SITE CHARACTERIZATION USING A DIOXIN SCREENING METHOD: FORMER SAWMILL, CALIFORNIA, UNITED STATES OF AMERICA

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Introduction

Evaluation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (dioxins/furans) can be a costly endeavor when data quality objectives require data adequate for a human health risk assessment. The cost for the analytical method typically used in the United States, U.S. Environmental Protection Agency (EPA) Method 8290, is two to five times higher per sample than analytical costs for other chemicals using standard U.S. EPA methods. Project costs, particularly those associated with sample collection and analysis, can quickly escalate when investigating a large area. For the project described here, future residential use is being considered for a large property. Typically, a higher density of sampling is required for residential properties, compared to industrial properties, to address potential future subdivision of the property into residential lots.

This paper provides a case study of a cost-effective site evaluation designed to address dioxins/furans in soil at a former sawmill site designated for future residential development. Once dioxins/furans were identified during preliminary sampling, additional sample collection was conducted and samples were analyzed using a screening laboratory analytical method with reporting limits at the California Human Health Screening Level (CHHSL)² for residential (unrestricted) site use (residential CHHSL). The screening method yielded results above or below the residential CHHSL as "positive" or "negative" results, respectively. The objective of the additional sampling was to characterize dioxin/furans in soil at or below the residential CHHSL to delineate soil acceptable for future residential use. Soil exceeding the residential CHHSL would require further evaluation or remediation. Analysis of samples by U.S. EPA Method 8290 was conducted on all samples with "negative" results from the screening method to confirm the "negative" results with data of sufficient quality for evaluating potential human health risks. The site was adequately characterized using the screening methodology and data from this method were used to delineate areas of soil that were currently acceptable for future residential use. The screening methodology cost is approximately one-half that of U.S. EPA Method 8290 and to date, this approach has resulted in laboratory analytical cost savings of approximately \$10,000 (U.S. dollars).

Background

The subject site consists of approximately 121 hectares, 32 hectares of which comprised former operations where lumber was milled and treated. The initial stages of investigation consisted of developing a conceptual site model from interviews with individuals familiar with the site operational history and from a review of environmental records and reports for the site. The background research indicated several areas within the former operations area where wood was treated with chemicals potentially containing pentachlorophenol or combustion of wood treated with such chemicals may have occurred. Dioxins/furans are present in pentachlorophenol as a byproduct of the chemical manufacturing.

An initial soil sampling investigation was subsequently conducted within the former operations area. Depthdiscrete soil samples were collected between the ground surface and 0.75 meters below ground surface (bgs) in the wood treatment and combustion areas and analyzed for dioxins/furans using U.S. EPA Method 8290¹. During this initial investigation, soil samples were also collected within the site property boundary, but outside of the former operations area, to establish background concentrations of dioxins/furans. This initial investigation revealed shallow bedrock (0.5 to 0.6 meters bgs) underlying a large portion of the former operations area of the site.

Concentrations of dioxins/furans in the background samples, expressed as 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents (2,3,7,8-TCDD TEQ), ranged from 1 to 2 picograms per gram (pg/g). Concentrations of 2,3,7,8-TCDD TEQ in soil from the former operations area ranged from 0.26 to 27,600 pg/g, with nearly half of the samples from near-surface soil (0 to 0.5 meters bgs) having concentrations above 4.6 pg/g, the CHHSL for residential soil. Concentrations of 2,3,7,8-TCDD TEQ in soil below 0.5 meters were generally consistent with background levels. All 2,3,7,8-TCDD TEQ concentrations were estimated using toxic equivalency factors (TEF) based on the weighting system proposed by the World Health Organization (WHO) in 2005³, and values equal to one-half the congener detection limit were used for non-detect congeners.

Based on the potential volume of near-surface soil with 2,3,7,8-TCDD TEQ concentrations above the CHSSL (approximately 38,000 cubic meters), further investigation was deemed necessary to more precisely delineate the areas where dioxin/furan concentrations were above or below the residential CHHSL. The volume of affected soil is important because of the potentially costly alternatives for site mitigation.

Methods

Subsequent to the initial investigation, more cost-effective and time-efficient alternatives to U.S. EPA Method 8290 were sought to determine the extent of dioxin/furan contamination over the 32-hectare former operations area. Alternative dioxin/furan screening methods, such as the RapidScreen⁴ method (originally developed by Eno River Labs, now offered by Pace Analytical), were considered for the purpose of identifying areas of contamination above or below the CHHSL for 2,3,7,8-TCDD TEQ concentrations in residential soil. RapidScreen is a gas chromatograph/mass spectrometer (GC/MS) method that reports results for 17 dioxin/furan congeners and 3 coplanar polychlorinated biphenyls (PCBs; dioxin-like compounds). As an alternative to U.S. EPA Method 8290, RapidScreen yields simplified results reported as positive or negative above a user-specified concentrations were greater than the residential CHHSL (4.6 pg/g). The RapidScreen analysis applies user-specified TEFs and one of three options for the treatment of non-detect congener measurements: zero values, values equal to one-half the congener detection limit, or values equal to the congener detection limit. Subsequent to this study, U.S. EPA published Method 4430 in December 2007⁵, an immunoassay-based screening method, which measures biological response in terms of total 2,3,7,8-TCDD TEQs to concentrations of 1 pg/g. U.S. EPA Method 4430 is the first screening method with U.S. EPA approval that can achieve this low detection limit.

For the subsequent investigation, 53 additional sampling locations were selected to further delineate dioxin/furans in soil, in areas where previous sampling results indicated 2,3,7,8-TCDD TEQ concentrations exceeding 4.6 pg/g. At least one depth-discrete sample was collected between 0 and 0.75 meters bgs at each location. Two depth-discrete samples were collected at most locations, one between the ground surface and 0.3 meters bgs and one between 0.3 meters bgs and 0.75 meters bgs. For sampling locations where two depth-discrete soil samples were collected, the shallow soil sample was analyzed using RapidScreen and the deeper sample was held by the analytical laboratory. If the RapidScreen result for the shallow sample was positive (2,3,7,8-TCDD TEQ concentration greater than 4.6 pg/g), then the deeper sample collected laterally (step-out) from the location to further characterize the extent of dioxins/furans. If the RapidScreen result for the shallow sample was negative (2,3,7,8-TCDD TEQ concentration less than 4.6 pg/g), then the deeper sample was not analyzed and no lateral step-out samples were collected.

In total (additional and step-out locations), 85 samples were collected and analyzed using RapidScreen. All RapidScreen results were based on the 2005 WHO TEFs and values equal to one-half the congener detection limit for non-detect congeners. Fifty-five of the 85 samples tested "positive" for dioxins/furans, 27 tested "negative," and results for three samples could not be reported by the laboratory. Twenty-three of the 27 samples with negative RapidScreen results were subsequently analyzed using U.S. EPA Method 8290 for confirmation of negative results. The negative RapidScreen results for the remaining four samples were not confirmed using U.S. EPA Method 8290 because the samples were very near other samples with positive RapidScreen results or because shallow bedrock was present at the sample location. Two samples with positive RapidScreen results, selected at random, were analyzed using U.S. EPA Method 8290 for confirmation of the positive results. Fewer positive results than negative results were confirmed because confirming potential false positive results was not considered critical for risk assessment. False positive results would indicate soil being designated for further evaluation that could have been designated for residential use. Verification of samples with negative results was considered more critical because false negative results could result in soil left in place that did not meet screening levels without further consideration.

Results and discussion

The results of the samples analyzed using RapidScreen and subsequently analyzed using U.S. EPA Method 8290 for confirmation of RapidScreen results are presented in Table 1. As presented, both samples that tested "positive" for dioxins/furans using RapidScreen had 2,3,7,8-TCDD TEQ concentrations above 4.6 pg/g based on U.S. EPA Method 8290, thus confirming the positive RapidScreen results. Furthermore, all but one of the 23 samples that tested "negative" for dioxins/furans using RapidScreen had 2,3,7,8-TCDD TEQ concentrations below 4.6 pg/g based on U.S. EPA Method 8290. Good agreement was therefore achieved between the RapidScreen and U.S. EPA Method 8290 results, with 24 of the 25 reported positive or negative RapidScreen results confirmed by U.S. EPA Method 8290 (96 percent agreement).

With confidence in the RapidScreen results, the combined set of RapidScreen and U.S. EPA Method 8290 data were used to delineate affected and unaffected areas of the site (Figure 1). Based on available data, approximately 80 percent of the 32 hectare former operations area (25.6 hectares) are considered affected by dioxins/furans, based on sample locations with positive RapidScreen results and/or 2,3,7,8-TCDD TEQ concentrations above 4.6 pg/g. However, included within the boundaries of the affected area are 3.5 hectares of former buildings beneath which no dioxin/furan data has been collected to date. Dioxins/furans may not be present above the residential CHHSL in these areas. Prior to developing a remedial approach, additional sample collection and analysis using the combined RapidScreen/U.S. EPA Method 8290 methods is anticipated to further refine the delineation of affected areas. To date, the laboratory analytical cost savings resulting from this approach is in the neighborhood of \$10,000 (U.S. dollars).

References

1. U.S. Environmental Protection Agency (U.S. EPA), 2007, Method 8290A, Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1, February.

2. Office of Environmental Health Hazard Assessment (OEHHA), California Environmental Protection Agency, 2005, Human-Exposure-Based Screening Numbers Developed to Aid Estimation of Cleanup Costs for Contaminated Soil, January Revision.

3. Van den Berg M., Birnbaum L. S., Denison M., DeVito M., Farland W., Feeley M., Fiedler H., Hakansson H., Hanberg A., Haws L., Rose M., Safe S., Schrenk D., Tohyama C., Trischer A., Tuomisto J., Tysklind M., Walker N. and Peterson R.E. *Toxicol Sci* 2006; 93(2): 223-24.

4. Pace Analytical Services, Inc., 2007, Standard Operating Procedure, RapidScreen Analysis of Samples for PCDDs and PCDFs, April.

5. U.S. EPA, 2007, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Method 4430, Office of Solid Waste and Emergency Response.

Sample ID ¹	RapidScreen Result	2,3,7,8-TCDD TEQ (Calculated from U.S. EPA Method 8290 Data) (in pg/g)	Sample ID ¹	RapidScreen Result	2,3,7,8-TCDD TEQ (Calculated from U.S. EPA Method 8290 Data) (in pg/g)
TP-2-1.5	negative	0.70	TP-35-1.5	negative	0.28
TP-6-0.5	not reportable	6.6	TP-38-1.5	negative	0.82
TP-9-0.5	negative	1.6	TP-39-0.5	negative	0.43
TP-11-0.5	not reportable	22.9	TP-40-0.5	negative	2.7
TP-13-0.5	positive	23.0	TP-41-1.0	negative	0.59
TP-14-0.5	negative	0.86	TP-42-1.0	negative	0.90
TP-16-0.5	negative	0.94	TP-43-1.0	negative	0.95
TP-23-1.5	negative	0.59	TP-44-1.0	negative	1.3
TP-24-0.5	negative	2.4	TP-47-1.0	negative	0.33
TP-25-1.5	negative	3.1	TP-52-1.0	negative	0.13
TP-27-0.5	negative	0.55	TP-59-0.5	negative	13.2
TP-28-0.5	negative	0.51	TP-60-0.5	negative	1.6
TP-31-1.5	negative	0.76	TP-63-1.0	positive	13.2
TP-32-1.5	negative	0.46	TP-66-0.5	not reportable	28.3

Table 1: Summary of RapidScreen and 2,3,7,8-TCDD TEQ Results

Notes:

1. Sample ID nomenclature: TP = test pit sample - location number - depth below ground surface. The bold value indicates the one case where the U.S. EPA Method 8290 results did not confirm the RapidScreen results.

