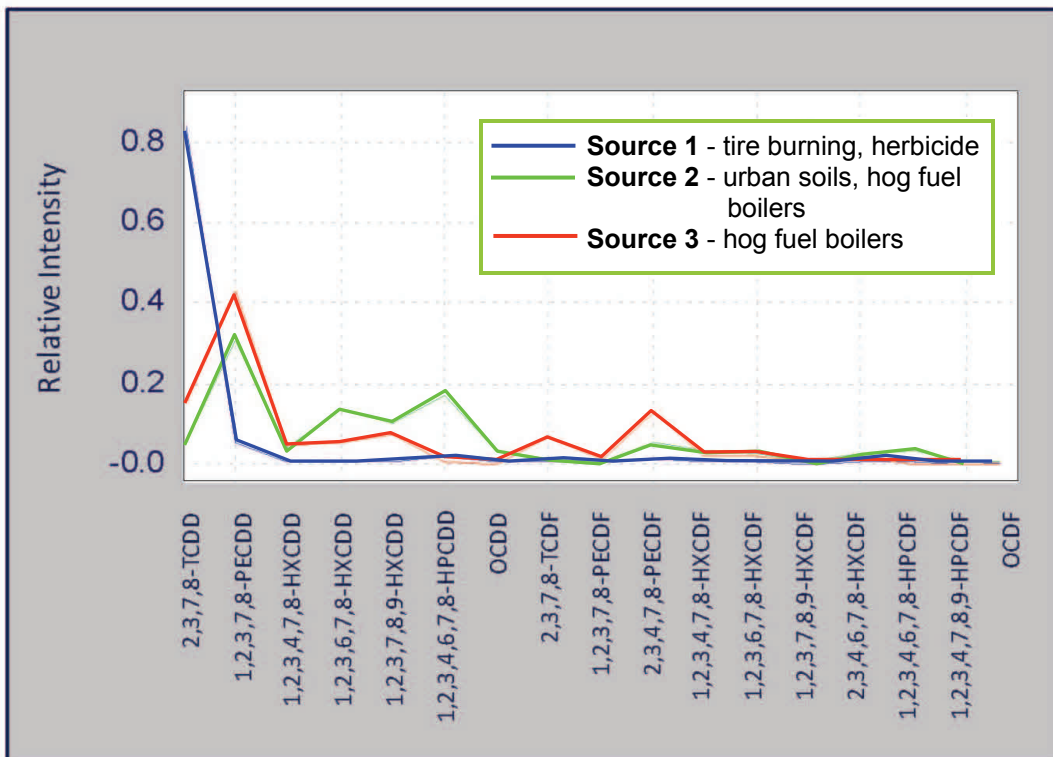
**Comparing profiles:** Unmixing is just the first step. The results then need to be interpreted by comparing them to known dioxin profiles. The consultant gathered data on several hundred profiles, including from hog fuel boilers burning salt-laden wood.

**Magnitude:** The analysis compares ranges of dioxins from this study to available soil dioxin studies. Data from grid samples in this study, taken as a whole, are higher than in studies of other urban areas. The same is true for forested areas (to the east in Figure 2). As in most other

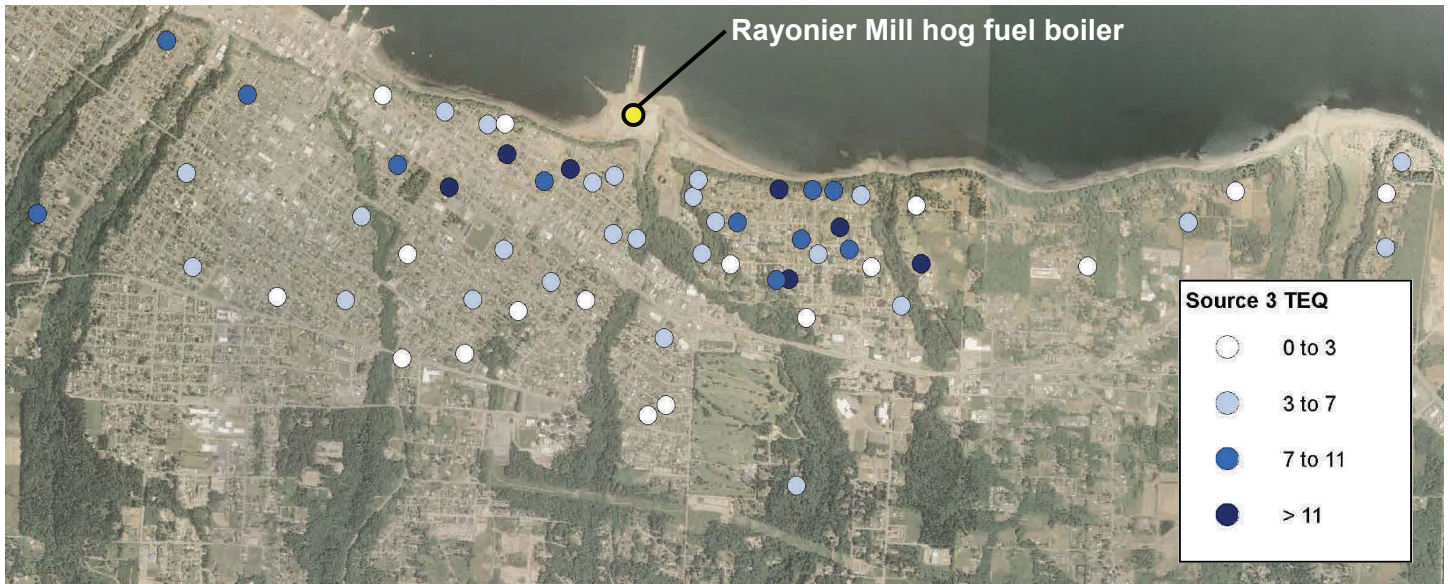


**Figure 3.** Total TEQ profiles for all samples (report fig 8-8)

The x-axis shows the 17 different dioxin and furans. Each line plots the relative amounts of the dioxins and furans in a single sample.



**Figure 4.** Unmixing model source profiles (report fig 8-10)



**Figure 5.** Map of source three dioxin levels (excluding forest, road, and upslope samples)

studies of urban soils, a few samples showed higher TEQ values (one as high 76 ppt).

**Spatial pattern:** Total TEQs do not show a clear pattern when mapping the samples (Figure 2). This is likely because more than one source is present in each sample.

**Chemical pattern methods:** The chemometric analysis provides several pieces of information based only on the relative contributions to TEQ in each sample. It creates a model to explain the variation in the measured data. It gives the number of dioxin sources, each of their profiles, and the contribution of each source to each sample. It also provides statistics on how well this model fits the actual data.

**Chemical pattern results:** The source profiles of all samples plotted together (Figure 3) do not show one clear pattern. However, after unmixing, three source profiles emerged (Figure 4).

- Source one is mostly made up of 2,3,7,8-TCDD. This profile has been found in some other urban soils and looks most like tire burning, or the herbicide 2,4,5-T.

- Source two is most similar to other urban soil samples. Its profile also looks like a few hog fuel boilers burning salt-laden wood. Source two may be a combination of typical urban sources and hog fuel boilers.
- Source three looks uniquely like hog fuel boiler profiles. No other sources the consultant looked at had this pattern.

**Source increment magnitudes:** Each soil sample has different proportions of the three source profiles found. If source three is removed from the forest samples, the remaining levels are similar to those found in studies of rural areas. Likewise, urban samples look more like urban background levels without source three.

**Source increment spatial patterns:** A map of source three profiles shows higher contributions closer to the Rayonier hog fuel boiler and lower values further away (see Figure 5). A few scattered properties show dominant source one contributions. This suggests that some activity on the property, like tire burning or herbicide use, contributed to the dioxin levels.

**Mass balance:** Over 67 years, Rayonier's hog fuel boiler likely produced enough dioxins to account for levels of source three dioxins found in soils in the area investigated. Ecology looked at several pieces of information to figure this out:

**Amount Rayonier produced:**

- Data from a 1995 test of stack emissions from the hog fuel boiler.
- Data showing that particulate emissions were much higher in the past, before pollution control improvements.

**Amount in Port Angeles soils:**

- Sampling data from this study.
- Information about how dioxins disperse in the environment and deposit in soils.

## Summary of Evidence:

### Magnitude



**Urban areas:** Average TEQ values from this study are higher than similar urban areas.



**Forested areas:** Average TEQs are far higher than three non-urban data sets.

### Chemical pattern

Unmixing analysis found three source profiles. Source three closely matches a hog fuel boiler profile, and not other profiles.

### Spatial pattern

TEQs for the entire data set do not follow a clear spatial pattern. However, source three is highest closer to the Rayonier hog fuel boiler location.

### Mass balance

Rayonier's hog fuel boiler likely produced enough dioxins to account for source three levels found in soils. No other local source Ecology looked at could account for that magnitude of source three dioxins in this study area.

## Contacts

This is a very complex and technical report. Please contact us if you have questions about the study findings or terminology in the report.

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