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Summary of Polychlorinated Biphenyls (PCBs) Results from Analysis of Selected Soil Samples Collected Within WMA C

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Abstract: This report presents an initial evaluation of polychlorinated biphenyls (PCBs) contamination associated with Waste Management Area (WMA) C. This evaluation of PCB contamination makes use of specific PCB congener analytical results obtained from selected direct push boreholes around WMA C. The analytical data were specifically obtained at shallow depths (0 to 5.5 m) at 10 of 13 soil sampling locations in the vicinity of tanks and selected ancillary equipment within WMA C.

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To: Mesford, Timothy B; Bergeron, Marcel P
Subject: RE: Emailing: RPP-RPT-58056 - Shortcut

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From: Mesford, Timothy B
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Marcel/Susan,

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Hi Tim

I approve this document as well. Please proceed with its final release.

Marcel

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Marcel,

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Thanks,
Tim

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RPP-RPT-58056
Revision 0

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M. P. Bergeron
Washington River Protection Solutions, LLC

Date published
November 2014

washington river protection solutions

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Office of River Protection

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EXECUTIVE SUMMARY

This report presents an initial evaluation of polychlorinated biphenyls (PCBs) contamination associated with Waste Management Area (WMA) C. This evaluation of PCB contamination makes use of specific PCB congener analytical results obtained from selected direct push boreholes around WMA C. The analytical data were specifically obtained at shallow depths (0 to 5.5 m) at 10 of 13 soil sampling locations in the vicinity of tanks and selected ancillary equipment within WMA C.

The overall purpose of this evaluation is to provide an initial screening-level assessment of the potential risk associated with PCB concentration levels in soil samples collected in the vicinity of WMA C. To accomplish this overall purpose, this assessment focused on:

- Providing comparisons of congeners and homolog distributions for each of the 10 soil sampling locations in and around WMA C where PCB congener data are available
- Evaluating total PCB congeners and their associated homolog distribution to assist in identifying potential sources of PCBs within WMA C
- Identifying the main carcinogenic congeners of concern and calculating their associated toxicity equivalents to determine if a potential for risks exists for PCBs within WMA C.

Results of the assessment showed that total PCB congeners for all sampled sites ranged from 0.06 µg/kg to 2.6 µg/kg over the depths sampled. The shallow (0 to 0.3 m) sampling at all except Site P showed the highest concentrations ranging from 0.18 µg/kg to 2.1 µg/kg, with the highest value coming from Site R.

Results of total PCB congeners ranged from 0.4 µg/kg to 2.6 µg/kg over the depths sampled at Site P near unplanned release site UPR 82. Concentrations in samples taken between 2.1 to 2.4 m had a slightly higher range compared to the deeper samples, ranging from 1.2 µg/kg to 2.6 µg/kg, with the highest concentrations coming from direct push site C6400 at 2.1 m.

Results of of the PCB congener analytical results from the shallowest samples (0 to 0.3 m) were also used to calculate a total 2,3,7,8-TCDD toxicity equivalent to evaluate the potential health risk associated with these constituents of concern. The results of these calculations were evaluated and found to be many times lower than the published *Revised Code of Washington* 70.105D, "Hazardous Waste Cleanup — Model Toxics Control Act" value at 0.5 mg/kg.

Based on review of these PCB congener analytical results, plans for continued *Resource Conservation and Recovery Act of 1976* Facility Investigation Phase 2 sampling and analysis were reevaluated and a recommendation was made to eliminate analysis of PCB congeners in further WMA C sampling activities, but continue to perform analyses of PCB Aroclors [Letter 11-TPD-020, "Organic Analyses Optimization for Waste Management Area (WMA) C"]. This recommendation was approved by the State of Washington Department of Ecology [Letter 11-NWP-053, "Re: Organic Analyses Optimization for Waste Management Area

(WMA) C"] and recommended changes for elimination of PCB congener analyses were incorporated in the work plan (RPP-PLAN-39114, *Phase 2 RCRA Facility Investigation/Corrective Measures Study Work Plan for Waste Management Area C*) and sampling and analysis plan (RPP-PLAN-38777, *Sampling and Analysis Plan for Phase 2 Characterization of Vadose Zone Soil in Waste Management Area C*).

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LIST OF TERMS

Abbreviations and Acronyms

bgs	below ground surface
BZ	Ballshmiter and Zell (1980)
CAS	Chemical Abstracts Service
CDD	chlorinated dibenzodioxin
CDF	chlorinated dibenzofuran
c-PAH	carcinogenic-polycyclic aromatic hydrocarbons
DOE	U.S. Department of Energy
Ecology	State of Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
GC/ECD	gas chromatography/electron capture detector
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HEIS	Hanford Environmental Information System
HRGC/HRMS	high resolution gas chromatography with high resolution mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
MTCA	Model Toxics Control Act
PCB	polychlorinated biphenyl
RCRA	*Resource Conservation and Recovery Act of 1976*
RFI	RCRA Facility Investigation
RFI/CMS	RCRA facility investigation/corrective measures study
SAP	sampling and analysis plan
TCDD	tetrachlorodibenzo-*p*-dioxin

TEF	toxicity equivalency factor
TEQ	toxicity equivalent
UPR	unplanned release
WAC	*Washington Administrative Code*
WHO	World Health Organization
WMA	Waste Management Area

1.0 INTRODUCTION

This report presents an initial evaluation of potential polychlorinated biphenyl (PCB) contamination associated with the WMA C area. This evaluation of PCB contamination makes use of specific PCB congener analytical results obtained from selected direct push boreholes from around WMA C (see Figure 1-1). The PCB congener analytical data examined were specifically obtained at selected shallow (0 to 5.5 m) depths from 10 of 13 direct push soil sampling locations in the vicinity of tanks and selected ancillary equipment within WMA C. These direct push soil samples were collected under the WMA C *Resource Conservation and Recovery Act of 1976* (RCRA) Facility Investigation (RFI) Phase 2 work plan (RPP-PLAN-39114, *Phase 2 RCRA Facility Investigation/Corrective Measures Study Work Plan for Waste Management Area C*) and Phase 2 sampling and analysis plan (SAP) (RPP-PLAN-38777, *Sampling and Analysis Plan for Phase 2 Characterization of Vadose Zone Soil in Waste Management Area C*). The selected ten locations are shown in Figure 1-2.

The overall purpose of this evaluation is to provide an initial screening-level assessment of the potential risks associated with PCB concentration levels in the vicinity of WMA C. To accomplish this overall purpose, this assessment focused on:

- Providing comparisons of congeners and homolog distributions for each of the 10 soil sampling locations in and around WMA C where PCB data are available
- Evaluating total PCB congeners and their associated homolog distribution to assist in identifying potential sources of PCBs within WMA C
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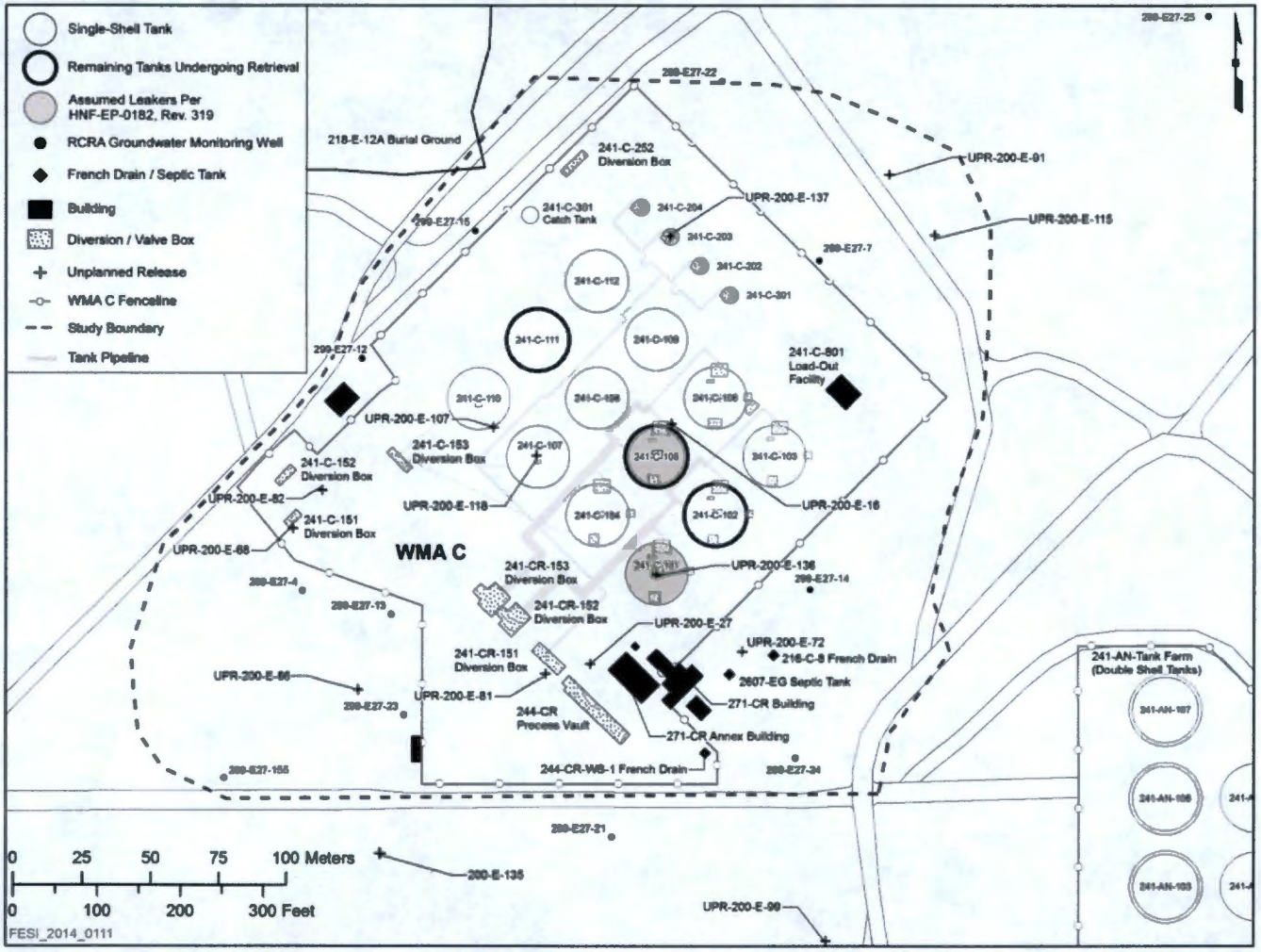
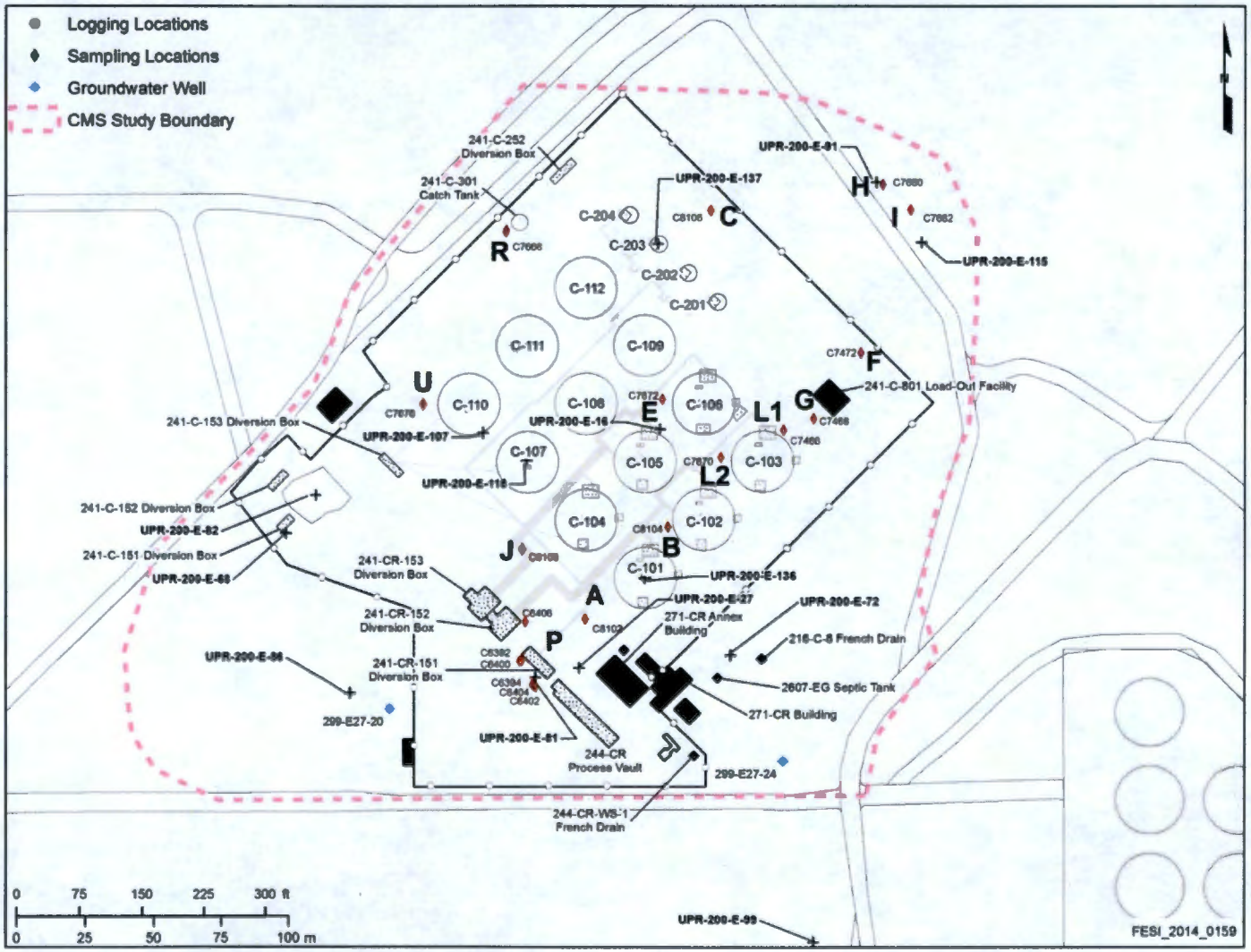
Figure 1-1. Location of Study Area Boundary and Single-Shell Tanks and Ancillary Facilities and Equipment in Vicinity of Waste Management Area C.



RCRA = *Resource Conservation and Recovery Act of 1976* WMA = Waste Management Area

Reference: HNF-EP-0182, *Waste Tank Summary Report for Month Ending July 31, 2014*, Rev. 319.

Figure 1-2. Waste Management Area C Soil Sample Locations Where Polychlorinated Biphenyl Congener Data Were Obtained.



CMS = corrective measures study

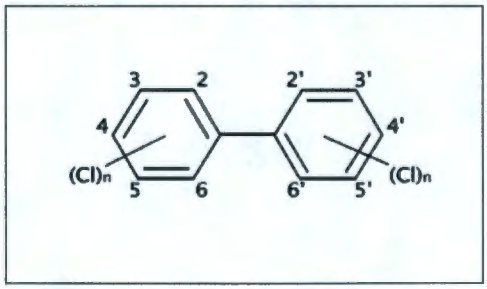
2.0 BACKGROUND

Over the years, evaluations of PCB contamination in environmental media have been conducted with either a focus using analyses of commercial mixtures of PCB compounds, known as Aroclors, or on more specific analyses of individual PCB congeners that make up the commercial mixtures themselves. Decisions on using one approach or the other depend on many factors that include the potential cost of analyses and what questions need to be addressed by the assessment.

Polychlorinated biphenyls are a group of man-made, chlorinated organic chemicals that were first introduced into commercial use in 1929 as insulating fluids for electric transformers and capacitors. In the United States, PCBs were produced by the Monsanto Company in Sauget, Illinois and given the trade name of Aroclor. After initial commercialization of PCBs, many other applications were developed including use as hydraulic fluids, paint additives, plasticizers, adhesives, and fire retardants. Production of PCBs in the United States was halted in 1977 because of uncertainty regarding toxicity of the ubiquitous and persistent environmental residues [*Toxicological Profile for Polychlorinated Biphenyls (PCBs)* (ATSDR 2000)].

Aroclors are commercial formulations of PCB congeners (Figure 2-1) defined by a four-digit number to describe the various constituent chlorine content. For example, the first two digits of Aroclor 1242 represent the 12 carbon atoms in biphenyl, and the second two digits represent the percentage by weight of chlorine (42%) within the mixtures. Aroclor 1016 is an exception to the general naming scheme, containing 12 carbons with 41% by weight chlorine content.

Figure 2-1. Basic Polychlorinated Biphenyl Structure



Polychlorinated biphenyls exist as mixtures containing 209 possible structural configurations (i.e., congeners) that vary by number and location of chlorine atoms on the base biphenyl structure. Number and ring substitution patterns of the chlorine atoms define each homologous congener. Only 36 congeners are considered relevant for human and ecological health based on their toxicity and occurrence in the environment ("Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: considerations for a congener-specific analysis" [McFarland and Clark 1989]). In general, PCB persistence and toxicity increase with the degree of chlorination within the commercial mixture (e.g., Aroclor 1254 is more persistent than Aroclor 1232) (ATSDR 2000). Octanol-water partition coefficients (K_{ow}) tend to increase and water solubilities tend to decrease as PCB chlorination increases. Because of slow metabolism in tissue and high K_{ow}, PCBs accumulate in fatty tissues and can be biomagnified in

the food chain ("Aerobic and anaerobic PCB biodegradation in the environment" [Abramowicz 1995]).

Polychlorinated biphenyl congeners are named by their International Union of Pure and Applied Chemistry (IUPAC) designated nomenclature and by a system of sequential numbering that has become known as the BZ number. In the IUPAC system the numbers in the beginning of the name specify the positions where chlorines are located on the two phenyl rings. The second and most common system developed by Ballschmiter and Zell ["Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography" (Ballschmiter and Zell 1980)] assigns a separate number ranging from 1 to 209 for each of the 209 specific PCB congeners. This correlates to the structural arrangement of the PCB congeners in an ascending order of the number of chlorine substitutions within each sequential homolog. For example, if each of the rings has a chlorine in the 3,3' and the 4,4' position then the IUPAC name would be 3,3',4,4'-tetrachlorobiphenyl and the assigned BZ number is 77. If the chlorine substitution for each of the phenyl rings occurs on the 3,4 and the 4',5 position the IUPAC name would be 3,4,4',5-tetrachlorobiphenyl and the assigned BZ number is 81 (Table 2-1). This example also points out that differences among BZ numbers may indicate a position change of the chlorines on the phenyl rings and not necessarily the total chlorine number.

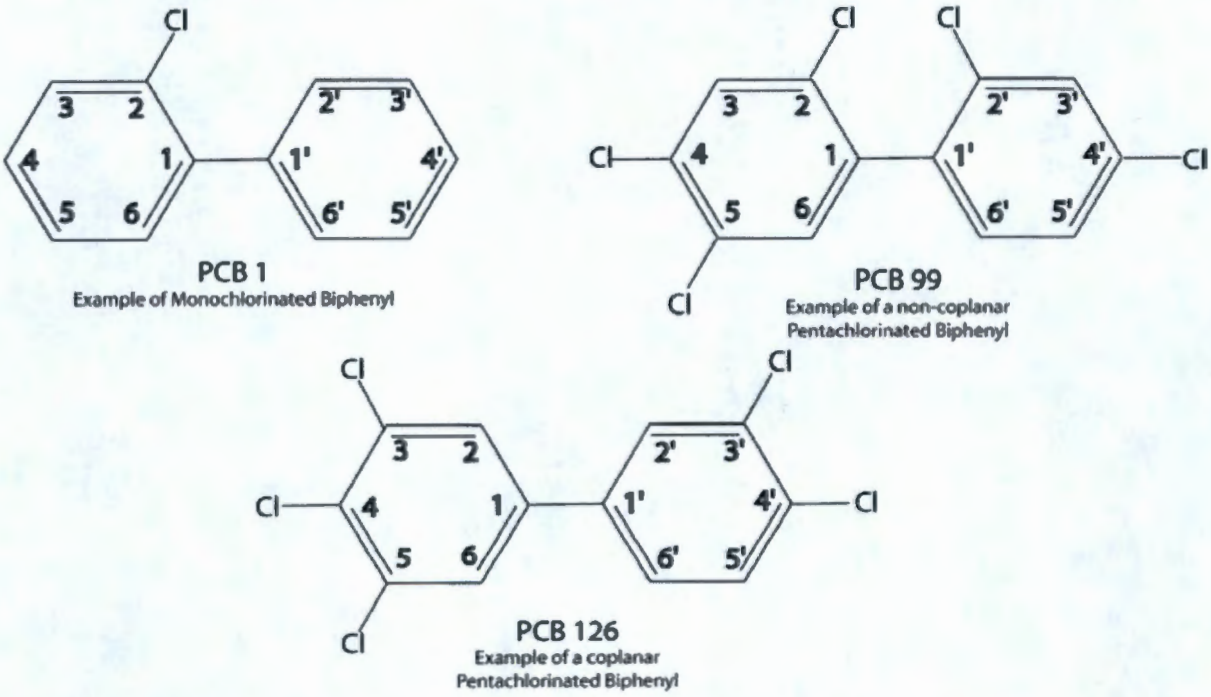
Table 2-1. Toxic Polychlorinated Biphenyl Congeners and Associated International Union of Pure and Applied Chemistry Nomenclature and Assigned Ballshmiter and Zell Numbers

Toxic Polychlorinated Biphenyl Congeners		
International Union of Pure and Applied Chemistry Name	**Empirical Formula**	**Ballschmiter and Zell Congener Number**
3,3',4,4'-Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	77
3,4,4',5-Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	81
2,3,3',4,4'-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	105
2,3,4,4',5-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	114
2,3',4,4',5-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	118
2,3',4,4',5'-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	123
3,3',4,4',5-Pentachlorobiphenyl	$C_{12}H_5Cl_5$	126
2,3,3',4,4',5-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	156
2,3,3',4,4',5'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	157
2,3',4,4',5,5'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	167
3,3',4,4',5,5'-Hexachlorobiphenyl	$C_{12}H_4Cl_6$	169
2,3,3',4,4',5,5'-Heptachlorobiphenyl	$C_{12}H_3Cl_7$	189

2.1 BIOCHEMICAL TOXICOLOGY

A subset of PCB congeners with chlorine constituents in the ortho positions of each phenyl group are restricted in ring rotation and thus cannot assume a co-planar structure. Polychlorinated biphenyls without ortho substitution or just mono ortho substitution can assume a co-planar structure (Figure 2-2). Co-planarity causes a PCB congener to resemble the polychlorinated dibenzo-*p*-dioxin known as TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) and thus imparts increased toxicity. Specifically, the TCDD binds to the aryl hydrocarbon receptor (Ah) and induces transcription of the cytochrome P-450 A1A gene. Increased synthesis of cytochrome P-450 A1A is associated with a host of biochemical reactions leading to various toxicological effects. Dioxin-like PCBs also have the potential to bind to (Ah) and by extension, tend to be more toxic than non-coplanar PCBs ("Polychlorinated Biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment" [Safe 1994]; "Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife" [Van den Berg et. al. 1998]).

Figure 2-2. Coplanar Versus Non-Coplanar Polychlorinated Biphenyls



To assess potential cancer risks from exposure to mixtures of PCB congeners, toxic equivalency factors (TEFs) are used to quantify the potential for each congener to exhibit dioxin-like toxicity. TEF values are used in combination with chemical residue data to calculate TCDD TEQ concentrations in a variety of environmental samples including animal tissue, soil, sediment, and water. Individual dioxin-like congeners are converted to TEQs by multiplying their initial concentrations by established TEFs. Toxicity equivalents are used in human health and ecological risk assessments in order to assess the impacts of a mixture of dixon-like compounds,

including chlorinated dibenzodioxins (CDDs), chlorinated dibenzofurans (CDFs), and co-planer PCBs (Van den Berg et. al. 1998).

The World Health Organization (WHO) has assigned TEFs to each of the dioxin-like PCB congeners to indicate their toxicity relative to 2,3,7,8-TCDD. Tetrachlorodibenzo-*p*-dioxin itself has been assigned a TEF of 1.0. A PCB congener with a TEF of 0.01 is considered to be 100 times less toxic than 2,3,7,8-TCDD. The WHO first established the TEF values in 1994 for application to humans and mammals. In 1998 WHO expanded and revised the TEFs to include separate values for fish and birds as well as for humans and mammals (Van den Berg et. al. 1998). In 2006 WHO reevaluated TEFs for dioxins and dioxin-like compounds ("The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds" [Van den Berg et al. 2006]) (Table 2-2).

Table 2-2. Current Animal Toxic Equivalency Factors for Dioxin-Like Polychlorinated Biphenyls That Have Been Evaluated by the World Health Organization

Ballschmiter and Zell/International Union of Pure and Applied Chemistry Number	International Union of Pure and Applied Chemistry Prefix	2005 World Health Organization Toxicity Equivalency Factors		
		Humans & Mammals	Fish	Birds
PCB-77	3,3',4,4'-Tetrachlorobiphenyl	0.0001	0.0001	0.05
PCB-81	3,4,4',5-Tetrachlorobiphenyl	0.0003	0.0005	0.1
PCB-105	2,3,3',4,4'-Pentachlorobiphenyl	0.00003	<0.000005	0.0001
PCB-114	2,3,4,4',5-Pentachlorobiphenyl	0.00003	<0.000005	0.0001
PCB-118	2,3',4,4',5-Pentachlorobiphenyl	0.00003	<0.000005	0.00001
PCB-123	2,3',4,4',5'-Pentachlorobiphenyl	0.00003	<0.000005	0.00001
PCB-126	3,3',4,4',5-Pentachlorobiphenyl	0.1	0.005	0.1
PCB-156	2,3,3',4,4',5-Hexachlorobiphenyl	0.00003	<0.000005	0.0001
PCB-157	2,3,3',4,4',5'-Hexachlorobiphenyl	0.00003	<0.000005	0.0001
PCB-167	2,3',4,4',5,5'-Hexachlorobiphenyl	0.00003	<0.000005	0.00001
PCB-169	3,3',4,4',5,5'-Hexachlorobiphenyl	0.03	0.00005	0.001
PCB-189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	0.00003	<0.000005	0.00001

Reference: "The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds" (Van den Berg et al. 2006).

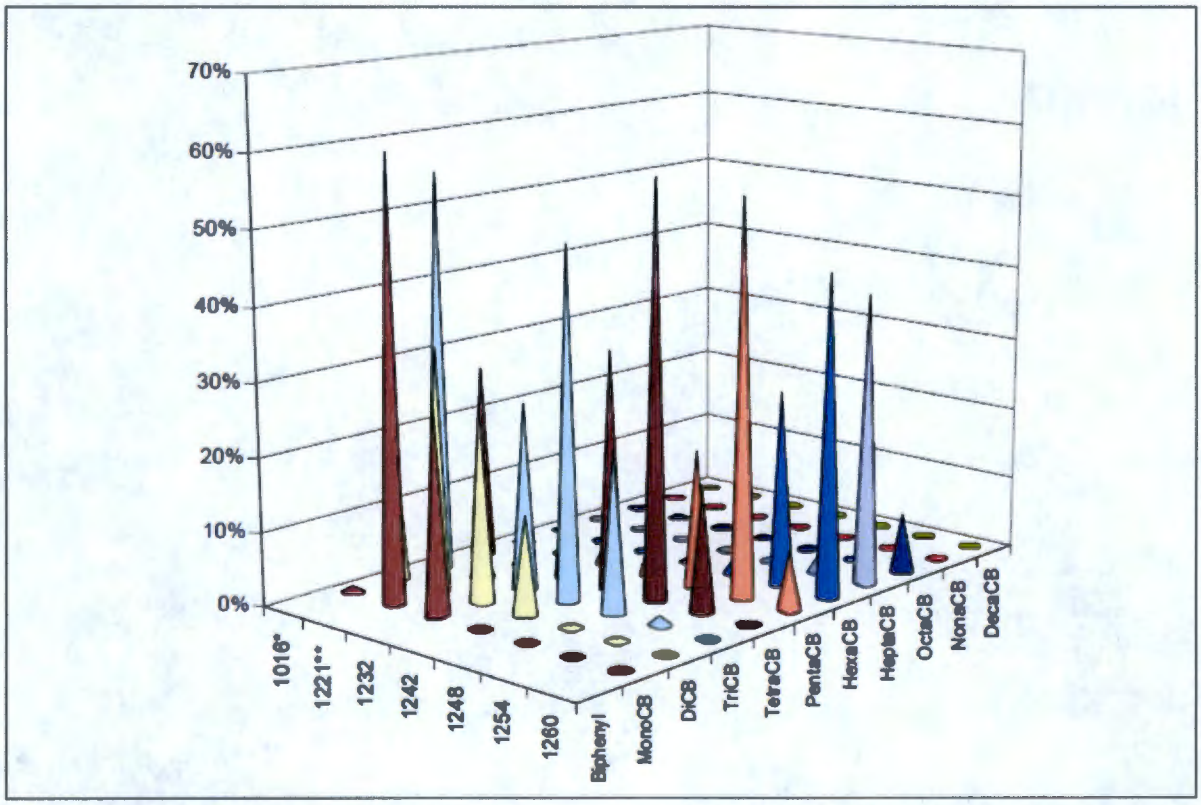
2.2 PERSISTENCE AND CHEMICAL DEGRADATION

Polychlorinated biphenyl mixtures with lower levels of chlorination (e.g., Aroclor-1221 as opposed to Aroclor-1260) are generally more soluble in water, more volatile, and more susceptible to biodegradation. These properties make the less-chlorinated PCBs less persistent in

the environment. In turn, PCB mixtures with higher levels of chlorination tend to be more persistent in the environment, bioaccumulating and remaining in environmental media (mainly soil) with little degradation over time.

The level of chlorination (21% in Aroclor-1221 and 60% in Aroclor-1260) is directly related to the prevalence of each isomer group, or homolog, in the mixture. Aroclor-1221 is less chlorinated than Aroclor-1260 and therefore has more congeners with mono, di, and tri homologs than Aroclor-1260, which contains more compounds in the penta, hexa, and hepta homologs (Figure 2-3). This information can be used by analysts to conduct source tracking and identification of PCB-related compounds.

Figure 2-3. Percentage of Isomer Homolog in Aroclor Mixtures



Source: Frame, J., 1996, *Journal of High Resolution Chromatography*, Vol.19 Dec. 1996, p. 657-668, Interpretation by Mark Marcus CH2MHill 5-22-2007.

2.3 ENVIRONMENTAL FATE OF AROCLORS

For Environmental Fate, PCBs enter the environment as commercially produced Aroclors, but the compositional mixture of congeners changes over time. Transformation in congener composition occurs through weathering, environmental partitioning, chemical transformation, bioaccumulation, and various biodegradation processes (EPA-440/4-79-029a, *Water-Related Environmental Fate of 129 Priority Pollutants, Volume I: Introduction and Technical*

Background, Metals and Inorganics, Pesticides and PCBs; EPA-440/4-79-029b, *Water-Related Environmental Fate of 129 Priority Pollutants, Volume II: Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds*). The persistence of PCBs lengthens as the degree of chlorination increases. For example, mono-, di- and tri-chlorinated biphenyls will biodegrade faster than tetra- and hepta-chlorinated biphenyls. However, persistence varies among the environmental compartments in which the PCBs are located (Table 2-3). Under laboratory conditions, bacteria that can metabolize PCBs to lower chlorinated congeners have been isolated, but under environmental conditions these organisms may not be functional, or alternatively, ambient conditions may not favor their transformation.

Table 2-3. Half-lives of Polychlorinated Biphenyls in Different Environmental Compartments

	Mean Half-life/Hours Air	Mean Half-life/Hours Water	Mean Half-life/Hours Soil	Mean Half-life/Hours Sediment
Dichloro-PCB	170 (~1 week)	5,500 (~8 months)	17,000 (~2 years)	17,000 (~ 2 years)
Heptachloro-PCB	5,500 (~8 months)	55,000 (~6 years)	55,000 (~6 years)	55,000 (~6 years)

PCB = polychlorinated biphenyl

Reference: *Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals, Volume 1: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs* (Mackay et al. 1992).

For example, within Hudson River sediments a combination of aerobic and anaerobic bacteria could transform higher chlorinated PCB congeners to lower, less toxic forms (Abramowicz 1995; *Hudson River PCBs Reassessment RI/FS Phase 3 Report: Feasibility Study* [EPA 2000]). These bacteria exhibit oxidation-reduction reactions that reduce the chlorine content, which in turn would reduce the potential health risk associated with PCB contamination. Nevertheless, PCB concentrations vary so greatly from one location to another that risk characterizations can be highly variable and uncertain, especially if they are conducted using broad-ranging Aroclor laboratory methodologies with their high detection limits. It is the persistence of PCBs in various environmental media that make it extremely important to properly characterize their risks for both human health and the environment.

2.4 POLYCHLORINATED BIPHENYL SOURCES

An estimated 2,000,000 tons of PCBs have been produced worldwide. A small fraction of these are still in use today in closed, highly regulated systems. Historical unregulated use of PCBs caused their widespread release and dissemination on land and water. Once released into the environment, PCBs bind intensively to soils and sediments but nevertheless partition from aqueous phases into air and thus continue to disperse worldwide. Polychlorinated biphenyls are deposited on vegetation and water surfaces by both precipitation and airborne particles. In

addition to environmental releases of commercial PCB formulations, various congeners can be formed during incomplete combustion of organic materials burned naturally or during agricultural burning ("Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions" [Eckhardt et al. 2007]).

The PCBs mainly bind to organic matter but have established equilibrium with water that allows them to accumulate throughout the food chain, concentrating in the fatty tissues of birds, marine mammals, and fish ("Contamination of Environmental Samples Prepared for PCB Analysis" [Alcock et al. 1994]). For the general public worldwide, contaminated fish consumption is the major source of PCB exposure.

2.5 POLYCHLORINATED BIPHENYL USE AND MANAGEMENT AT THE HANFORD SITE

Materials and equipment known to contain PCBs have been used across the Hanford Site, as the chemicals were widely used worldwide. For the most part, sources along the river corridor and inland areas were similar in nature. Sites and equipment such as electrical substations, transformers, capacitors, roofing material, and caulking can be found at various locations across the Hanford Site indiscriminant of operable unit. Historical onsite disposal areas, such as burial and dumping grounds, are a main feature of past Hanford Site operations. Inland sources of PCBs are primarily confined to the 200, 400, and 600 Areas. Polychlorinated biphenyl-containing materials and equipment are likely found within tank farms such as the WMA C.

The U.S. Environmental Protection Agency (EPA), U.S. Department of Energy (DOE), and State of Washington Department of Ecology (Ecology) agreed upon and signed the *Framework Agreement for Management of Polychlorinated Biphenyls (PCBs) in Hanford Tank Waste* (Ecology et al. 2000). This agreement directed quantification of PCBs in double-shell and single-shell tanks to ensure vitrification plant waste acceptance limits and requirements of risk-based disposal levels are met. As a result, the tank farm contractor at that time formulated a PCB characterization program, establishing PCB inventories for all 177 underground storage tanks. Prioritization strategies and characterization scheduling can be found in Revision 4 of RPP-6693, *Fiscal Year 2004 PCB Characterization Plan for Tank Farm Waste*.

As of July 2003, according to a prioritized characterization schedule, aqueous phase media analysis for PCBs has been completed in 52 tanks, with the remaining tanks awaiting characterization at that time. Polychlorinated biphenyls were detected at very low levels in only one of those tanks. Levels detected were 4.3 and 1.8 ppb for Aroclor-1248 and Aroclor-1254, respectively. One tank was observed as having a separable organic phase, and analysis of that phase resulted in detectable levels of Aroclor-1254. This organic phase was adsorbed onto the solid phase after tank pumping had been completed. Analysis of these solids revealed PCB detections in 15 out of 49 tanks sampled (Revision 3 of RPP-6693, *Fiscal Year 2003 PCB Characterization Plan for Tank Farm Waste*).

In summary, a total of 17 tanks were identified as containing PCBs, in water and/or sediment, and all of these tanks contained the mixture Aroclor-1254. In 2 of the 17 tanks, Aroclor-1248 was also detected, and in one case Aroclor-1260 was detected. Assuming that tank waste confirmed for PCBs contained materials from a variety of sources (e.g., transformer oil, paint, caulking, and other storage facilities in the 100-N and 100-K basins), and considering Aroclor persistence (described above), then Aroclor-1248, Aroclor-1254, and Aroclor-1260 would represent the most prevalent PCB mixtures on the Hanford Site, with Aroclor-1254 and Aroclor-1260 being the most prevalent. Because of the variation in detection limits associated with analytical methods for Aroclors, these results can be subjective at best, and a more specific analysis is required.

For example, analytical methods for Aroclors include the EPA-approved SW-846 Method 8082 ["Method 8082. Polychlorinated Biphenyls (PCBs) by Gas Chromatography" (EPA 1996)], which uses a capillary column with gas chromatography (GC)/electron capture detector (ECD). This method typically has quantitation limits that range as low as 10 μg/kg and often has high as 540 μg/kg wet weight in sediment and soil. Other methods are available with lower reporting limits that can be achieved through only improved sample cleanup and concentration steps, but are not practical. On the other hand, homolog-based quantification methods using GC/mass spectrometry (MS) and congener-specific analyses can achieve very much lower quantitation limits (0.02 to 0.6 μg/kg), with very reliable results, but have a drawback of generally higher costs.

2.6 LABORATORY METHODS FOR POLYCHLORINATED BIPHENYLS

Two methods are typically used to analyze for PCBs in environmental samples. The total PCB or Aroclor method (e.g., SW-846 Method 8082) extracts PCBs from a sample, analyzes the extract by GC and then uses a certain subset of peaks to determine the concentration of the PCB mixture. A pattern-recognition technique is used to qualitatively determine whether or not an Aroclor mixture is present; then a set of standards using that particular Aroclor is used for quantification. This method can measure the total amount of PCBs present in a sample, but has only limited ability to identify and quantify each of the 60 to 80 individual PCB congeners within any Aroclor mixture. Rather, the analyst uses the presence and ratio of a select subset of individual PCB congeners to identify which Aroclor is represented. The total amount of material can be related to a total amount of Aroclor. Individual PCB congener concentrations are not reported.

The second approach is the congener-specific method (e.g., EPA-821-R-07-004, *Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*). This process uses a high-resolution gas chromatograph spectrometer (GC/MS) to determine the concentration of each individual PCB congener in the sample. There are no presumptions regarding the PCB source material, whether it is an Aroclor or PCBs from combustion or some other source. The results are concentrations of each individual congener, subject to some technical limitations on the ability to resolve a handful of co-eluting congeners.

The two methods differ considerably in reported parameters, detection limits, availability and cost. The total PCB/Aroclor method is readily available and relatively inexpensive, but may not provide detection limits required for making decisions about closure-related activities. On the other hand, the congener-specific method can provide low detection limits for individual constituents and enable assessment personnel to determine homolog distribution, which will have the potential for source tracking and bioavailability comparison in fish or mammal tissue. However, it is nearly an order of magnitude more expensive than the other method.

2.7 SW-846 METHOD 8082

One of the major sources of interference in the analysis of PCBs is that organochlorine pesticides are co-extracted from the samples. Several of the commonly found pesticides and associated degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several PCB GC peaks and therefore cannot be accurately measured. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in the total PCB values generated.

Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters respond on electron capture detectors, usually as late-eluting peaks, and can interfere in PCB quantification.

Typically, increased sensitivity of SW-846 Method 8082 is achieved via three mechanisms:

- Hardware modifications and/or optimization of the operating conditions of the instrument
- Use of sample clean-up procedures to eliminate or minimize interferences
- Introduction of more sample into the instrument.

The primary objective is to perform sample preparation techniques that result in reliable, ultra-low-level Aroclor quantization. However, interferences inherent to the sample matrix or introduced during the sample preparation may be enhanced by use of these techniques. If non-target background signal and laboratory contamination can be controlled, significant gains in sensitivity can be achieved.

A large volume or mass of sample is solvent-extracted by the laboratory. After concentration of the sample extract to a small volume, the extract is subjected to gel permeation chromatography (GPC) followed by a large-volume silica gel column cleanup to remove PCB-interfering pesticides and other non-target interferences. These cleanups are followed by concentrated sulfuric acid treatment to remove biogenic interferences.

Further cleanup is performed using elemental mercury to precipitate sulfur, which interferes with the accurate quantitation of Aroclors. Samples are injected into the gas chromatograph using a pressure-programmed LVI that allows the injection of up to 100 μL of sample extract, which essentially results in further concentration of the sample in the instrument. This technique has been used successfully on discharge water, receiving water, sewage influents/effluents, sediment,

and tissue. Aroclor reporting limits are 5 ng/L (ppt) for water and 10 µg/kg (ppb) for tissue and sediment. Experimentally-derived detection limits are 2 to 5 times lower than the reporting limit, depending on the Aroclor. The PCB congener reporting limits by this method are 5 ng/L (ppt) for water and 0.5 µg/kg (ppb) for tissue and sediment.

Common concerns for Aroclor testing:

- PCBs have been present in the environment for many decades, possibly changing the congener profile over time due to degradation and weathering
- Often there are many interfering compounds in a sample, masking the identifying chromatogram peak pattern
- A significant amount of PCBs may be present in a sample, yet the chromatogram does not show a peak pattern consistent with any Aroclor standard available
- Recent data has shown that 12 individual PCB congeners are more toxic than the others
- It is possible a sample with a significant amount of PCB congeners present is not as much of an ecological risk as a sample with fewer but more toxic PCB congeners present.

As a result, there has been an increased interest in the analysis for individual PCB congeners rather than the analysis for PCB Aroclors.

2.8 EPA METHOD 1668

The EPA Method 1668 is used to analyze individual PCB congeners by high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS) using isotope dilution. This method was originally developed by the EPA to determine the concentrations of the 12 toxic PCB congeners as designated by WHO. In 1999, EPA released Revision A of the method, which expanded its scope to include all 209 PCB congeners. However, approximately 30% of the PCB congeners co-elute and are reported either as pairs, triplets, or even quadruplets. Method 1668A is applicable to aqueous, solid, multiphase and tissue matrices. It is used under many different regulatory programs including the *Clean Water Act of 1972* and RCRA.

Advantages to Method 1668A:

- The detection limits are up to one thousand times (1000x) lower than the traditional Aroclor analysis
- There are fewer problems with matrix interferences in a complex sample
- The identification and quantification of individual PCB congeners is more accurate than SW-846 Method 8082 and its modifications

- The quantification of the 12 toxic PCB congeners allows measurement of relative toxicity and more accurately determines the ecological risk at a site
- The low-level PCB congener composition can be interpreted to determine the amount of aging that occurred in a complex PCB mixture
- Aroclor concentrations can be estimated from the congener concentrations.

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3.0 METHODOLOGY

This section summarizes the methodology used to evaluate PCB congeners and Aroclor analytical results collected at 10 direct push locations within WMA C.

3.1 SAMPLE NUMBER AND LOCATION

The 10 soil sample locations within WMA C where PCBs were analyzed for are previously shown in Figure 1-2. The soil samples from these locations were collected under the WMA C RFI Phase 2 work plan (RPP-PLAN-39114) and Phase 2 SAP (RPP-PLAN-38777). To date, implementation of characterization activities under these two plans resulted in the collection and analysis of soil samples at 13 sampling locations (A, B, C, E, F, G, H, I, J, L1/L2, P, R, and U). Under these same plans, PCB congener data were specifically collected at 10 of the 13 locations (E, F, G, H, I, J, L1/L2, P, R, and U) with the specific purpose of delineating the nature and extent of PCB congener contamination within WMA C. A summary of Phase 2 RFI sampling sites, their general locations within WMA C, and their overall RFI Phase 2 characterization objectives are summarized in Table 3-1.

3.2 SAMPLE DEPTHS

Depending on location, samples were collected from 0 to 5.5 m and at various intervals. Sampling intervals for all locations except for the unplanned release (UPR) site UPR 81 (Site P) included depth intervals of 0 to 0.3 m, 2.1 m, and 4.9 to 5.5 m. At the Site P sample location, no surface samples were taken and the intervals included 2.1 to 2.4 m and 4.9 to 5.5 m.

3.3 DATA USED

The PCB congener data from 2009 to 2010 for 10 locations (E, F, G, H, I, J, L1/L2, P, R, and U) at WMA C are used for this assessment. The PCB Aroclor data collected from all 13 locations (A, B, C, E, F, G, H, I, J, L1/L2, P, R, and U) collected between 2009 and 2011 at WMA C are also considered in this assessment. The analytical data were extracted from the Hanford Environmental Information System (HEIS) and processed to obtain a single set of results per sampling location for only polychlorinated biphenyl congener and Aroclor results. In total, 9,196 PCB-related (including PCB congeners, Aroclors, and Co-elution PCBs) records were obtained from HEIS with detects reported for 133 out of 209 congeners and 2 out of 7 Aroclors. A subsequent review of the HEIS data revealed that the lab qualifier flags in the data set used for this evaluation had not been reported correctly for a small number of PCB congener samples. The net effect for data processing was that 52 samples originally reported as non-detects were actually detects. Because this evaluation used a bounding approach, this discrepancy is not expected to have any substantive effect on the evaluation conclusions. The evaluation included both upper- and lower-bound calculations, where detects and non-detects were summed together to get upper bound total PCB concentrations and non-detects were excluded to get lower bound total PCB concentrations.

Table 3-1. Waste Management Area C Grouped Sampling Locations

Grouped Sampling Sites[a]	General Location Within Waste Management Area C (see Figure 1-1)	Phase 2 Characterization Objective[b]
A + B	Area near tank 241-C-101	Characterize releases and refine conceptual models 1, 2 and 4
C	Area near 241-C-200 series tanks	Determine if C-200 tanks actually leaked, refine conceptual models 1, 2, and 4, and determine if any C-200 tank leaked during retrieval
E	Area between tanks 241-C-106 and 241-C-109	Assess ^{60}Co and refine conceptual models 1, 2, and 4
F + G	Area near tank 241-C-103 and Bldg. C-801, and Bldg. C-801 chemical drain	Assess release of Plutonium Uranium Extraction plant waste, ^{137}Cs and ^{99}Tc, and ^{60}Co and refine conceptual models 1, 2, and 4
H + I	Area northeast of UPR-200E-91 and UPR-200E-115	Assess surface exposures, and assess ^{60}Co and surface release conceptual models
J	Area near tank 241-C-104	Assess suspected release and refine conceptual models 1, 2 and 4
L1 + L2	Area between tanks 241-C-103 and 241-C-106	Update logging data for ^{60}Co, ^{137}Cs, uranium, and moisture and assess potential release and refine conceptual models 1, 2, and 4
P	Area near UPR 81	Characterize release and refine conceptual models 1, 2, and 4
R	Area near 241-C-301 catch tank	Assess potential catch tank release and refine conceptual models 1, 2, and 4
U	Area near tank 241-C-110	Characterize tank 241-C-110 release and conceptual models 1, 2, and 4

[a] Sampling sites, in bold, are locations where polychlorinated biphenyl congeners were evaluated.

[b] Conceptual models 1, 2, and 4 refer to alternative conceptualizations of contaminant release and subsequent migration from Waste Management Area C infrastructure. Conceptual model descriptions are provided in Section 3.3 of RPP-PLAN-39114, *Phase 2 RCRA Facility Investigation/Corrective Measures Study Work Plan for Waste Management Area C.*

3.4 DATA PROCESSING AND REDUCTION

All data extracted from HEIS including non-detects were used in this assessment. The purpose of this was to get an upper bound and a lower bound estimate of ranges for PCB congeners from each location and sample depth. Any sample that was flagged with an R qualifier was considered unusable and rejected from this analysis. Sample results were then grouped by location and depth.

3.5 TOXICITY EQUIVALENCY FACTOR DETERMINATION

When establishing and determining compliance with cleanup levels and remediation levels for mixtures of PCBs under the 2007 *Revised Code of Washington* 70.105D, "Hazardous Waste Cleanup — Model Toxics Control Act" (MTCA) cleanup regulation [*Washington Administrative Code* (WAC) 173-340-708, "Human Health Risk Assessment Procedures," subsection (8) "Carcinogenic potency factor"], the mixture shall be considered a single hazardous substance. This means that a target cancer risk level of one in one million (10^{-6}) is used when calculating cleanup levels under Method B.

As described in *Evaluating the Toxicity and Assessing the Carcinogenic Risk of Environmental Mixtures Using Toxicity Equivalency Factors* (Ecology 2007) (WAC 173-340-708), the TEF methodology was developed by EPA to evaluate the toxicity and assess the risks of a mixture of structurally related chemicals with a common mechanism of action. A TEF is an estimate of the relative toxicity of a chemical compared to a reference chemical.

Ecology uses the TEF methodology to evaluate the toxicity and assess the risks for environmental mixtures of dioxins/furans and carcinogenic-polycyclic aromatic hydrocarbons (c-PAHs). This methodology may also be used to evaluate the toxicity of PCBs.

Toxicity equivalency factors are developed for PCBs as described in the Section above. The methodology used to determine PCB TEFs is also described in WAC 173-340-708(8).

The TEFs from Table 3-2 are used to evaluate the TEQ for each dioxin-like PCB and assess the risk for the 12 dioxin-like PCBs (4 non-ortho and 8 mono-ortho PCBs). These values were taken from Van den Berg et al. 2006.

3.6 TOXICITY EQUIVALENT DETERMINATION

According to information provided by WHO, the health risk of these 12 dioxin-like PCB congeners can be related to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) through a TEF. Toxicity equivalents were determined by multiplying the concentration of each of the 12 PCB congeners by its own TEF, to derive the TEQ concentration of 2,3,7,8-TCDD. Each of those 12 PCB congeners' TEQs were then added together to generate the concentration equivalent of 2,3,7,8-TCDD for the entire PCB mixture. These calculations are shown as Equations 3-1 and 3-2 below.

$$\text{(Individual PCB congener concentration)} \times \text{TEF} = \text{(congener 2,3,7,8-TCDD TEQ)} \quad (3\text{-}1)$$

$$\text{Sum of all 12 (congener-specific TEQ)} = \text{(Total 2,3,7,8-TCDD TEQ)} \quad (3\text{-}2)$$

Table 3-3 shows an example calculation of congener TEQ and sample TEQ using concentration results for the 12 dioxin-like PCB congeners in a hypothetical sample where each congener is present at a median reporting limit for Method 1668a.

Table 3-2. World Health Organization Toxicity Equivalent Factor Values for Dioxin-like Polychlorinated Biphenyl Congeners

Chemical Abstracts Service Number	Dioxin-like Polychlorinated Biphenyl Congener	Polychlorinated Biphenyl Congener-Specific Toxicity Equivalency Factor (Unitless)[a]
32598-13-3	3,3',4,4'-Tetrachlorobiphenyl (PCB 77)	0.0001
70362-50-4	3,4,4',5- Tetrachlorobiphenyl (PCB 81)	0.0003
32598-14-4	2,3,3',4,4'-Pentachlorobiphenyl (PCB 105)	0.00003
74472-37-0	2,3,4,4',5-Pentachlorobiphenyl (PCB 114)	0.00003
31508-00-6	2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	0.00003
65510-44-3	2',3,4,4',5-Pentachlorobiphenyl (PCB 123)	0.00003
57465-28-8	3,3',4,4',5-Pentachlorobiphenyl (PCB 126)	0.1
38380-08-4	2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156)	0.00003
69782-90-7	2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157)	0.00003
52663-72-6	2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167)	0.00003
32774-16-6	3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169)	0.03
39635-31-9	2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189)	0.00003

[a] As described in WAC 173-340-708, "Human Health Risk Assessment Procedures" and "The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds" (Van den Berg et al. 2006).

Table 3-3. Example Calculation of Congener Toxicity Equivalents Using Hypothetical Polychlorinated Biphenyl Congener Concentrations and Associated Toxicity Equivalent Factors.

Dioxin-like Polychlorinated Biphenyl (PCB) Congener	Hypothetical PCB Congener Concentrations (Pg/g)	PCB Congener-specific Toxicity Equivalency Factor (unitless)	Median Method 1668a Reporting Limit (Pg/g)	Calculated PCB-specific Toxicity Equivalent Concentrations (Pg/g)
3,3',4,4'-Tetrachlorobiphenyl (PCB 77)	77	0.0001	40	0.004
3,4,4',5- Tetrachlorobiphenyl (PCB 81)	81	0.0003	40	0.012
2,3,3',4,4'-Pentachlorobiphenyl (PCB 105)	105	0.00003	20	0.0006
2,3,4,4',5-Pentachlorobiphenyl (PCB 114)	114	0.00003	40	0.0012
2,3',4,4',5-Pentachlorobiphenyl (PCB 118)	118	0.00003	40	0.0012
2',3,4,4',5-Pentachlorobiphenyl (PCB 123)	123	0.00003	40	0.0012
3,3',4,4',5-Pentachlorobiphenyl (PCB 126)	126	0.1	20	2.0
2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156)	156	0.00003	40	0.0012
2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157)	157	0.00003	40	0.0012
2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167)	167	0.00003	40	0.0012
3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169)	169	0.03	20	0.6
2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189)	189	0.00003	40	0.0012
Total				2.625

Pg/g = picograms per gram
Note: Calculated 2,3,7,8-TCDD toxic equivalent in this hypothetical sample is 2.625 pg/g.

Reference: EPA-821-R-07-004, *Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS.*

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4.0 RESULTS

For total PCB congeners, both upper bound and lower bound concentrations were examined to see if any variation is apparent. These bounded calculations include non-detected results for the upper bound and exclude the non-detected results for the lower bounded results.

Total PCB congeners for all sites, except for UPR 81 (Site P), ranged from 0.06 µg/kg to 2.1 µg/kg depending on depth. The shallow (0 to 0.3 m) sites showed the highest concentrations, ranging from 0.18 µg/kg to 2.1 µg/kg, with the highest coming from Site R (Figures 4-1 through 4-4). The shallow sites had two samples taken from 0 to 0.3 m (considered shallow samples) and are labeled #1 for the first sample taken and #2 for the second sample taken. The subsurface 2.1 to 3.7 m sample concentrations ranged from 0.08 µg/kg to 0.5 µg/kg (Figures 4-5 through 4-9) with the highest coming from Site G at 2.1 m (Figure 4-5). The last subsurface 4.9 to 5.5 m sample concentration, as expected, was much lower than the other sample depths and ranged from 0.06 µg/kg to 0.038 µg/kg, with Sites G and L1 having the highest concentrations (Figures 4-10 and 4-11).

Total PCB congeners for UPR 81 (Site P) ranged from 0.4 µg/kg to 2.6 µg/kg depending on depth (Figures 4-12 through 4-15). The 2.1 to 2.4 m sample range had a slightly higher concentration range compared to the deeper samples, from 1.2 µg/kg to 2.6 µg/kg, with the highest concentrations coming from C6400 at 2.1 m (Figure 4-12). Samples from the 1.1- to 1.5-m depths ranged from 0.4 µg/kg to 2.4 µg/kg with the highest concentrations coming from C6406 at 3.7 m (Figure 4-14).

Total 2,3,7,8-TCDD TEQ was also calculated for all shallow (0 to 0.3 m) samples (see Figure 4-16 and Table 4-1) and for a number of deeper (2.1 to 4.9 m) samples collected near Site P (see Figure 4-17). Results of these calculations showed the total 2,3,7,8-TCDD TEQ for the shallow (0 to 0.3 m) samples ranged from 5.5 E-05 to 1.6 E-04 µg/kg when non-detects were included and from 7.6 E-08 to 1.0 E-04 µg/kg when non-detects were excluded (see Table 4-1). The total 2,3,7,8-TCDD TEQ for the deeper (2.1 to 4.9 m) samples near Site P ranged from 1.5 E-04 to 2.2 E-04 µg/kg when non-detects were included. All totals were several orders of magnitude lower than the 2007 MTCA Standard Method B direct contact soil cleanup level for total PCBs of 0.5 mg/kg [WAC 173-340-740, "Unrestricted Land Use Soil Cleanup Standards," subsection (3) "Method B soil cleanup levels for unrestricted land use."].

Homolog analysis for all the samples showed a consistent pattern, with the most prevalent being from the Penta, Hexa, Hepta, and Octa. This is consistent with very weathered PCB patterns with little resemblance to any Aroclor patterns from any commercial mixture produced. This becomes apparent when side-by-side samples were analyzed for both Aroclors and congeners. The results showed the total congeners values 20 to 30 times lower than the reported Aroclor results in Table 4-2. All three highlighted samples were collected from the same depth, but with much different detection limits and results.

Figure 4-1. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 0 to 0.3 Meters at Selected Sample Locations at Waste Management Area C. Upper Bound (Sample #1 Detects and Non-detects Summed).

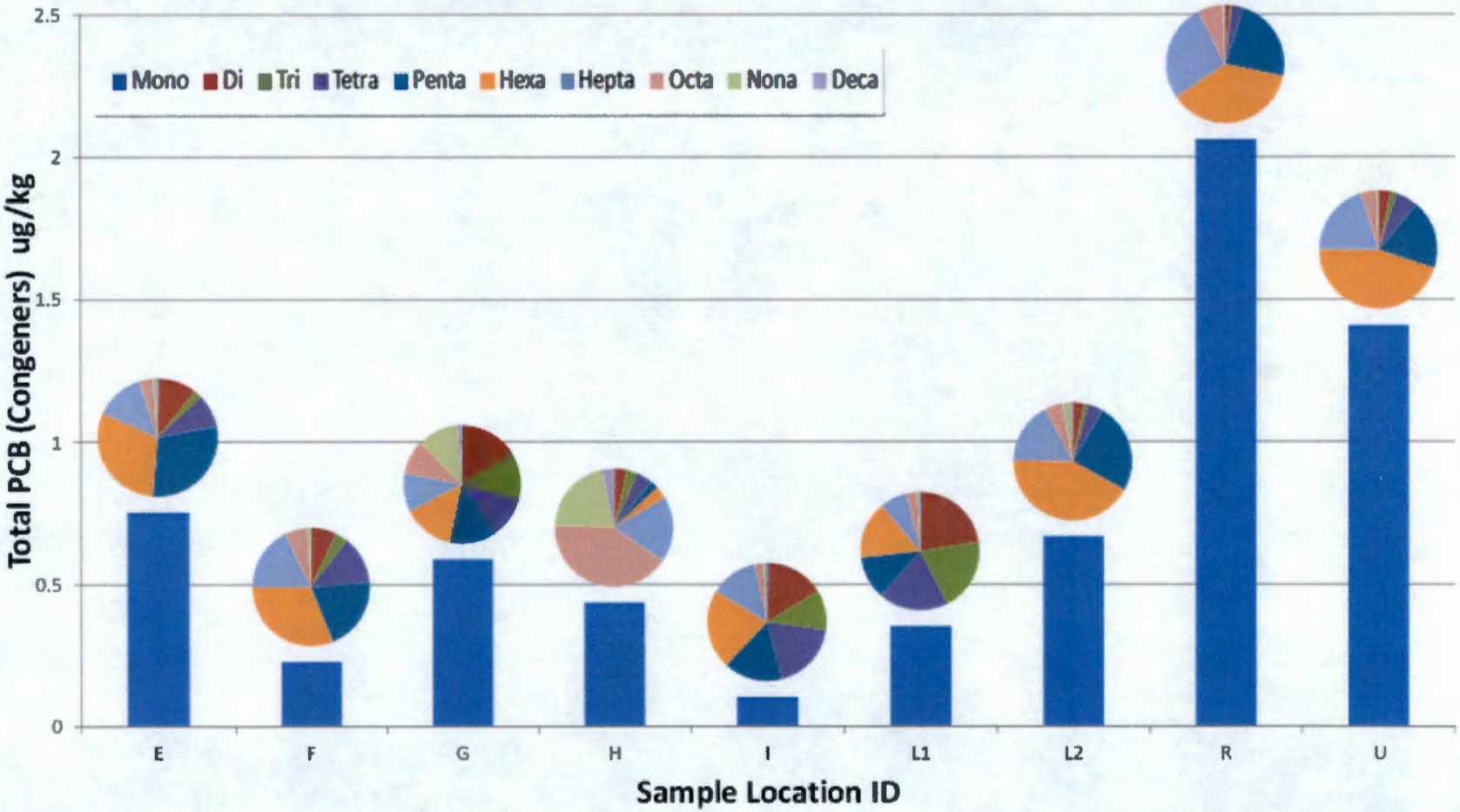


Figure 4-2. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 0 to 0.3 Meters at Selected Sample Locations at Waste Management Area C. Upper Bound (Sample #2 Detects and Non-detects Summed).

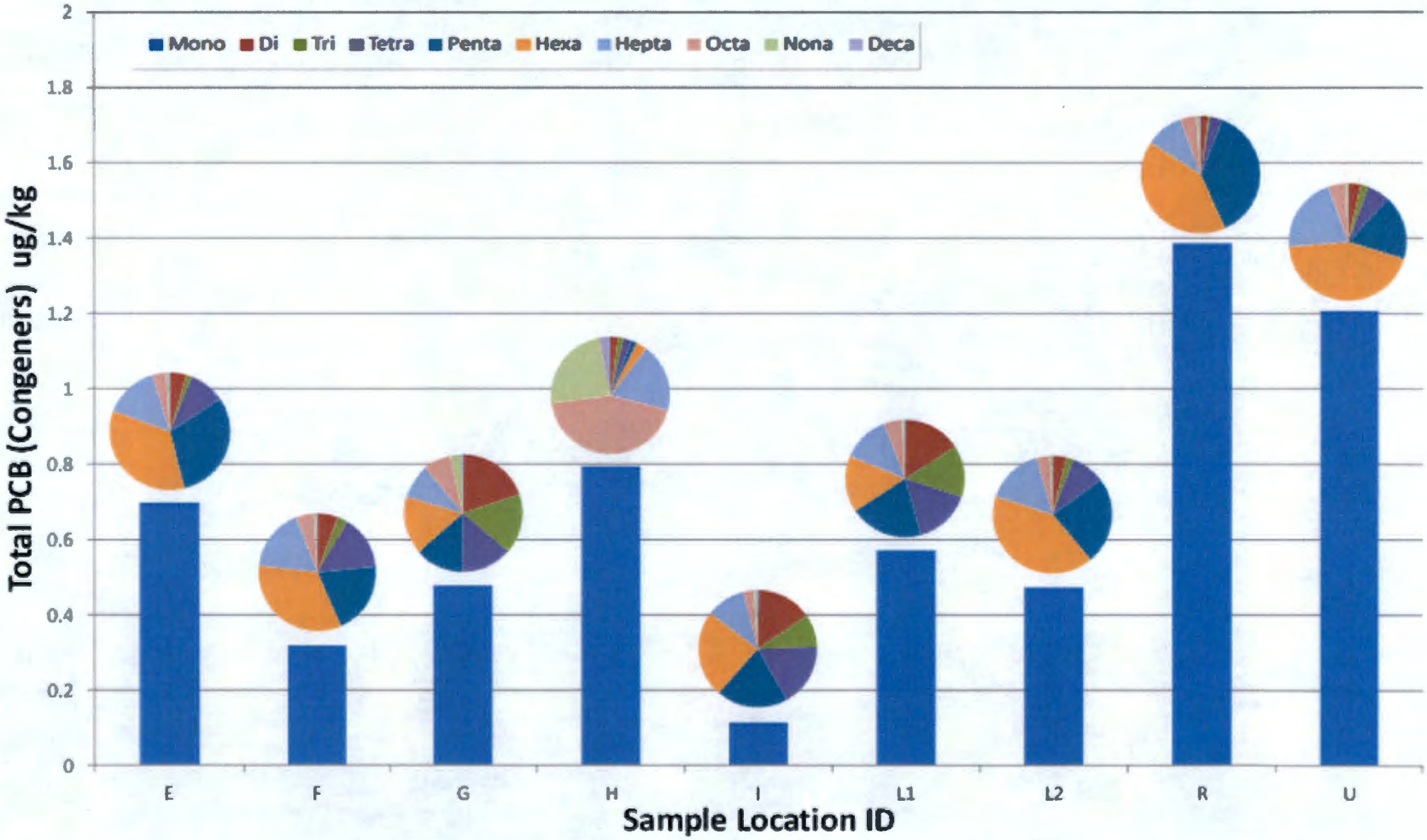


Figure 4-3. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 0 to 0.3 Meters at Selected Sample Locations at Waste Management Area C (Sample #1 Detects only Summed).

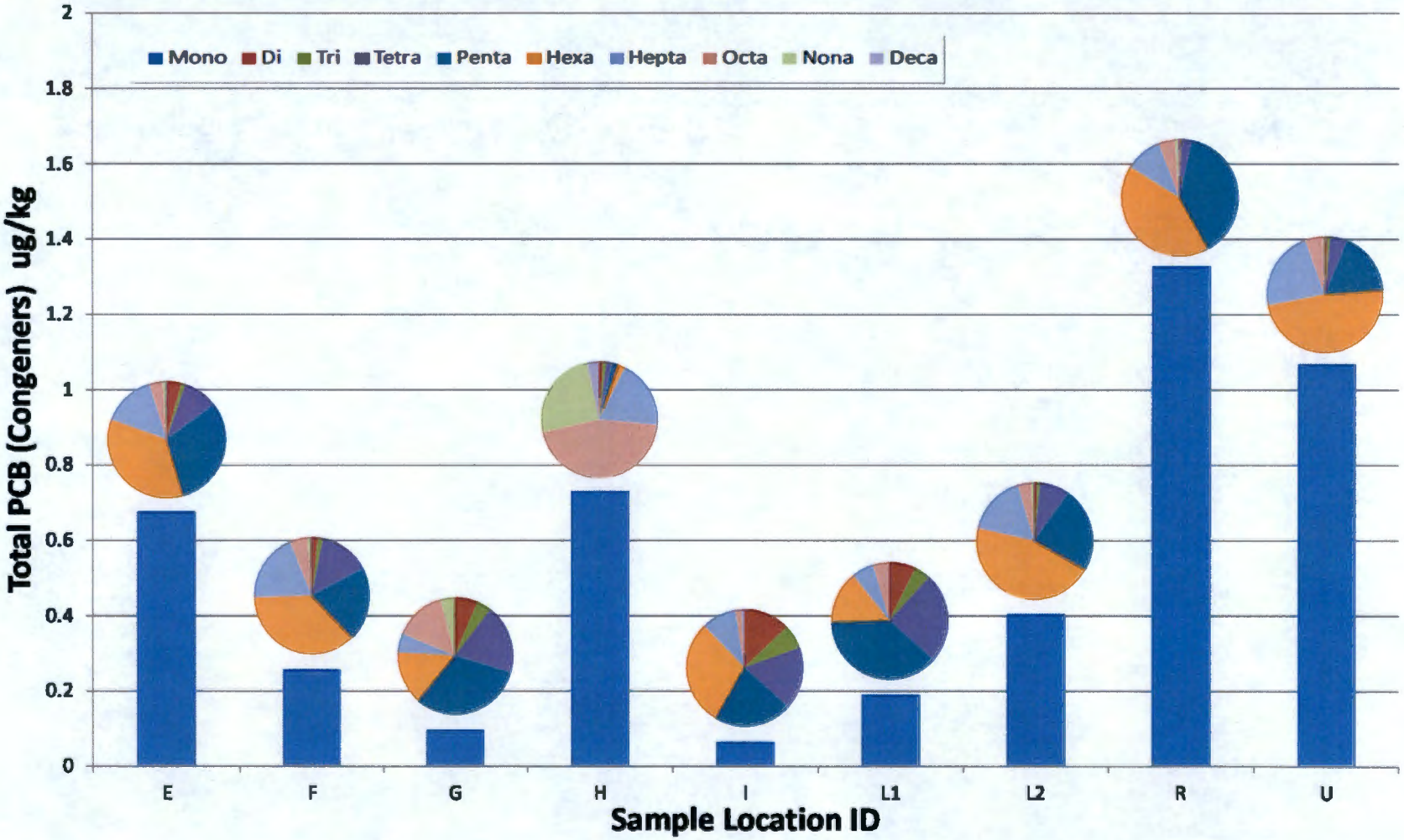


Figure 4-4. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 0 to 0.3 Meters at Selected Sample Locations at Waste Management Area C (Sample #2 Detects only Summed).

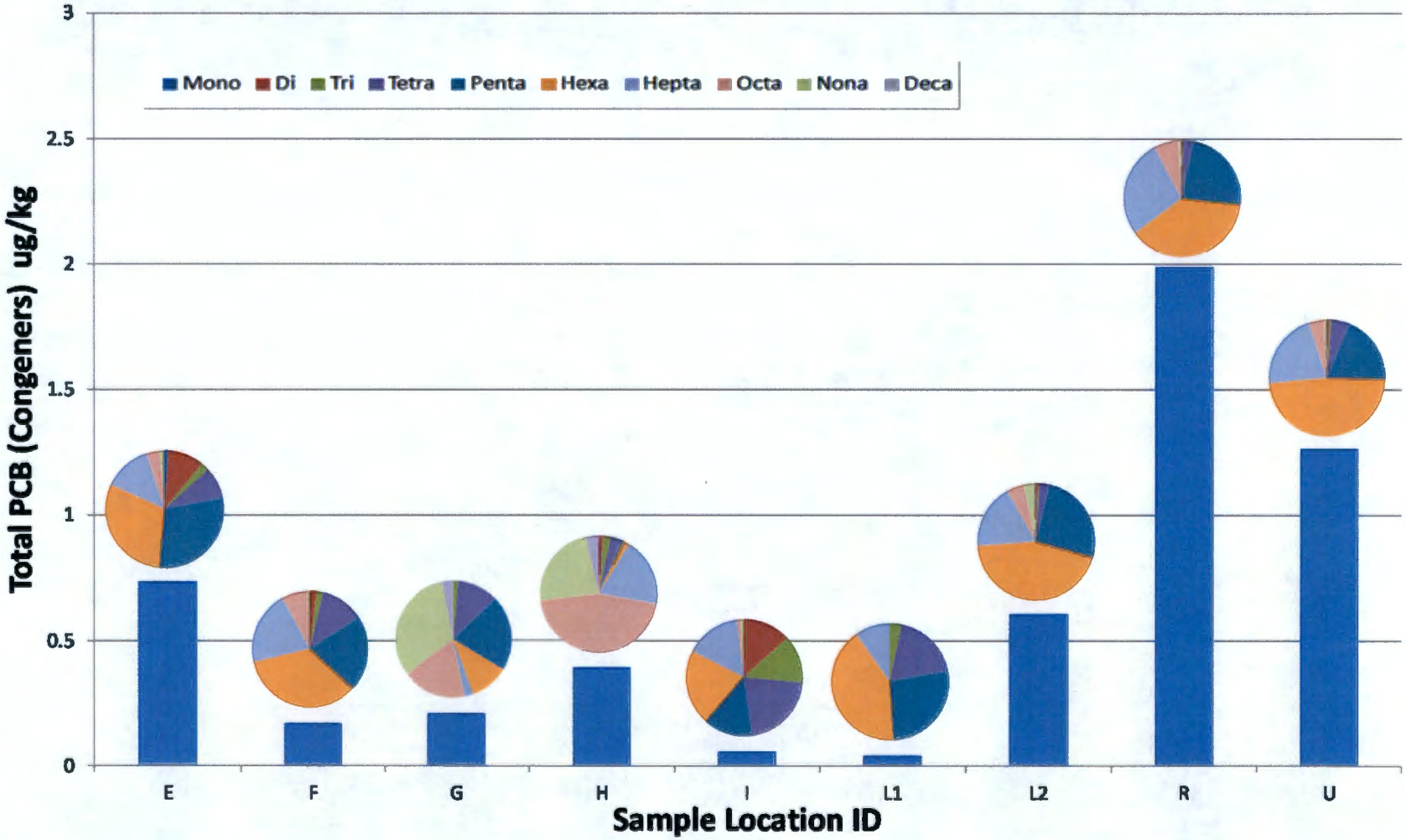


Figure 4-5. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected at 2.1 Meters at Selected Sample Locations at Waste Management Area C (Detects and Non-detects Summed).

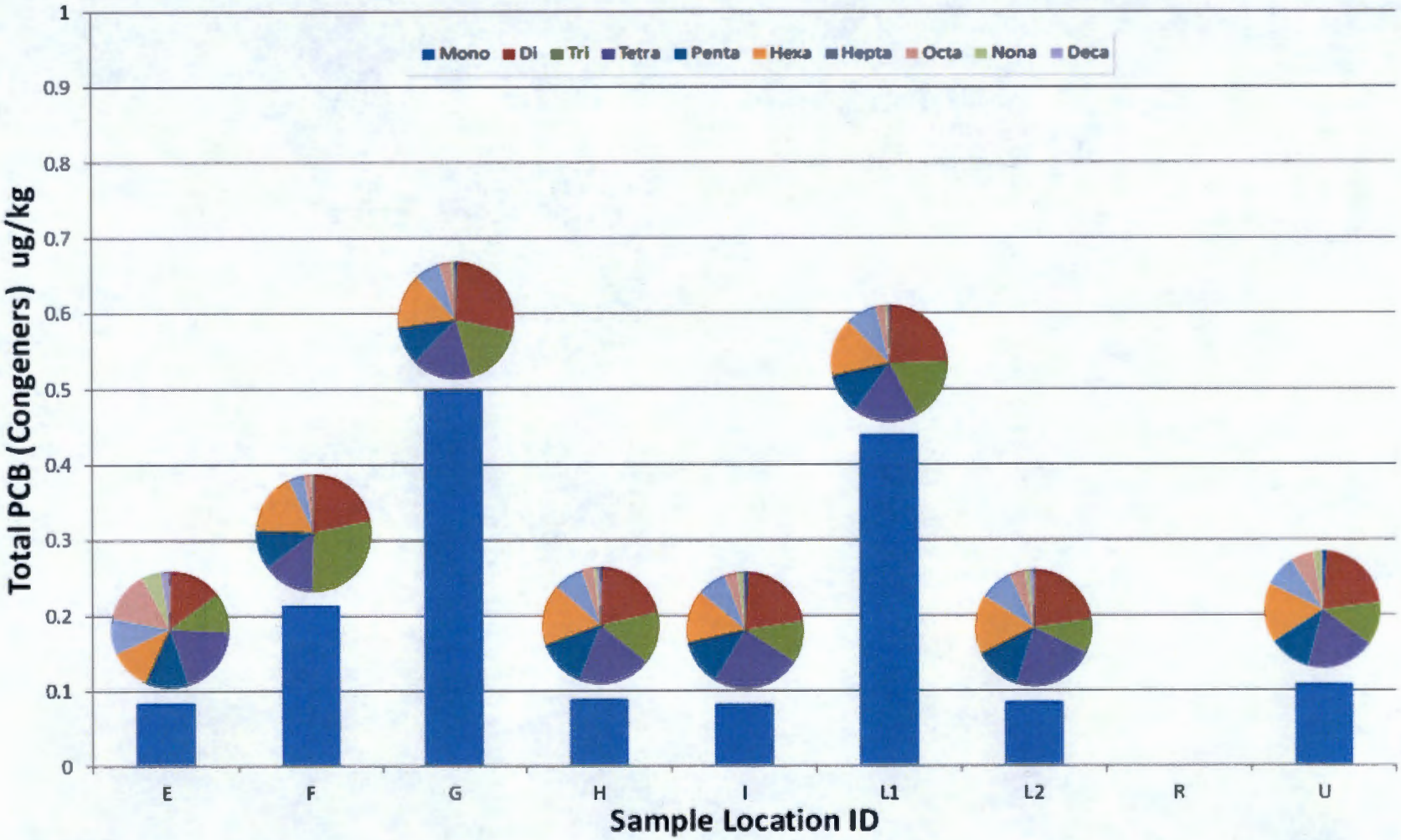


Figure 4-6. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected at 2.1 Meters at Selected Sample Locations at Waste Management Area C (Detects only Summed).

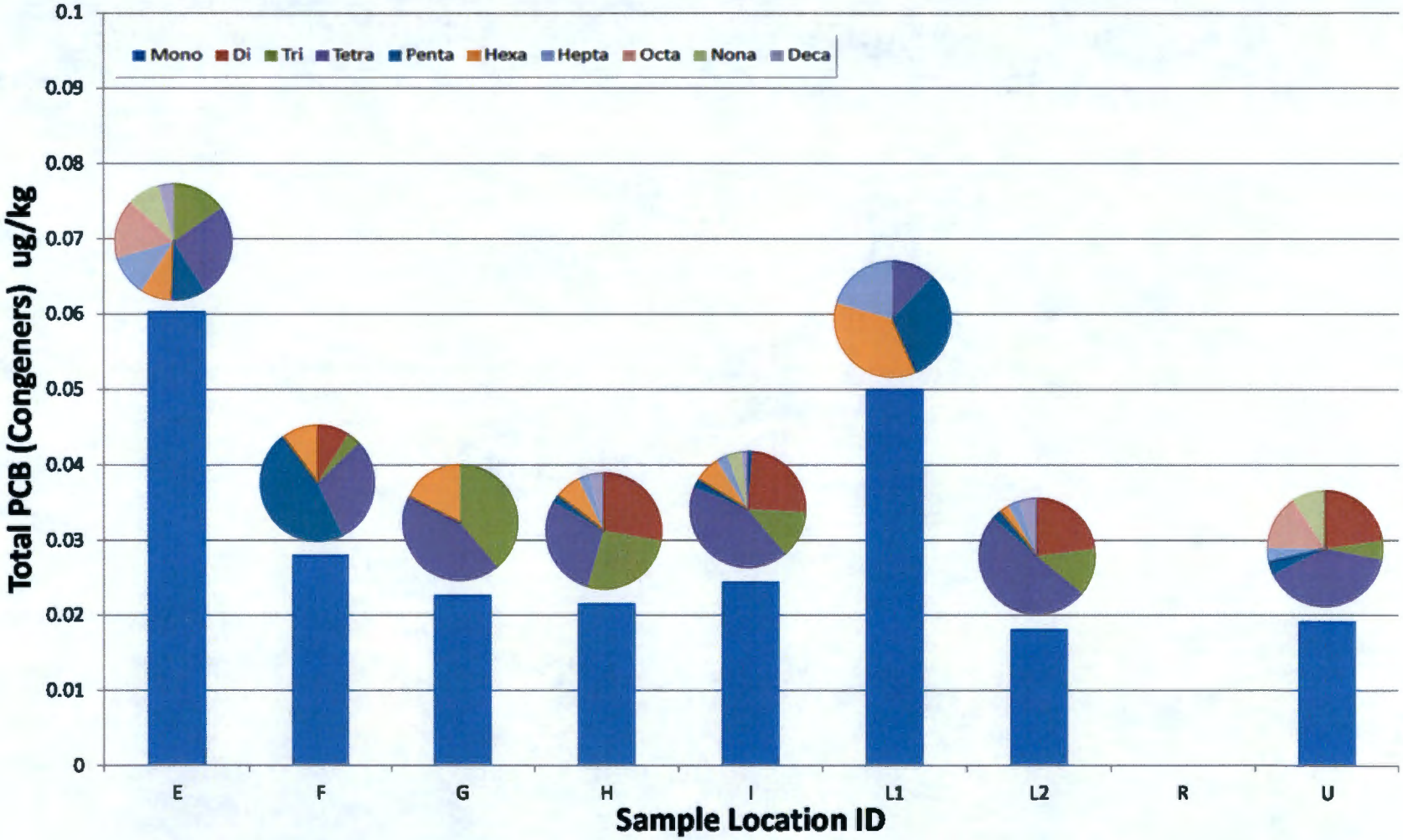


Figure 4-7. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected at 3.7 Meters at Selected Sample Locations at Waste Management Area C (Detects and Non-detects Summed).

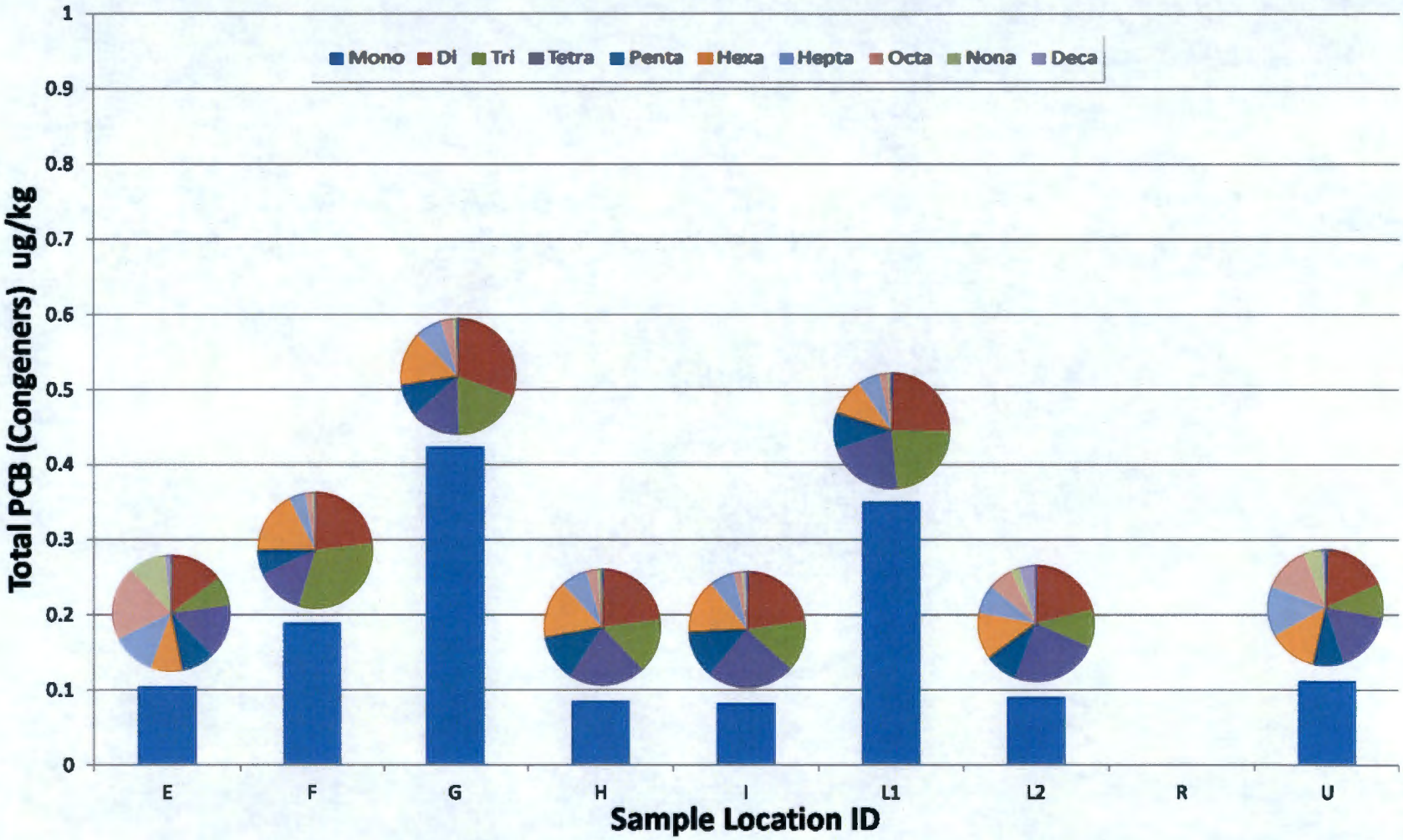


Figure 4-8. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected at 3.7 Meters at Selected Sample Locations at Waste Management Area C (Detects only Summed).

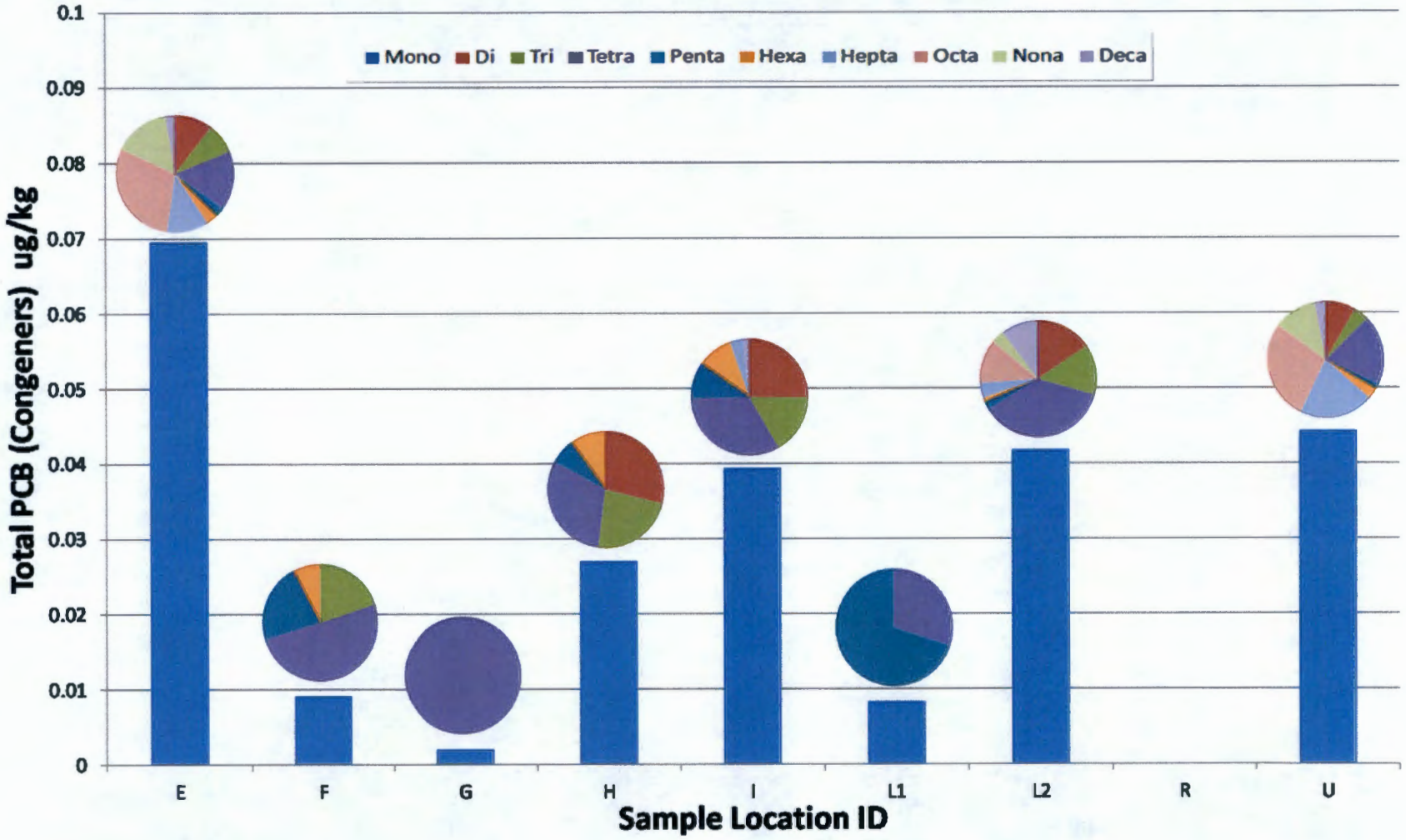


Figure 4-9. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 4.9 to 5.5 Meters at Selected Sample Locations at Waste Management Area C (Detects and Non-detects Summed).

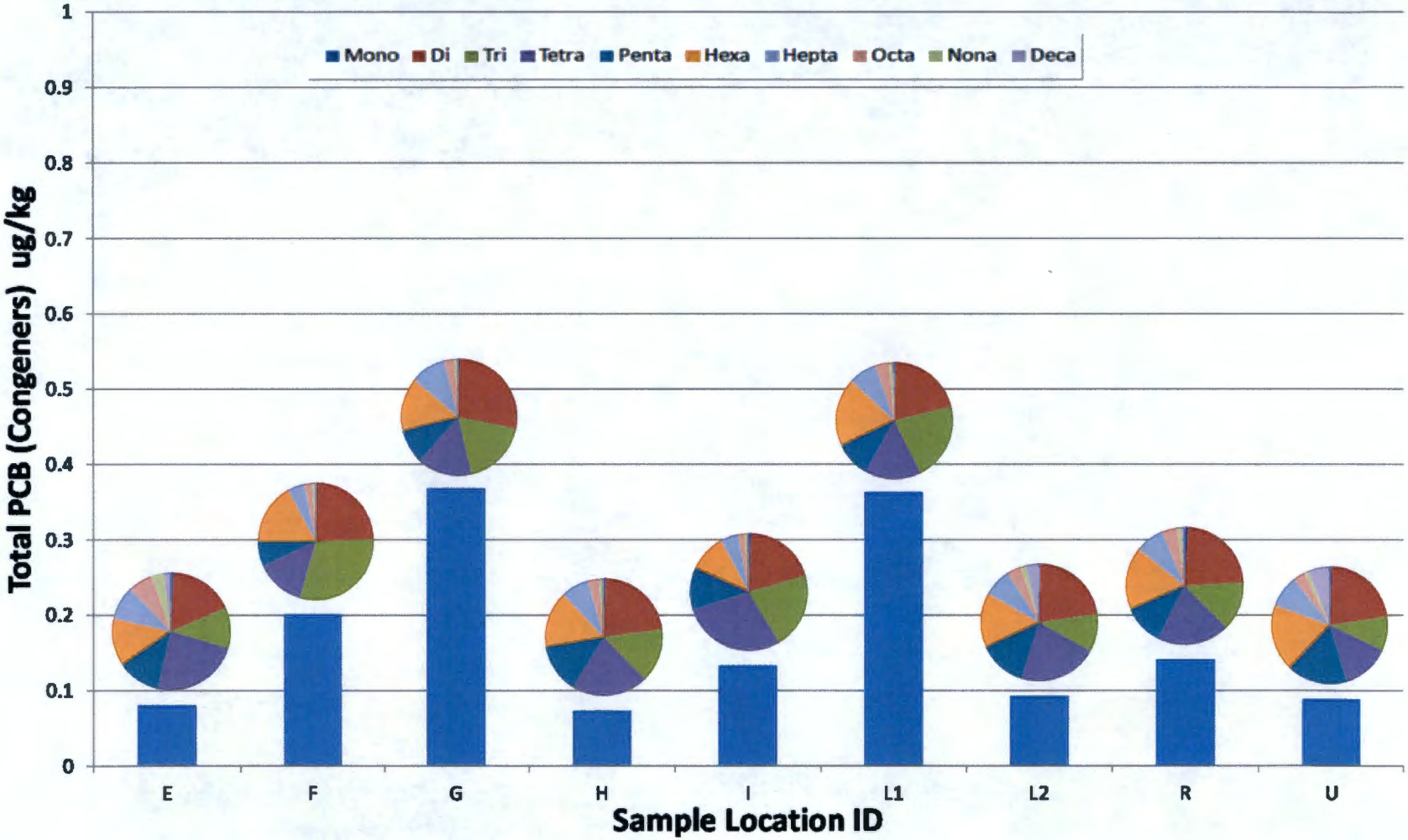


Figure 4-10. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 4.9 to 5.5 Meters at Selected Sample Locations at Waste Management Area C (Detects only Summed).

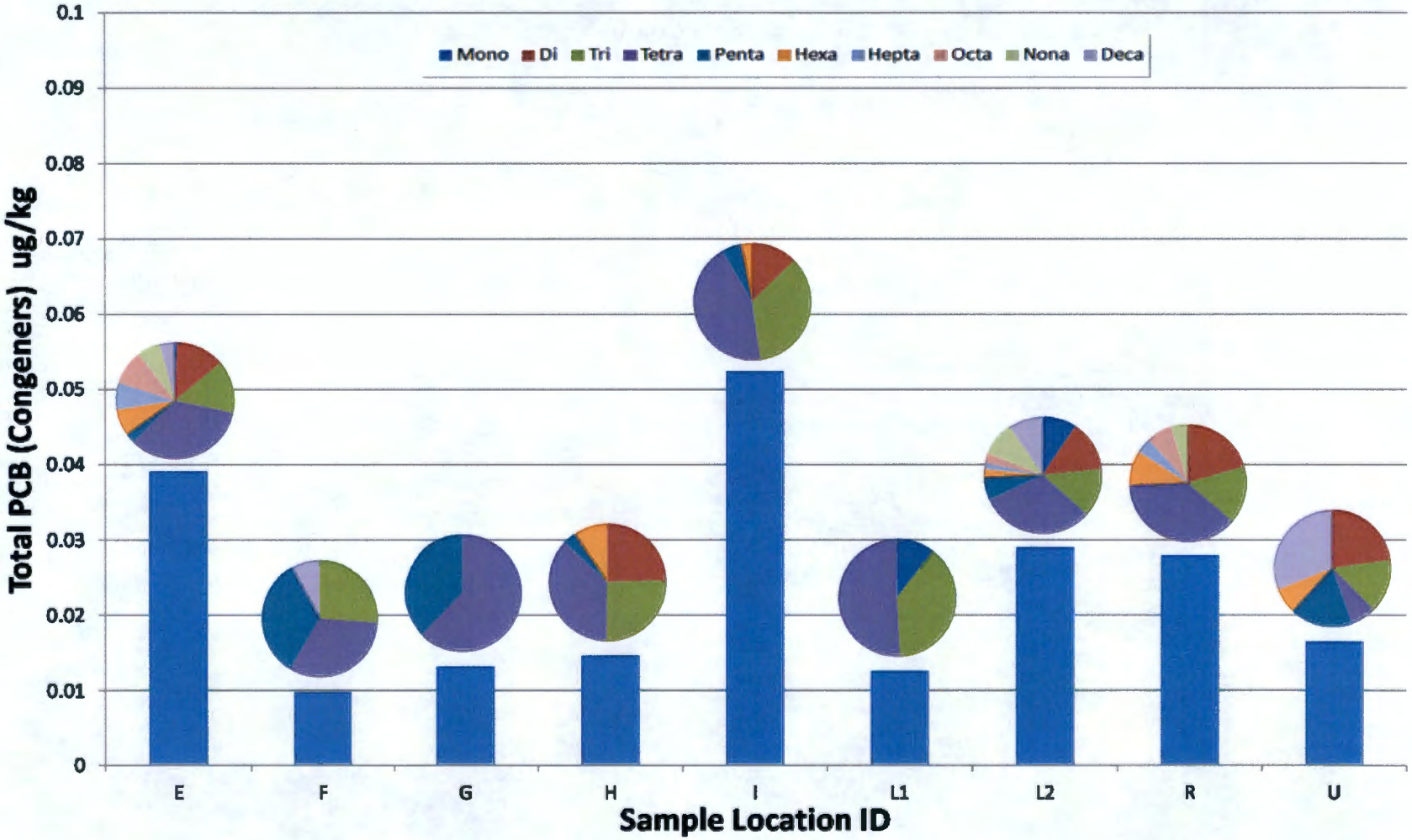


Figure 4-11. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 2.1 to 2.4 Meters at Site P at Waste Management Area C (Detects and Non-detects Summed).

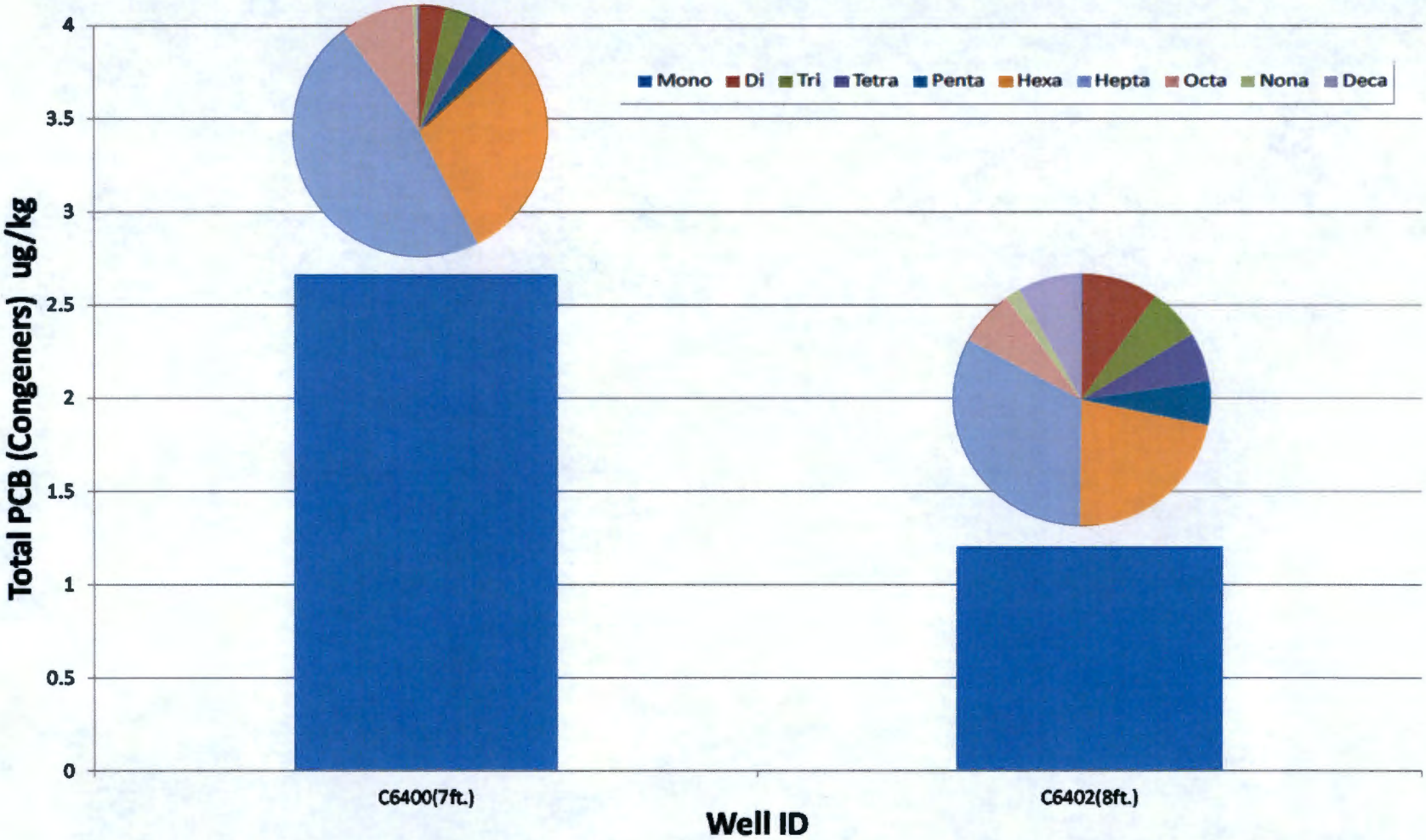


Figure 4-12. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 2.1 to 2.4 Meters at Site P at Waste Management Area C (Detects only Summed).

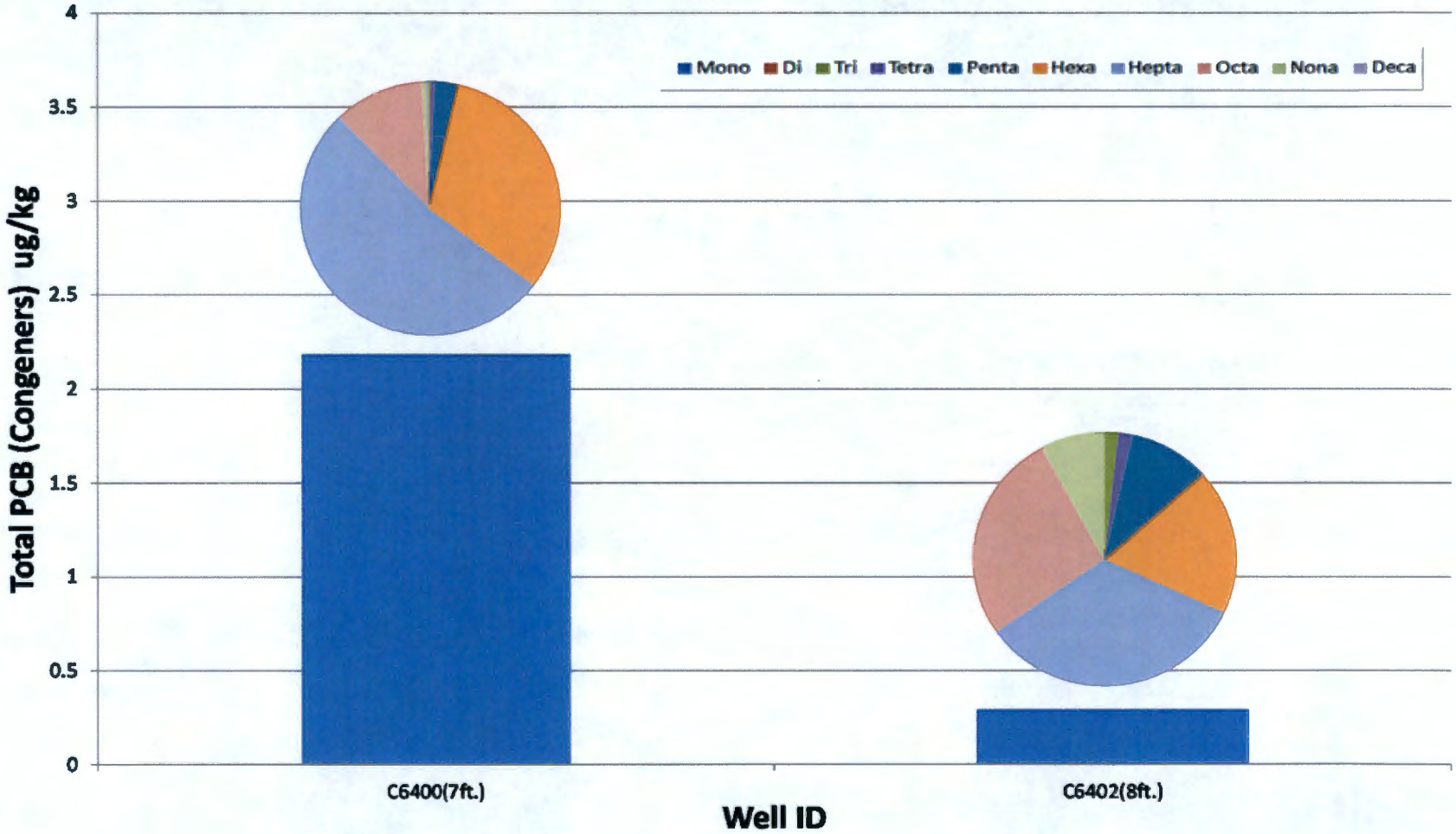


Figure 4-13. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 3.7 to 4.9 Meters at Site P at Waste Management Area C (Detects and Non-detects Summed).

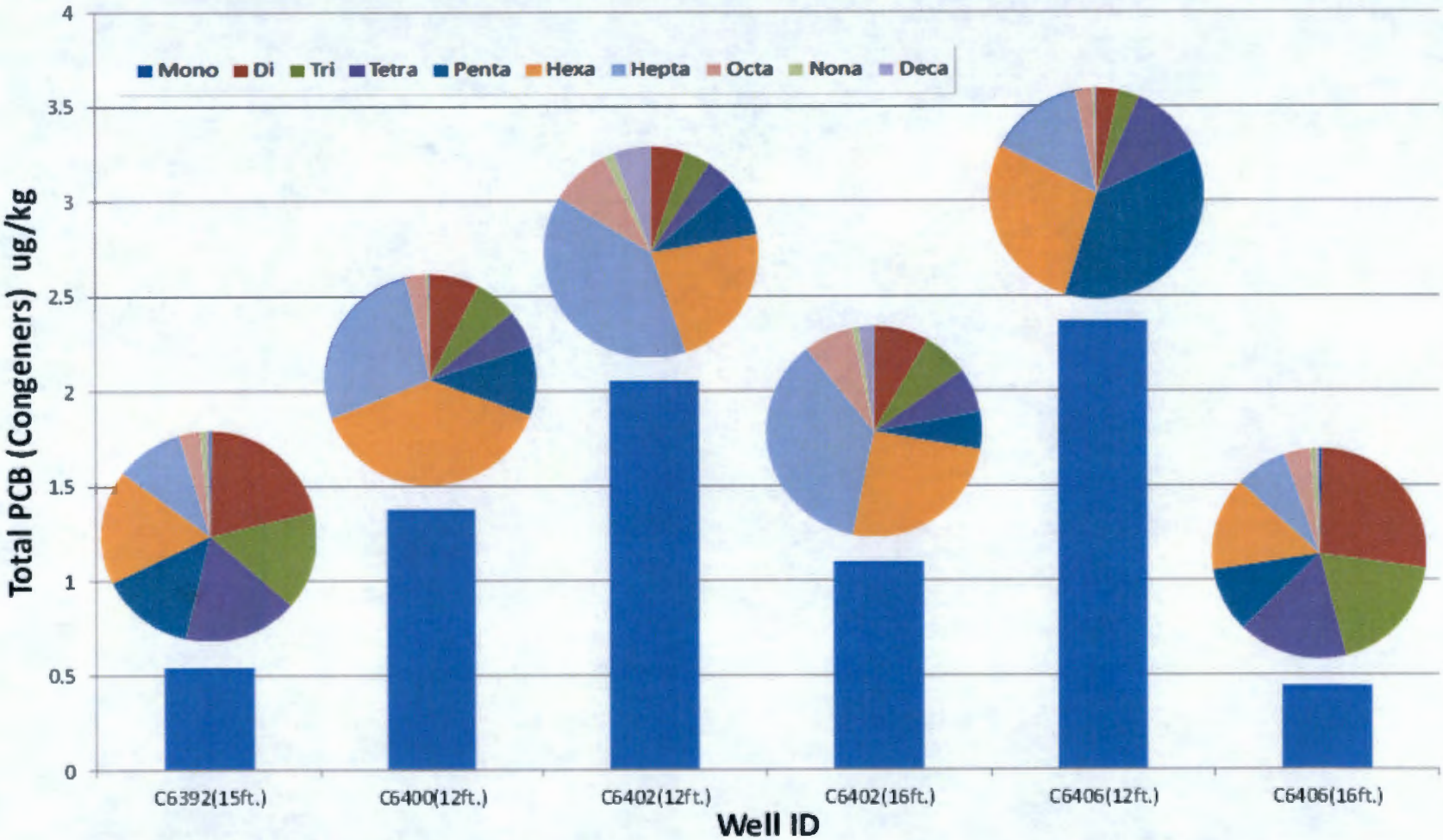


Figure 4-14. Homolog Distribution Comparison to Total Polychlorinated Biphenyl (Congener) in Soils Collected from 3.7 to 4.9 Meters at Site P at Waste Management Area C (Detects only Summed).

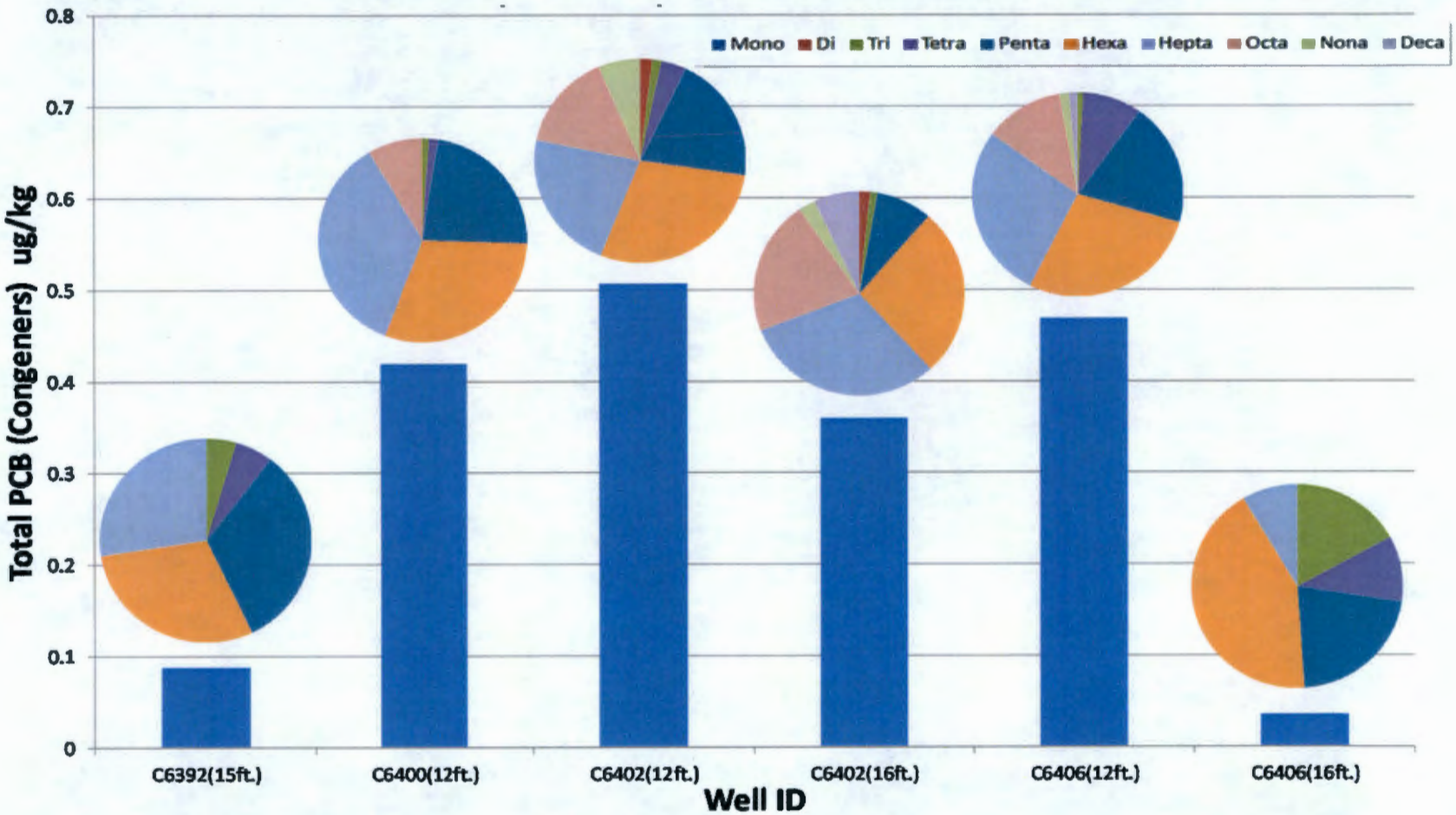
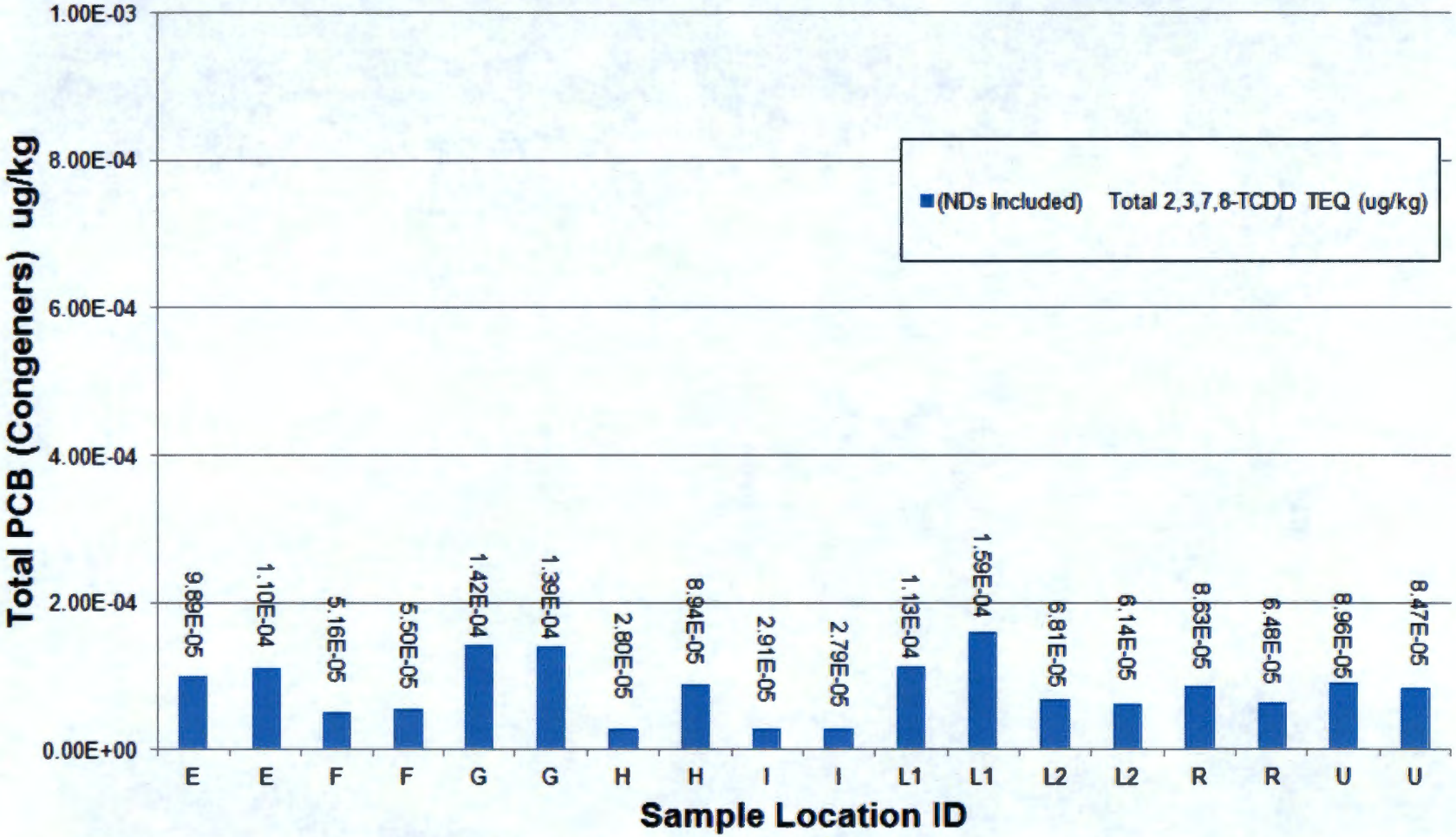
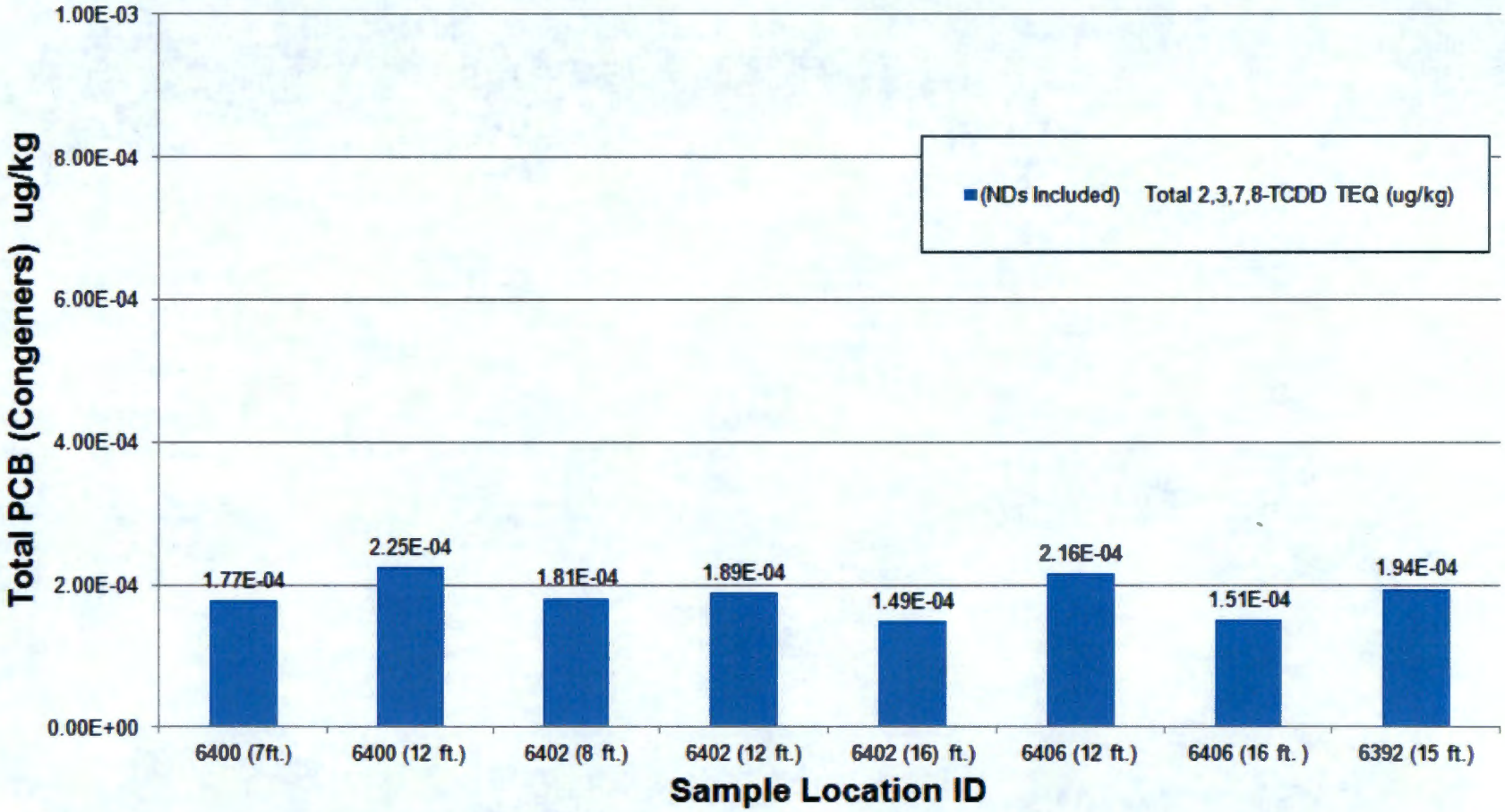


Figure 4-15. Samples #1 and #2 Total Calculated Upper Bound 2,3,7,8-TCDD Toxic Equivalence for Soils Collected from 0.0 to 0.3 Meters at Selected Sample Locations at Waste Management Area C.



ND = Non-detect TEQ = toxicity equivalent

Figure 4-16. Total Calculated Upper Bound 2,3,7,8-TCDD Toxic Equivalence for Soils Collected from 2.1 to 4.9 Meters at Selected Sample Locations near Site P at Waste Management Area C.



ND = Non-detect TEQ = toxicity equivalent

Table 4-1. Total Calculated 2,3,7,8-TCDD Toxic Equivalence by Sample Locations at Waste Management Area C.

Sample Location	Depth (m)	HEIS ID	(Non-Detects Excluded) Total 2,3,7,8-TCDD Toxicity Equivalent (ug/kg)	(Non-Detects Included) Total 2,3,7,8-TCDD Toxicity Equivalent (ug/kg)
E	0.3	B26JK2	9.85E-05	9.89E-05
E	0.3	B26JK3	1.04E-04	1.10E-04
F	0.3	B236N5	2.79E-06	5.16E-05
F	0	B236N8	2.58E-06	5.50E-05
G	0.3	B215L0	2.89E-06	1.42E-04
G	0.3	B215L1	2.71E-07	1.39E-04
H	0.3	B26JK8	9.02E-06	2.80E-05
H	0.3	B26JK9	8.81E-05	8.94E-05
I	0.3	B26JL0	7.62E-08	2.91E-05
I	0.3	B26JL1	1.56E-07	2.79E-05
L1	0.3	B215K8	1.44E-07	1.13E-04
L1	0.3	B215K9	6.34E-06	1.59E-04
L2	0.3	B23KN7	5.14E-05	6.81E-05
L2	0.3	B23R25	1.80E-06	6.14E-05
R	0.3	B23TK2	9.81E-06	8.63E-05
R	0.3	B23TK5	8.91E-06	6.48E-05
U	0.3	B26JK6	1.01E-05	8.96E-05
U	0.3	B26JK7	7.21E-06	8.47E-05

HEIS ID = Hanford Environmental Information System identification number

Table 4-2. Comparison of Detected Aroclors and Total Polychlorinated Biphenyl (Congener) Value at Selected Sample Locations at Waste Management Area C.

Site Location	HEIS Number	Well Name	Analyte Name	Depth	Value Reported	Minimum Detection Limit	Units	Total Congener Value
A	B2B1L9	C8102	Aroclor-1254	1.3 cm	6.46	6.02	ug/kg	
B	B2FPF1	C8104	Aroclor-1254	0.23 m	8.59	6.06	ug/kg	
B	B2FPF2	C8104	Aroclor-1254	0.23 m	8.33	5.95	ug/kg	
G	B211Y6	C7468	Aroclor-1260	3.35 m	20.6	18.9	ug/kg	0.42
P	B1YTH3	C6400	Aroclor-1260	3.35 m	25.2	20.2	ug/kg	1.38
P	B20XV9	C6402	Aroclor-1260	3.35 m	26.8	19.3	ug/kg	2.05

HEIS = Hanford Environmental Information System

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5.0 SUMMARY AND CONCLUSIONS

Soil samples were obtained and analyzed for PCB congeners at selected shallow (0 to 5.5 m) depths from 10 of 13 direct push soil sampling locations in the vicinity of tanks and selected ancillary equipment within WMA C. These direct push soil samples were collected under the WMA C RFI Phase 2 work plan (RPP-PLAN-39114) and Phase 2 SAP (RPP-PLAN-38777).

Results of the assessment showed that total PCB congeners for all sampled sites ranged from 0.06 µg/kg to 2.6 µg/kg over the depths sampled. The shallow (0 to 0.3 m) sampling at all except Site P showed the highest concentrations ranging from 0.18 µg/kg to 2.1 µg/kg, with the highest value coming from Site R.

Results of total PCB congeners ranged from 0.4 µg/kg to 2.6 µg/kg over the depths sampled for Site P near UPR 82. Concentrations in samples taken between 2.1 to 2.4 m had a slightly higher range compared to the deeper samples, ranging from 1.2 µg/kg to 2.6 µg/kg, with the highest concentrations coming from direct push site C6400 near Site P at 2.1 m.

Results of of the PCB congener analytical results from the shallowest samples (0 to 0.3 m) were also used to calculate a total 2,3,7,8-TCDD TEQ to evaluate the potential health risk associated with these constituents of concern. The results of these calculations were evaluated and were found to be many times lower than the 2007 MTCA Method B soil direct contact cleanup value for total PCBs of 0.5 mg/kg.

Based on review of these PCB congener analytical results, plans for continued RFI Phase 2 sampling and analysis were reevaluated and a recommendation was made to eliminate analysis of PCB congeners in further WMA C sampling activities, but continue to perform analyses of PCB Aroclors [Letter 11-TPD-020, "Organic Analyses Optimization for Waste Management Area (WMA) C"]. This recommendation was approved by Ecology [Letter 11-NWP-053, "Re: Organic Analyses Optimization for Waste Management Area (WMA) C"] and recommended changes for elimination of PCB congener analyses were incorporated in the work plan (RPP-PLAN-39114) and SAP (RPP-PLAN-38777).

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6.0 REFERENCES

11-NWP-053, 2011, "Re: Organic Analyses Optimization for Waste Management Area (WMA) C" (letter from J. J. Lyon to R. W. Lober, U.S. Department of Energy, Office of River Protection, June 1), State of Washington Department of Ecology, Richland, Washington.

11-TPD-020, 2011, "Organic Analyses Optimization for Waste Management Area (WMA) C" (letter from T. W. Fletcher to J. J. Lyon, State of Washington Department of Ecology, March 23), U.S. Department of Energy, Office of River Protection, Richland, Washington.

Abramowicz, D. A., 1995, "Aerobic and anaerobic PCB biodegradation in the environment," *Environmental Health Perspectives*, Vol. 103 (Suppl 5), pp. 97–99.

Alcock, R. E., C. J. Halsall, C. A. Harris, A. E. Johnston, W. A. Lead, G. Sanders, and K. C. Jones, 1994, "Contamination of Environmental Samples Prepared for PCB Analysis," *Environmental Science and Technology*, Vol. 28, pp. 1828–1842.

ATSDR, 2000, *Toxicological Profile for Polychlorinated Biphenyls (PCBs)*, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia. (http://www.astdr.cdc.gov/toxprofiles/tp17.pdf)

Ballschmiter, K. and M. Zell, 1980, "Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography," *Fresenius Zeitschrift für Analytische Chemie*, Vol. 302, pp. 20–31.

Clean Water Act of 1972, 33 USC 1251 et seq.

Eckhardt, S., K. Breivik, S. Mano, and A. Stohl, 2007, "Record high peaks in PCB concentrations in the Arctic atmosphere due to long-range transport of biomass burning emissions," *Atmospheric Chemistry and Physics*, Vol. 7, pp. 4527–4536.

Ecology, 2007, *Evaluating the Toxicity and Assessing the Carcinogenic Risk of Environmental Mixtures Using Toxicity Equivalency Factors*, State of Washington Department of Ecology, Olympia, Washington.

Ecology, EPA, and DOE, 2000, *Framework Agreement for Management of Polychlorinated Biphenyls (PCBs) in Hanford Tank Waste*, State of Washington State Department of Ecology, U.S. Environmental Protection Agency, U.S. Department of Energy, Richland, Washington.

EPA, 1996, "Method 8082. Polychlorinated Biphenyls (PCBs) by Gas Chromatography," Rev. 0. Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods. EPA SW-846, Third Ed., 8000 series, pp. 8082-1 – 8082-42. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

EPA, 2000, *Hudson River PCBs Reassessment RI/FS Phase 3 Report: Feasibility Study*, TAMS Consultants, Inc. for U.S. Environmental Protection Agency, Region 2 and U.S. Army Corps of Engineers , Kansas City District.

EPA-440/4-79-029a, 1979, *Water-Related Environmental Fate of 129 Priority Pollutants, Volume I: Introduction and Technical Background, Metals and Inorganics, Pesticides and PCBs*, Office of Water Planning and Standards, Office of Water and Waste Management, U.S. Environmental Protection Agency, Washington, D.C.

EPA-440/4-79-029b, 1979, *Water-Related Environmental Fate of 129 Priority Pollutants, Volume II: Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, Miscellaneous Compounds*, Office of Water Planning and Standards, Office of Water and Waste Management, U.S. Environmental Protection Agency, Washington, D.C.

EPA-821-R-07-004, 2003, *Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*, U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Washington, D.C.

HNF-EP-0182, 2014, *Waste Tank Summary Report for Month Ending July 31, 2014*, Rev. 319, Washington River Protection Solutions, LLC, Richland, Washington.

Mackay, D., W. Y. Shiu, and K. C. Ma, 1992, *Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals, Volume 1: Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*, Lewis Publishers, Chelsea, Michigan.

McFarland, V.A. and J. U. Clark, 1989, "Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: considerations for a congener- specific analysis," *Environmental Health Perspectives*, Vol. 81, pp. 225–239.

RCW 70.105D, "Hazardous Waste Cleanup — Model Toxics Control Act," *Revised Code of Washington*, as amended.

RPP-6693, 2002, *Fiscal Year 2003 PCB Characterization Plan for Tank Farm Waste*, Rev. 3, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-6993, 2003, *Fiscal Year 2004 PCB Characterization Plan for Tank Farm Waste*, Rev. 4, CH2M HILL Hanford Group, Inc., Richland, Washington.

RPP-PLAN-38777, 2012, *Sampling and Analysis Plan for Phase 2 Characterization of Vadose Zone Soil in Waste Management Area C*, Rev. 3, Washington River Protection Solutions, LLC, Richland, Washington.

RPP-PLAN-39114, 2012, *Phase 2 RCRA Facility Investigation/Corrective Measures Study Work Plan for Waste Management Area C*, Rev. 2, Washington River Protection Solutions, LLC, Richland, Washington.

Safe, S. H., 1994, "Polychlorinated Biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment," *Critical Reviews in Toxicology*, Vol. 24, Issue 2, pp. 87–149.

Van den Berg, M., L. Birnbaum, A. T. C. Bosveld, B. Brunstrom, P. Cook, M. Feeley, J. P. Giesy, A. Hanberg, R. Hasegawa, S. W. Kennedy, T. Kubiak, J. C. Larsen, F. X. Rolaf van Leeowen, A.K. Djien Liem, C. Nolt, R. E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, and T. Zacharewsk, 1998, "Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife," Environmental Health Perspectives, Vol. 106, pp. 775–792.

Van den Berg, M., L. S. Birnbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker, and R. E. Petersonq, 2006, "The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds," *Toxicological Sciences*, Vol. 93, pp. 223–241.

WAC 173-340-708, "Human Health Risk Assessment Procedures," *Washington Administrative Code*, as amended.

WAC 173-340-740, "Unrestricted Land Use Soil Cleanup Standards," *Washington Administrative Code*, as amended.

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