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Phytoremediation of airborne polychlorinated biphenyls

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PHYTOREMEDIATION OF AIRBORNE POLYCHLORINATED BIPHENYLS

by

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CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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INTRODUCTION AND OBJECTIVES

1.1 Background

Polychlorinated biphenyls (PCBs) are a group of 209 compounds known as congeners, each with different numbers and configurations of chlorine atoms substituted on a biphenyl moiety. The positioning and number of chlorines results in varying physical and chemical properties. PCBs are useful in several applications including dielectric fluids for transformers and plasticizers, flame retardants, and adhesives (Giesy and Kannan 1998). Properties such as inflammability and high chemical stability that contribute to their usefulness in industrial applications are the same properties that cause them to be persistent environmental pollutants (Beyer and Biziuk 2009).

PCBs were manufactured from the beginning of 1929 until the mid-1970s when their production was banned in the United States. Although their production has ceased, PCBs continue to contaminate the environment including air, soil, water, and biota (Beyer and Biziuk 2009). This poses a threat to the environment and human beings.

PCBs are listed as a Persistent Organic Pollutant (POP) by the Stockholm Convention. Classification for POPs is based on characteristics such as: widespread distribution in the environment as a result of natural processes involving soil, water, and air; accumulation in fatty tissues of living organisms and bioaccumulation in the food chain; and toxic to humans and wildlife (UNEP 2001). This international treaty is in place in order to reduce or eliminate the production and use of these harmful chemical substances.

1.2 Iowa Superfund Research Program- Project 5

The research for this project is part of Project 5 of the Iowa Superfund Research Program. Aim 3 of the project is to test the ability of plants to phytoremediate PCB congeners from the air and other airborne sources such as dredged sediments at the planned Confined Disposal Facility in East Chicago. The focus of the research is on higher chlorinated congeners that are typically found in Chicago air. Higher chlorinated congeners are known to have high toxicity and are persistent in the environment.

1.3 PCB Structure

PCBs are comprised of two benzene rings with a bond linking the carbon located in the carbon 1 position of the first ring with the carbon in the 1' position of the second ring. PCBs are classified based on the number of chlorines attached to the ring. Chlorines attach to the structure by replacing a hydrogen atom. A PCB molecule with a single chlorine molecule attached is classified as a monochlorobiphenyl, a PCB molecule with two chlorines attached is classified as a dichlorobiphenyl, and so forth. The classification scheme of PCB congeners can be seen in Table 1-1 (Ballschmiter and Zell 1980).

The location of the chlorine atom can be identified by the following: ortho, meta, or para. Chlorines that are located on carbons in the 2, 2', 6, or 6' position are in the ortho position, those in the 3, 3', 5, or 5' position are in the meta position, and those in the 4 or 4' position are in the para position. Figure 1-1 shows the general chemical structure of PCBs including the numbering and naming scheme.

PCB toxicity can be attributed to not only the number of chlorines present on the biphenyl ring, but the position as well. Congeners with a chlorine substitution at the para

positions and at least two meta position substitutions on the biphenyl ring, but no ortho substitutions are considered to be "dioxin like" and are the most toxic (McFarland and Clarke 1989).

The single carbon-carbon bond linking the two phenyl rings allows for unconstrained rotational freedom. Rotation about the bond has two configurations, planar and non-planar. In a planar configuration the two rings are in the same plane whereas in the non-planar configuration where the two rings are at a 90° angle to one another (ATSDR, 2000). A non-planar conformation is preferred for degradation of all PCBs because it minimizes steric interference of rotation about the bond that connects the two rings (McKinney and Singh 1981).

1.4 PCB Toxicity

Human exposure to PCBs can be attributed primarily to fish consumption from contaminated water bodies or inhalation of contamination in the air (Kimbrough 1987). The lipophilicity of PCBs contributes to the ability of PCBs to bioaccumulate and biomagnify in the food chain (Ritter, et al. 1995). This leads to accumulation of PCBs in the fatty tissues of humans (Roberston and Hansen 2001).

1.5 Physical-Chemical Properties of PCBs

Each individual congener has its own physical-chemical properties unique to its chemical configuration. These properties affect the environmental distribution and toxicity for each congener. Differences in the number of chlorines and their location result in differences in properties such as the octanol-air partition coefficient, solubility in water, Henry's Law constant, and vapor pressure. The physical-chemical properties of the PCBs of interest can be seen in Table 1-2.

The ease of movement across plant membranes is dependent on the lipophilicity of a chemical. The lipophilicity can be described as the balance between the affinity of a chemical for aqueous phases and that for lipid-like phases (Trapp and McFarland 1995). The octanol-water partition coefficient (K_{ow}) is used to assess the lipophilicity of a chemical.

Vapor pressure is a property that can be used to assess the volatility of a compound. Vapor pressure and solubility in water are both related to saturation and can be considered measurements of the maximum capacity that a phase has for dissolved chemical (Mackay, Shiu and Kuo 1997). With vapor pressure as the property related to solubility in air, these two properties can be used to describe air-water partitioning tendency as denoted by Henry's law constants. Henry's law explicitly stated is the solubility of a gas is directly proportional to the partial pressure of a gas above the solution (Silberber 2006). Henry's law constant is the ratio of the vapor pressure to its solubility in water.

In regard to PCBs, highly-chlorinated congeners are less water-soluble and less volatile than lower-chlorinated congeners (Mackova, et al. 2006). Volatility decreases with increasing chlorination, while lipophilicity increases with increasing chlorination (Loganathan and Kannan 1994). The behavior and presence of each congener is dependent on these physical-chemical properties.

1.6 PCBs in the Environment

PCBs were first detected in the environment in 1966 by Jensen (1966). Due to their high volatility and stability, PCBs have been largely dispersed by atmospheric transport (Van Aken, Correa and Schnoor 2009). PCB contamination is widespread and

can be found everywhere including both the Arctic and Antarctic (Risebrough, et al. 1976). Near contamination sites, a large fraction of higher-chlorinated congeners are present. This can be attributed to the volatility and biodegradability of lower-chlorinated congeners, which results in migration or biotransformation of these compounds (Mackova, et al. 2006). The highly chlorinated congeners that contaminate source areas degrade to lower-chlorinated congeners over time. Remote areas accumulate high contamination of lower-chlorinated congeners due to the mobility of these congeners, which allows them to be transported by atmospheric currents (Mackova, et al. 2006). As semi-volatile chemicals, they enter a cycle of repeated condensation onto cool surfaces such as plants and re-volatilization during warm, dry periods (Barber, Kurt, et al. 2002).

Due to the persistence of PCBs, only two natural processes of degradation are possible: photolysis and biodegradation (Hooper, Pettigrew and Sayler 2009). Microbial biodegradation is the only feasible natural eliminator of PCBs from the environment. Lesser chlorinated PCBs typically undergo aerobic degradation while anaerobic degradation is a more likely for higher chlorinated (four or more chlorine atoms) congeners (Borja, et al. 2005). High concentrations of PCBs and specific conditions are necessary in order for nature to eliminate PCBs from the environment (Lang 1992). Thus, remediation strategies are necessary in order to eliminate PCB contamination.

1.7 PCB Cycling

The ability of vegetation to scavenge PCBs from the air could be a contributing factor in buffering local air concentrations (Barber, Thomas, et al. 2004). A model of the 'Forest Filter Effect' shows the importance of vegetation in regard to filtering airborne organic pollutants from the atmosphere to the soil (McLachlan and Horstmann 1998).

High deposition velocities and large canopy densities of forests result in the large uptake of organic pollutants from the air. This reduces atmospheric concentrations and thus increases soil concentrations when leaves are deposited on the ground, increasing concentrations below the canopy (Barber, Thomas, et al. 2004). Predictions show that there is a dip in concentrations during the Spring while leaves are developing (Wania and McLachlan 2001).

1.8 Deposition of Gas-Phase Pollutants

PCBs undergo dry gaseous deposition as the primary mechanism of deposition (Thomas, et al. 1998). Deposition of gas-phase PCBs from the atmosphere involves movement through bulk air to the boundary layer surrounding to the leaf, transfer across the boundary layer to the leaf surface and partitioning into the plant (Barber, Thomas, et al. 2004). A model study showed that atmospheric uptake is the important pathway for chemicals with a log K_{oa} value greater than 6 and that for chemicals with a log K_{oa} value greater than 9 atmospheric uptake is dominated by particle-bound deposition (Cousins and Mackay 2000).

1.9 Leaf Anatomy

Plant leaves have an epidermis on both the upper and lower sides. Epidermal cells have a relatively thick waterproof cuticle on the atmospheric (upper) side that contains cutin (Nobel 2009). Cutin is a thin non-living lipid surface structure that serves as a barrier against water loss and pathogen invasion (Kerstiens 1996). The mesophyll tissue is contained between the two epidermal layers and is the leaf's primary photosynthetic tissue. The upper region of the mesophyll is the palisade mesophyll which consists of elongate cells that are oriented perpendicular to the epidermis and

found directly beneath it (Beck 2010). The spongy mesophyll is composed of irregularly shaped, loosely packed cells containing intercellular airspace is located beneath the palisade mesophyll layer. The lower epidermis contains the stomata, which is comprised of stomatal aperture and two enclosing guard cells. The aperture of the stomata fluctuates depending on factors such as light intensity, air humidity, or carbon dioxide concentration (Wilmer and Fricker 1996). Figure 1-2 is an illustration of the leaf cell structure.

1.10 Leaf Capture

Two pathways in parallel transfer PCBs into the leaf: uptake through the cuticle and uptake through the stomata. POPs are believed to enter the plant via the cuticle due to their high solubility in lipids (Riederer 1990). Riederer later created a model that showed the importance of the stomatal pathway increases with decreasing cuticle permeability (Trapp and McFarland 1995). The model predicts that in plants with a relatively impermeable cuticle, PCBs with a low log K_{oa} (e.g. PCB 18, 28, 52) may largely be taken up by the stomata, while higher log K_{oa} PCBs are not (e.g. PCB 153)and that plants with a very permeable cuticle will have nearly no stomatal uptake (Barber, Kurt, et al. 2002). The uptake pathway is largely variable depending on the permeability of the cuticle and the number of stomata and the congener's physical-chemical properties.

1.11 Vascular System

A plants vascular system is made up of two main components the xylem and the phloem. The vascular system is found within the roots, stems, and leaves of plants. Within the trunk of a tree, the phloem consists of a layer of the bark and the xylem constitutes nearly all the wood (Nobel 2009). The xylem is primarily responsible for the

movement of water and nutrients from the soil through the roots up toward the leaves (Nobel 2009). The phloem is responsible for the movement of most organic compounds throughout the plant.

1.12 Phloem Transport

The phloem is responsible for movement of solutes over long distances. Long-distance transport in the phloem occurs by mass flow, driven by differences in hydrostatic pressure in the direction of areas with lower osmotic pressure (Lambers, Chapin and Pons 2008). Movement in the phloem is generally in the downward direction, but has been shown to be bidirectional (Peterson and Currier 2006). In regard to lipophilic compounds such as PCBs, transport by the phloem is rarely observed (Simonich and Hites 1995).

1.13 Remediation Technologies for PCBs

Traditional remediation techniques to eliminate PCBs from contaminated sites require soil excavation and transport prior to off-site treatment by solvent extraction, thermal alkaline dechlorination, incineration or landfilling (Campanella, Bock and Schroder 2002). The removal of PCBs from sediments results in the volatilization of PCBs into the air. Airborne PCBs should be taken into more consideration since the atmosphere is the major route of exposure and transfer among other matrices such as water and sediment (Hansen 1999). The remediation of airborne PCBs has not been well studied. However, the use of vegetation as a biological monitor for PCB contamination has been studied (Dushenko, Grundy and Reimer 1996) (Gaggi, et al. 1985). Phytoremediation is a cost-effective, *in situ* treatment option to implement at sites that are contaminated with PCBs.

1.14 Phytoremediation

Phytoremediation is a form of bioremediation used to remediate contaminated soils and waters. Phytoremediation incorporates the use of plants to mitigate environmental pollutants without excavation of the contaminated material. Plants serve as solar-driven pumping and filtering systems as they take up water soluble contaminants through their roots and transport/translocate them through various plant tissues where they can be metabolized, sequestered or volatilized (McCutcheon and Schnoor 2003).

Plants use several different mechanisms for removal of environmental chemicals including: phytoextraction, phytoaccumulation, phytostabilization, phytotransformation, phytovolatilization, rhizodegradation, and air scavenging. Phytoextraction is the uptake of contaminants by plant tissues resulting in phytoaccumulation when the plant is unable to degrade the contaminant (Susarla, Medina and McCutcheon 2002). Plants that have undergone phytoaccumulation can be harvested and disposed of at an appropriate landfill. Phytostabilization reduces the mobility of contaminants and stabilizes them in the soil. Phytotransformation uses the plant and its associated microorganisms to degrade contaminants (Salt, Smith and Raskin 1998). Phytovolatilization involves the removal of a contaminant from soil or water by volatilizing the pollutant (Salt, Smith and Raskin 1998). Rhizodegradation is treatment that is enhanced by the microbial activity in the rhizosphere of plants (Susarla, Medina and McCutcheon 2002). Airborne contaminants can be uptaken by the leaves and bark of trees by air scavenging.

1.15 Phytoremediation of PCBs in Groundwater/Soil

Liu (2008) studied the fate of lesser-chlorinated PCBs in whole hybrid poplar trees. The experiment showed that PCBs were more likely to accumulate in the wood of

the plant rather than in the leaves. Lesser chlorinated congeners were translocated from the roots to the secondary stem while higher chlorinated congeners were bound to the roots and prevented from translocating. This behavior can be attributed to the hydrophobicity of each congener.

1.16 Phytoremediation of Airborne PCBs

Barber et al. (2002) studied the uptake of airborne PCBs by two slow-growing evergreen shrubs, *Skimma japonica* Thunb. and *Hebe*. *Skimma* plants are large leafed waxy plants with thick cuticles and *Hebe* plants are small leafed waxy plants. The first experiment compared the uptake of PCB 153 by both plant species under a constant airflow of 2 m/s. The experiment showed that uptake rates were higher in *Hebe* leaves than in *Skimma* leaves, which is likely due to variations in plant structure and morphology. The second experiment compared the short and long-term uptake of PCB 31 and PCB 18 under fanned and unfanned conditions. The results indicate a two-phase uptake, the first phase occurring within hours and the second continuing over days or weeks. The experiment also showed that uptake rate constants tend to increase in correlation to increased chlorination.

1.17 Objectives

The overall objective of the research project is to determine if poplar trees can effectively reduce the amount of airborne transfer of PCBs from nearby sources to receptors, thus preventing human exposure. The objectives can be more specifically defined as the following:

1) Determine the amount of PCBs that volatilize into an experimental exposure system of poplar plants

2) Determine the amount of semi-volatile PCBs that the plant can scavenge from the air onto the leaves from a specific congener mix based on a range of physical-chemical properties
3) Determine if translocation occurs downward from the leaves into the roots
4) Develop a mass balance for the entire exposure system
5) Using GC-ECD, determine if the plant produces any detectable metabolites from the specific congener mix of parent compounds

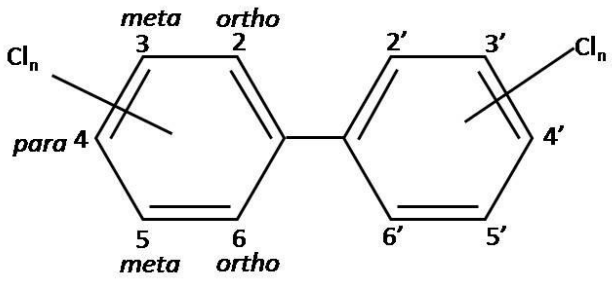

Figure 1-1. General PCB Structure

Table 1-1. PCB Congener Classification

Classification	Molecular Formula	Congers of Interest
Monochlorobiphenyls	$C_{12}H_9Cl$	PCB-3
Dichlorobiphenyls	$C_{12}H_8Cl_2$	PCB-15
Trichlorobiphenyls	$C_{12}H_7Cl_3$	PCB-28
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	PCB-52 & PCB-77
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	-
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	PCB-153
Heptacholobiphenyls	$C_{12}H_3Cl_7$	-
Octachlorobiphenyls	$C_{12}H_2Cl_8$	-
Nonachlorobiphenyls	$C_{12}HCl_9$	-
Decachlorobiphenyls	$C_{12}Cl_{10}$	-

Table 1-2. Physical-Chemical Parameters for selected PCB congeners

IUPAC No.	Molecular Weight (g/mol)	log K_{ow} [a]	log K_{oa} [b]	-log (mol/L) Solubility in water at 25 °C [c]	-log HLC ($atm \cdot m^3/mol$) at 25 °C [d]	Vapor Pressure $\times 10^7$ (atm) at 25 °C [e]
PCB 3	188.65	4.69	6.64	5.14-5.39	3.56	26-227
PCB 15	223.1	5.3	7.34	6.61-6.79	3.64	0.18-59.2
PCB 28	257.54	5.67	7.6	6.34	3.54	0.29-19.7
PCB 52	291.99	5.84	7.72	6.43	3.5	0.0058-6.4
PCB 77	291.99	6.36	8.74	8.73	3.99	0.0058-6.4
PCB 153	360.88	6.92	9.09	8.62	3.78	0.0019-0.5

[a] (Hawker and Connell 1988)

[b] calculated from log K_{ow} values (Hawker and Connell 1988)

[c,d] (Dunnivant and Elzerman 1992)

[e] (Dickerson and Korte 1994)

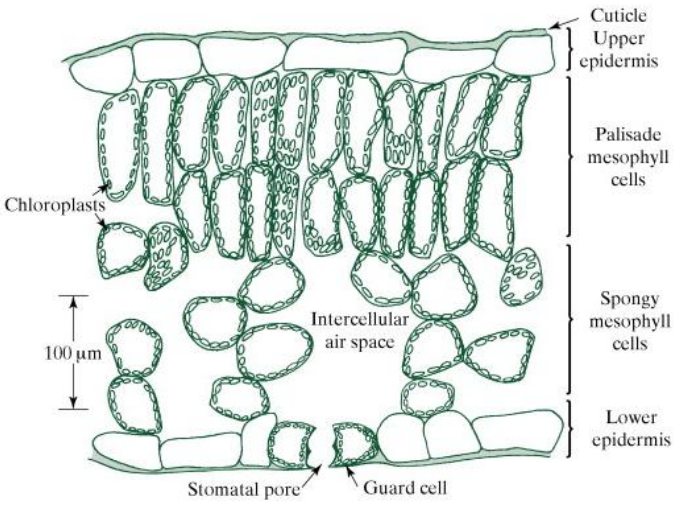

Figure 1-2. Traverse section through a leaf, indicating the arrangement of various cell types (Nobel 2009)

CHAPTER 2
PHYTOREMEDIATION OF AIRBORNE POLYCHLORINATED BIPHENYLS

2.1 Introduction

Studies have shown that PCB congeners are present in the air or can become airborne due to dredging of contaminated sediments. Based on the work of Project 4 of the Iowa Superfund Basic Research Program, congeners of interest were selected that represent a range of physical-chemical properties that were found in Chicago air. Phytoremediation could be used a cost-effective solution for in situ remediation of these contaminants to reduce the exposure to humans and the environment.

The purpose of this project is to determine if PCBs can be scavenged from the air by the leaves of poplar trees and what happens to the PCBs within the plant. Previous studies have shown that poplar trees make ideal candidates for the uptake and remediation of PCB congeners at dredged material sites where exposure to PCBs is through slurry-mixtures in the root system (Liu and Schnoor 2008). The results of this project could be used to further the use of poplar trees for remediation of PCBs in the air from nearby sources.

2.2 Experimental Setup

2.2.1 Exposure Setup

Cuttings (8-inch) of DN-34 hybrids of poplar trees (*Populus deltoids* × *nigra)* were obtained from Hramor Nursery in Manistee, Michigan. The cuttings were grown hydroponically using half strength Hoagland's nutrient solution adjusted to pH 6.8 using

1.0 M NaOH (Epstein 1972) under growth lamps in the laboratory. Live plants were grown for 30 days in hydroponic solution. Dead plants were dried for 20 days prior to exposure. For exposure, cuttings were placed in individual screw-topped 500 mL flasks with two sampling ports. Cuttings were fitted with pre-drilled screw caps and sealed with silicone sealant to eliminate the transfer of PCBs between the two flasks. The lower flask was wrapped in aluminum foil and filled with 400 grams of half strength Hoagland's solution. The upper flask was inverted to enclose the upper half of the plant. A closed system was designed to allow for mass balance analysis.

Compressed air was blown into a small screw-capped vial containing solid PCB standards, which was connected to the top flask via an L-shaped glass tube. The exit port of the top flask was fitted with a column containing XAD-2 resin. The exposure setup for the experiment can be seen in Figure 2-1 and Figure 2-2. The entire exposure system was enclosed in a fume hood equipped with fluorescent growth lights on a 16 hour day and 8 hour night cycle. The lower flask was weighed daily and deionized water was added in order to replenish water lost due to transpiration. Transpiration rates during the exposure ranged from 2-5 mL/day.

2.3 Materials and Methods

2.3.1 Chemicals and Materials

Six congeners were selected for exposure including: PCB 3 (4-monochlorobiphenyl), PCB 15 (4,4'-dichlorobiphenyl), PCB 28 (2,4,4'-trichlorobiphenyl), PCB 52 (2,2',5,5'-tetrachlorobiphenyl), PCB 77 (3,3',4,4'-tetrachlorbiphenyl), and PCB 153(2,2',4,4',5,5'-hexachlorobiphenyl). All solid PCB standards were purchased from AccuStandard©, Inc. (New Haven, CT) and were 99.5%

pure or higher. PCB 14 (3,5-dichlorobiphenyl), PCB 65 (2,3,5,6-tetrachlorobiphenyl), and PCB 166 (2,3,4,4',5,6- hexachlorobiphenyl) were selected as surrogate standards and PCB 204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) was selected as internal standard for analysis. Acetone was purchase from Sigma Aldrich. Methyl-tert butyl ether (MTBE) and hexane were purchased from Fisher Scientific.

Amberlite® XAD-2 polymeric adsorbent was purchased from Sigma-Aldrich. Hexane, acetone, methanol, dichloromethane used for XAD purposes were pesticide grade. These solvents were all purchased from Fisher Scientific.

2.3.2 PCB Exposure

Solid PCB standards were placed inside a small screw-capped vial with varying masses for each exposure. For the first two exposures, all six congeners were placed into a single vial. The live sample vial for Exposure 1 was filled with 500 µg of PCB 3, 3000 µg of PCB 15, 200 µg of PCB 28, 100 µg PCB 52, 100 µg PCB 77, and 100 µg of PCB 153. A duplicate live experiment was run for Exposure 1. The vial for the duplicate experiment for Exposure 1 was filled with 400 µg of PCB 3, 300 µg of PCB 15, 300 µg of PCB 28, 200 µg PCB 52, 100 µg PCB 77, and 100 µg of PCB 153. The dead sample vial for Exposure 1 was filled with 500 µg of PCB 3, 300 µg of PCB 15, 300 µg of PCB 28, 100 µg PCB 52, 200 µg PCB 77, and 100 µg of PCB 153. Both the live and dead sample vials for Exposure 2 contained 500 µg of PCB 3, 300 µg of PCB 15, 200 µg of PCB 28, 100 µg PCB 52, 200 µg PCB 77, and 100 µg of PCB 153. For Exposure 3, only one congener was placed in each vial. The first vial contained 500 µg of PCB 3 and the second contained 100 µg of PCB 77. PCBs were blown into the upper flask of the system at 100 mL/min during exposure. Based on the volume of the flask and the air flow rate,

the residence time of the air in the upper flask is 5 min. The duration of each exposure lasted for a total of 10 days.

2.3.3 XAD Cleaning

The XAD-2 resin was precleaned prior to its use in order to remove any trace PCBs or other contamination. A 24-h Soxhlet extraction was performed with methanol, acetone, hexane, and 50/50 hexane/acetone prior to sampling (Peck and Hornbuckle 2005). The cleaned XAD-2 resin was stored in amber glass containers until it was used for exposure.

2.3.4 Sampling

Plant samples were separated into the following components: leaves, secondary stem, upper bark, lower bark, upper wood, lower wood, and roots. The upper half consist of the section enclosed in the top flask and the lower half consists of the section within the lower flask that is immersed in solution. Extraction occurred immediately after the exposure was complete.

All samples were weighed and cut into separate sections. The leaves and roots were ground with a mortar and pestle in liquid nitrogen. The other plant samples were cut into small pieces using stainless steel blades and scissors. In order to minimize the amount of cross-contamination, all tools were rinsed with reagent-grade acetone in between samples.

2.3.5 PCB Extraction from XAD-2 Resin

PCBs were extracted from the XAD cartridge using Accelerated Solvent Extraction (ASE 300, Dionex, Sunnyvale, CA) using a method described by Hu et al.

(Hu, Martinez and Hornbuckle 2008). Samples were extracted with acetone/hexane (1:1, *v:v*). Prior to extraction samples were spiked with surrogate standards PCB 14, PCB 65, and PCB 166. The resulting extracts were further reduced to approximately 500 µL by a Turbovap workstation (Martinez Araneda 2010). The samples were transferred to a column with 0.1 gram activated silica gel and 1 gram of acid silica gel and injected with internal standard PCB 204 prior to analysis.

2.3.6 PCB Extraction from Solution

The extraction and cleanup of PCBs from solution was performed using the methods described by Liu and Schnoor (2008). Surrogate standards (PCB 14, PCB 65, and PCB 166) were added to all samples prior to extraction. In order to extract PCBs from the hydroponic solution, 50 mL of hexane/MTBE (1:1 *v/v*) was poured into the reactor and shaken overnight. A second extraction was performed with an additional 50 mL of hexane/MTBE (1:1 *v/v*) and shaken for 30 minutes. The combined 100 mL of extract was concentrated by rotary evaporation at 40 °C to approximately 1 mL. Approximately 1 mL of concentrated H_2SO_4 was used to partition the extract in order to remove proteins, lipids, and trace water. The extract was then centrifuged for 5 minutes at 3000 rpm and the organic phase was separated and combined with internal standard (PCB 204) for GC analysis.

2.3.7 PCB Extraction from Poplar

Extraction of PCBs from plant tissue was performed using the methods described by Liu and Schnoor (2008). Prior to extraction, surrogate standards (PCB 14, PCB 65, and PCB 166) were added to all the samples. In order to extract PCBs from the plant tissue, approximately 5 mL of hexane/acetone (1:1 *v/v*) g^{-1} of sample was added and

shaken overnight. A second extraction was performed with an additional 5 mL of hexane g^{-1} of sample and shaken for 30 minutes. The combined extract was concentrated by rotary evaporation at 40 ℃ to approximately 1 mL. The extract was then treated with 1 mL of concentrated H_2SO_4 and centrifuged for 5 minutes at 3000 rpm. The organic phase was transferred and an additional 1 mL of hexane was added to the acidic phase and centrifuged again. The combined organic phase was transferred to a column with 0.1 gram activated silica gel and 1 gram of acid silica gel. The extract was eluted with 10 mL of hexane after column extraction. The extract was concentrated and mixed with internal standard (PCB 204) for GC analysis.

2.3.8 Chemical Analysis

The following analysis was performed as described by Liu (2008). Analysis of all extractions was performed using an Agilent 6890 gas chromatography equipped with ^{63}Ni electron capture detector (GC/μECD) and an autosampling device.

The GC-ECD was operated as follows: injection port, 250 ℃ with splitless mode; high purity of helium carrier gas at 1 mL min^{-1} constant flow rate; detector, 300 ℃; 95% argon and 5% methane make-up gas at 60 mL min^{-1} flow rate. The oven program was set for 2 min at 70 ℃, first ramp at 10 ℃ min^{-1} to 200 ℃ (17 min hold), second ramp at 3 ℃ min^{-1} to 260 ℃ (25 min hold), and post run for 5 min at 300 ℃. Peaks were identified by comparing retention times with standards. To ensure quality control the surrogate standard peak was identified and analyzed.

2.4 Previous Results and Discussion

2.4.1 Results from (Liu 2008)

Unpublished data from the same laboratory exists that were included as part of an effort in the interest of satisfying the objects set forth for this project. The results from this work are shown in Table 2-1 and Table 2-2. Based on the octanol-air partition coefficient, it is expected that PCB 15, PCB 28, and PCB 52 will behave similarly while PCB 3 will be more volatile than these compounds and PCB 77 and PCB 153 less volatile. According to Liu's results, nearly all the PCB 3 (>99.5%), over 98% of PCB 15 and 28, 65% of PCB 52, and no more than 10% of PCB 77 were blown into the upper flask.

The results show that most significant amount (76% of the mass applied) of PCB 3 was found in the XAD-2 cartridge. Due to its high volatility, PCB 3 did not effectively sorb to the plant leaves and was blown through the system to the cartridge. The amount of PCB 15, 28, and 52 found in the XAD cartridge ranged from 19-23% of the mass applied, confirming that these three compounds have similar volatilities to one another. The amount of PCB 77 applied found on the cartridge was not-detectable.

The leaves of all the live samples were able to capture all five congeners. In general, the higher the congener number the higher the capturing efficiency. Only 3.4 percent of the mass applied of PCB 3 was found in the leaves. Similar amounts of PCB 15 and 28 were captured, 51 and 58 percent of the mass applied, respectively. The leaves were able to capture 68 percent of the mass applied of PCB 52 and 67.4 percent of the mass applied of PCB 77.

The mass of PCBs decreased throughout the plant moving downward. The percentages found in the upper bark were higher for all congeners than that found in the upper wood. Only 1.9 percent of the mass applied of PCB 3 was retained in the upper bark. There was higher retention of PCB 15, 28, and 52 in the upper bark with 11, 9.5, and 6.7 percent of the mass applied, respectively. The percentages of the mass applied were found to be 0.40, 1.0, 1.0, 0.97, and 0.87% for PCB 3, 15, 28, 52, and 77, respectively.

The lower wood tended to have higher retention than that in the lower bark for all congeners except for PCB 3, which had the highest retention in the lower bark compared to all other congeners (0.021 percent of the mass applied). The lower bark contained only 0.0021 and 0.0025 percent of the mass applied of PCB 28 and 52, respectively. PCB 15 and 77 were found to be not-detectable in the lower bark. The lower wood contained 0.018, 0.069, 0.056, 0.033, 0.036 percent of the mass applied of PCB 3, 15, 28, 52, and 77, respectively.

For the dead controls, the same trends were found on the XAD cartridge. The highest percentage of the mass applied (61%) of PCB 3 was found on the XAD cartridge. The percent of the mass applied ranged from 40 to 48% for PCB 15, 28, and 52. Only 17 percent of the mass applied of PCB 77 was found on the XAD cartridge.

Compared to the live trees all the dead samples had lower percentages for all congeners found in the leaves. PCB 3 was captured the least efficiently, with only 7.9 percent of the mass applied retained. The percent of the mass applied for PCB 15, 28, and 52 were 25, 28, and 28%, respectively. PCB 77 was captured on the leaves the most efficiently, with 52 percent of the mass applied retained on the leaves.

For the dead trees, detections were found for all congeners in the upper bark but not in the upper wood. The only detectable congener in the upper wood was PCB 28 (0.047 percent of the mass applied). The upper bark retained 5.4 percent of the mass applied of PCB 3. There was 11 percent of the mass applied found in the top bark for PCB 15 and 28. There was 7.9 and 1.5 percent of the mass applied of PCB 52 and 77 found in the top bark, respectively.

Significantly lower masses of all congeners were found in the bottom half, though a consistent trend was not found. There was 0.046, 0.37, 0.019, 0.014 percent of the mass applied of PCB 3, 15, 28, and 52 found in the lower bark for the dead sample, respectively. The lower wood contained 0.0033, 0.0097, 0.025, 0.019 percent of the mass applied of PCB 3, 15, 28, and 52, respectively. PCB 77 was not detectable in the lower bark or lower wood.

2.4.2 Discussion of (Liu 2008)

Based on the octanol-air partition coefficient, it is expected that PCB 15, PCB 28, and PCB 52 will behave similarly while PCB 3 will be more volatile than these compounds and PCB 77 less volatile. This is consistent with the results for all congeners aside from PCB 52, which only had 65% of the mass applied reach the upper flask while PCB 15 and 28 had over 98% of the mass applied reach the upper flask.

Due to its high volatility, PCB 3 did not effectively sorb to the plant leaves and was blown through the system to the cartridge. Over 50% of PCB 15, 28, 52, and 77 that entered the flask interacted with the poplar. Of the percent applied that interacted with the poplar, a majority of the mass was retained in the leaves.

The leaves of both the live and dead trees were able to capture PCBs. In nearly all cases, the live trees were able to capture higher quantities of all the applied congeners compared to the dead trees. This can likely be attributed to the fact that the waxy layer of the dead leaves is damaged and that there is a smaller surface area available on the dead leaves to capture the PCBs.

The PCBs that were captured on the leaves were detected in nearly all regions of the remainder of the plant. Higher masses were found in the upper bark compared to the upper wood for all the congeners applied. The trend in the lower half of the tree was not as consistent. A higher mass of PCB 3 was found in the lower bark than the lower wood. For PCB 28 and 52, higher masses were found in the lower wood than in the lower bark. PCB 15 and 77 were not detected in the lower bark, but were detected in the lower wood.

The masses of all congeners found in the upper bark of the dead tree were of equal or higher masses for all congeners except for PCB 77. However, there were no detections in the upper wood of the dead tree except for PCB 28. A consistent trend is not present for the lower half of the dead tree. Higher mass percentages were found in the lower bark than in the lower wood for PCB 3 and 15. For PCB 28 and 52, the percent found in the lower wood was higher than that in the lower bark. There were no detections for PCB 77 in the lower bark or lower wood in the dead tree.

2.5 Results from this Research

2.5.1 Exposure 1

The PCB mass distribution for the congeners of interest throughout the various segments of the plant samples for the Exposure 1 system can be seen in Table 2-3. The leaves of both live samples were able to capture all six congeners to an extent. In

general, the mass of PCBs measured decreases throughout the plant in the downward direction from the leaves. The leaves of the live tree were able to capture 40.5, 22.6, 15.4, 88.3, 0.51, and 0.89 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. The secondary stem retained 2.1, 1.0, 0.51, 2.1, 0.025, and 0.036 µg of PCB 3, 15, 28, 52, 77, and 153, respectively.

The masses found in the upper bark were higher than that found in the upper wood for every congener. The masses of PCB 3, 15, 28, 52, 77, and 153 found in the upper bark were 25.1, 7.9, 4.0, 19.5, 0.57, 0.023, and 0.12 µg, respectively. The masses of PCB 3, 15, 28, 52, 77, and 153 found in the upper wood were 3.2, 0.65, 0.30, 1.54, 0.004, and 0.025 µg, respectively.

For the lower half of the tree, the trend was not consistent for all six congeners. The following masses were found in the lower bark 0.008, 0.025, 0.057, 0.092, 0.019, and 0.002 µg for PCB 3, 15, 28, 52, 77, and 153, respectively. The masses found in the lower wood were 0.027, 0.017, 0.066, 0.029, 0.006, and 0.001 for PCB 3, 15, 28, 52, 77, and 153, respectively. The roots were found to retain several of the higher chlorinated congeners, but no detections were found for PCB 3 or 15. The masses of PCB 28, 52, 77, and 153 were 0.002, 0.015, 0.008, and 0.001, respectively.

For the duplicate live sample, the leaves were able to also capture all six congeners. The trends were similar to those found in the other live sample, but the masses retained were not similar overall. The leaves for the duplicate sample were able to capture 47.6, 5.0, 16.4, 20.9, 0.020, and 0.072 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. The secondary stem retained 7.64, 1.8, 4.9, 2.1, 0.012, 0.051 µg of PCB 3, 15, 28, 52, 77, and 153, respectively.

The upper half of the duplicate sample consistently retained a higher mass of all six congeners in the upper bark compared to the upper wood. The upper bark contained 21.1, 4.7, 12.1, 16.7, 0.023, 0.096 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. There was 1.45, 0.072, 0.12, 0.12, 0.016, and 0.001 µg of PCB 3, 15, 28, 52, 77, and 153 found in the upper wood, respectively.

The lower half of the duplicate sample was also inconsistent when comparing the masses of the six congeners found in the lower bark and lower wood. The lower bark contained 0.75, 0.49, 0.15, 0.92, 0.006, and 0.010 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. PCB 3, 15, 28, 52, 77, and 153 were found in the lower wood with masses of 1.03, 0.20, 0.43, 0.79, 0.038, and 0.61 µg, respectively. There were also no detections for PCB 3 or 15 found in the roots of the duplicate sample. There were 0.006, 0.024, 0.015, and 0.003 µg of PCB 28, 52, 77, and 153 in the roots, respectively.

A consistent trend was not found with respect to the dead control. The leaves captured 14.8, 2.5, 7.6, 12.5, 0.049, and 0.10 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. There was no secondary stem sample for the dead plant. The mass for all six congeners retained in the upper wood was found to be higher than leaves. The upper bark contained 17.3, 4.6, 10.1, 13.5, 0.11, and 0.17 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. The upper wood had lower masses than the upper bark for all congeners except PCB 153. The masses retained in the upper wood for PCB 3, 15, 28, 52, 77, and 153 were found to be 1.1, 0.22, 0.52, 0.83, 0.025, 0.65 µg, respectively.

There was no consistent trend found in the lower half of the dead plant in regard to the lower bark and lower wood. The masses of PCB 3, 15, 28, 52, 77, and 153 retained in the lower bark were found to be 0.051, 0.065, 0.066, 0.11, and 0.002 µg,

respectively. The lower wood retained 0.11, 0.066, 0.24, 0.43, and 0.014 µg, for PCB 3, 15, 28, 52, and 153, respectively. There were no detections in the lower wood for PCB 77. The dead plant sample contained no roots.

Table 2-4 shows the PCB mass distribution for the non-plant compartments for the Exposure 1 system. The masses of PCB 3, 15, 28, 52, 77, and 153 that remained in the input vial for the live tree were 313.8, 1009.2, 268.4, 1073.7, 2.5, and 238.6 µg, respectively. There were no detections found in the solution for any of the PCB congeners. There were no detections in the upper flask for PCB 3 or 15. There were 0.030, 0.028, 0.030, and 0.015 µg of PCB 28, 52, 77, and 153 in the upper flask, respectively. The XAD-2 sample for the live tree was ruined during analysis.

The duplicate live sample inlet vial contained 2.3, 1382.9, 268.4, 890.7, 46.8, and 238.6 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. There were no detections in the solution of the live duplicate sample. There were also no detections of PCB 3 or 15 in the upper flask for the duplicate sample. There were 0.007, 0.008, 0.040, and 0.012 µg of PCB 28, 52, 77, and 153 found in the upper flask for the duplicate live sample, respectively. The XAD-2 cartridge retained 2725.3, 5053.3, 6.9, 31.8, 32.4, and 6.9 µg of PCB 3, 15, 28, 52, 77, and 153, respectively.

The inlet vial for the dead plant control contained 274.5, 950.3, 137.0, 791.5, 33.3, and 211.5 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. There were no detections in the solution of the dead plant sample. The upper flask sample for the dead plant was also ruined during analysis. The XAD-2 cartridge for the dead plant sample contained 583.9, 395.6, 488.9, 1155.0, and 7.9 µg of PCB 3, 15, 28, 52, 77, and 153, respectively.

Table 2-5 shows the mass balance calculations for the Exposure 1 system. Summations of the masses in the plant and non-plant compartments were used to determine the total mass of PCBs in the system. The initial mass added was used to determine the percent recovered from the system. The percent recovered from the live plant system for PCB 3, 15, 28, 52, 77, and 153 was 14.2, 10.7, 10.1, 111.6, 0.65, and 1.1%, respectively. The percent recovered from the live plant duplicate system was 701.2, 1688.5, 13.7, 38.0, 32.5, and 7.7% for PCB 3, 15, 28, 52, 77, and 153, respectively. There was 123.4, 134.4, 169.1, 1182.3, 20.3, and 8.8% recovered of PCB 3, 15, 28, 52, 77, and 153 from the dead plant system, respectively.

Figure 2-3, Figure 2-4, and Figure 2-5 show the distribution of PCBs throughout the plant measured in μg/g of plant sample for live plant sample, duplicate live plant sample, and dead plant sample, respectively. Figure 2-6 shows the mass of each congener retained on the leaves versus the log K_{oa} value for each.

2.5.2 Exposure 2

Table 2-6 shows the PCB mass distribution for the congeners of interest throughout the various segments of the plant samples for Exposure 2. Again, the live leaf sample was able to somewhat capture all six congeners. The mass of PCBs measured throughout the plant tends to decrease moving downward throughout the plant. The leaves of the live sample were able to capture 23.3, 31.4, 40.8, 144.4, 1.5, and 0.88 μg of PCB 3, 15, 28, 52, 77, and 153, respectively. The secondary stem retained smaller masses for each congener. The masses found in the secondary stem for PCB 3, 15, 28, 52, 77, and 153 were 5.4, 3.1, 3.1, 5.4, 0.23, and 0.070, respectively.

The upper bark of the live plant sample contained higher masses of all congeners except PCB 3 in comparison to the upper wood. The upper bark contained 4.3, 5.6, 6.5, 25.6, 0.22, and 0.13 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. There were 5.6, 3.1, 3.0, 9.7, 0.082, and 0.030 µg of PCB 3, 15, 28, 52, 77, and 153 found in the upper wood, respectively.

Comparisons for the lower half of the live plant sample could not be made since the lower bark sample was ruined before analysis. The lower wood contained 0.38, 0.049, 0.056, 0.011, 0.041, and 0.019 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. Detections were found in the roots for all samples except PCB 15. There were 0.071, 0.0097, 0.042, 0.020, and 0.013 µg of PCB 3, 28, 52, 77, and 153 found in the roots, respectively.

The leaf sample of the dead plant sample was also able to capture all six congeners. The dead leaf sample contained 30.6, 27.8, 17.9, 1.4, 0.30, 0.11 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. The dead plant sample contained no secondary stem sample. The upper bark retained higher masses of all six congeners compared to the upper wood sample. The upper bark contained 5.8, 5.3, 3.3, 0.33, 0.068, and 0.020 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. The upper wood contained 5.0, 1.9, 0.98, 0.12, and 0.015 µg of PCB 3, 15, 28, 52, and 153, respectively. There were no detections for PCB 77 in the upper wood.

There were higher detections in the lower bark compared to the lower wood for all congeners except PCB 77 for the dead plant sample. The lower bark of the dead plant sample contained 0.47, 0.037, 0.017, 0.14, 0.040, and 0.014 µg of PCB 3, 15, 28, 52, 77, and 152, respectively. The lower wood contained 0.37, 0.011, 0.049, 0.041, and 0.014 µg

of PCB 3, 15, 28, 52, 77, and 153, respectively. There were no detections for PCB 15 in the lower wood. There were no root samples for analysis in the dead plant sample.

Table 2-7 shows the PCB mass distribution for the congeners of interest throughout the various compartments of the non-plant samples for Exposure 2 system. There were 0.066, 237.3, 105.8, 598.1, 44.8, and 141.7 µg remaining in the inlet vial of PCB 3, 15, 28, 52, 77, and 153 for the live tree, respectively. There were no detections in the solution samples for any of the PCB congeners. There were 0.14, 0.14, 0.042, 0.08, 0.90, and 0.33 µg of PCB 3, 15, 28, 52, 77, and 153 found in the upper flask for the live sample, respectively. The XAD-2 cartridge for the live sample retained 53.9, 42.9, 10.4, 5.8, 31.5, and 2.2 µg of PCB 3, 15, 28, 52, 77, and 153, respectively.

The remaining masses found in the input vial dead plant sample were 19.9, 393.5, 107.3, 1.3, 206.4, and 100.8 µg of PCB 3, 15, 28, 52, 77, and 153, respectively. There were no detections for any congeners in the solution sample. There were 0.53, 0.27, 0.21, 0.016, 0.041, and 0.019 µg of PCB 3, 15, 28, 52, 77, and 153 found in the upper flask for the dead sample, respectively. The XAD-2 cartridge retained 73.6, 44.2, 7.0, 6.0, 32.4, and 2.1 µg of PCB 3, 15, 28, 52, 77, and 153, respectively.

Table 2-8 shows the mass balance calculations for the Exposure 2 system. The same calculations were done for Exposure 2 as in Exposure 1. The percent recovered from the live plant system for PCB 3, 15, 28, 52, 77, and 153 was 18.9, 28.8, 32.0, 191.5, 17.3, and 3.7%, respectively. The percent recovered from the dead plant duplicate system was 24.5, 28.8, 14.7, 8.0, 16.5, and 2.3% for PCB 3, 15, 28, 52, 77, and 153, respectively.

Figure 2-7 and Figure 2-8 show the distribution of PCBs throughout the plant measured in μg/g of plant sample for live plant sample and dead plant sample, respectively. Figure 2-9 shows the mass of each congener retained on the leaves versus the log K_{oa} value for each.

2.5.3 Exposure 3

Table 2-9 shows the mass distribution for PCB 3 and 77 throughout the various segments of the plant samples for Exposure 3. Figure 2-10 shows the distribution of PCB 3 and 77 throughout the plant measured in μg/g of plant sample for each system, respectively. Overall the mass of each congener decreased throughout the plant in the downward direction. The tree exposed to PCB 3 retained 20.9 μg on the leaves. There was 3.9 μg of PCB 3 found in the secondary stem. There were 5.8, 1.10, 0.45, 0.22, 0.044 μg found in the upper bark, upper wood, lower bark, lower wood, and roots, respectively.

There was 10.1 μg retained on the leaves of the plant exposed to PCB 77. The remainder of the tree contained lower masses of PCB 77 moving downward. The secondary stem contained 0.15 μg of PCB 77. The upper bark and upper wood contained 0.35 and 0.16 μg, respectively. There were 0.28, 0.34, and 0.046 μg found in the lower bark, lower wood, and roots, respectively.

Table 2-10 shows the PCB mass distribution of PCB 3 and77 throughout the various compartments of the non-plant samples for Exposure 3 system. The input vial for the PCB 3 and PCB 77 systems contained 16.4 and 125.8 μg, respectively. There were no detections in the solution of either system. The upper flask contained 0.05 and 11.09

µg of PCB 3 and 77, respectively. The XAD-2 cartridge captured 0.52 and 0.03 µg of PCB 3 and 77, respectively.

Table 2-11 shows the mass balance calculations for the Exposure 3 system. The same calculations were done for Exposure 3 as in Exposure 1. There was only 9.9% of the mass recovered for the PCB 3 system and 22.6% of the mass recovered for the PCB 77 system.

2.5.4 Quality Control

The concentration of PCB 14 in the surrogate standard was 50 ng/L. The surrogate recovery of PCB 14 for plant samples ranged from 76-120%. The surrogate recovery of PCB 14 for the non-plant samples ranged from 62-95%.

2.6 Discussion from this Research

As a result of further analysis, it was determined that the balance sensitivity was not adequate to accurately measure the input mass. For several samples, the mass remaining in the input vial after exposure that was measured on the GC-ECD was higher than the mass that was originally measured on the balance. The same samples were rerun using the GC-MS, which confirmed that the masses remaining in the input vial were higher than the mass that was initially entered into the inlet vial. To compensate for these errors, known masses of each congener were measured on the balance then analyzed using the GC-ECD in an attempt to create correction factors. The measured correction factors did not follow the expected trends based on the physical-chemical properties for each congener and confirmed the random error that is seen throughout the rest of the results.

Overall the trends that were found in the previous study were confirmed in this study. Direct comparison of the results is not possible due to the inability to properly determine the mass of PCBs that were blown into the system for the current research. In general, the percent recovered values for this research compared to Liu's were significantly lower. The humidity and temperature inside the reactors were never measured during any of the experiments. These factors have a large influence on uptake of airborne contaminants. Plant concentrations increase as temperature decreases (Barber, Thomas, et al. 2004). For later experiments, smaller plants were used to ensure that leaves were not pressed against the glass. This could be a contributing factor for lower leaf capturing efficiency. Larger plants tend to increase the humidity inside the reactor, resulting in higher amounts of condensation inside the reactor and potentially larger uptake by the plant.

The highest mass of each congener was retained on the leaves for both the live and dead samples. In all cases except for PCB 3 in Exposure 2, theactual mass found in the dead sample were lower than that found in the live sample as was expected. This is likely due to the waxy layer of the dead leaves being damaged and a smaller surface area available on the dead leaves

The PCBs that were captured on the leaves were detected in nearly all regions of the reminder of the plant including the roots for several of the congeners. Detections of PCB 3, 28, 52, 77, and 153 in the roots are a new finding as a result of this work. The only congener that was not detected in the roots was PCB 15. The masses found in the lower half of the tree did not follow a consistent trend. There was no clear trend based on congener that explains whether the mass was higher in the lower bark or lower wood.

Overall, the masses in the upper regions were higher than those in the lower regions, as expected from the literature. The masses in the upper bark were also consistently higher than those found in the upper wood.

Due to the inability to accurately measure the initial mass put into the inlet vial, mass balance calculations result in extremes in the percent of the mass recovered. In general, the mass retained in the plant was below the mass added to the system. The non-plant components contributed to the high percent recovered values for Exposure 1. All the masses recovered for Exposure 2 were below 100% except for PCB 52 in live sample due to a high retention on the leaves. The percent recovered for PCB 3 and 77 for Exposure 3 were also below 100%, but were significantly lower than would be expected. Low percent recovery values are likely due to low capture by the XAD resin. This could be attributed to insufficient amounts of XAD resin in the cartridge or humidity effects causing the PCBs to not adhere to the XAD.

For the figures depicting the PCB concentration throughout the plant it is expected that as chlorination increases the mass fraction will decrease. Figure 2-3 shows this downward trend aside from PCB 52 which shows an unexpected peak. The mass fractions decrease throughout the plant in the downward direction as expected. Figure 2-4 shows an unexpected trend of increasing mass fractions from PCB 15 to PCB 52. The trend of decreasing mass fraction downward through the plant is consistent with expectations. Figure 2-5 shows the same trend as in Figure 2-4 except with higher mass fractions.

Plots of the mass on the leaf sample versus log K_{oa} were made in order to illustrate the relationship between the two parameters. As the log K_{oa} value increases, the

mass retained on the leaves is expected to decrease due to decreasing volatility. PCB 3 is the most volatile congener and has the largest percent entering the system while PCB 153 is the least volatile and has the smallest percent entering the system. In addition to its volatility, there is also the highest mass added of PCB 3 to the inlet vial. Figure 2-6 does not confirm these expectations. The trend for the live sample shows an overall decrease aside from PCB 52 (as indicated by log K_{oa} 7.72), which has an unexpected peak. The peak of PCB 52 is consistent for all the samples in Exposure 1. The trend for the duplicate live sample and the dead control are similar to one another with a sharp decrease followed by a slight increase then another decrease.

The profile depicted in Figure 2-7 for the live plant sample does not follow the expected trend. As chlorination increases, the mass fraction increases. However, the mass fractions decrease throughout the plant moving in the downward direction as expected. Figure 2-8 for the dead plant sample best depicts the expected profile. The mass fractions decrease with increased chlorination and throughout the plant in the downward direction. The mass fractions found in the dead plant are higher than those found in the live plant. This can be attributed to water content found in the leaves. The live leaves weighed 2.8 grams and the dead leaves weighed 0.84 grams, indicating approximately 73% water content. A study of the hybrid poplar species *Populus deltoids* showed that the relative water content of is approximately 72% (Braatne, Hinckley and Stettler 1992).

Figure 2-9 shows the mass of leaf sample versus log K_{oa} for Exposure 2. As explained earlier, the trend is expected to decrease from left to right with increasing log K_{oa}. The live sample does not follow this trend and includes a peak at log K_{oa} (PCB 52)

for Exposure 2 as was seen in Exposure 1. The dead control shows the downward trend with increased chlorination as expected.

Figure 2-10 shows the PCB distribution throughout the plant for Exposure 3. The concentration of PCBs decreases throughout the plant in the downward direction as expected. In general, the mass fraction of PCB 3 is higher than PCB 77 as expected. The mass fraction values for Exposure 3 are lower than the previous exposures.

2.7 Recommendations

In order to more accurately quantify the mass of each congener the following recommendations are suggested as a result of this work:

1) Expose each tree to just one congener at a time to allow for more accurate quantification of the amount of PCBs that volatilize in order to determine the mass going into the system to determine a proper mass balance
2) Use higher masses in order to compensate for balance sensitivity issues (i.e. mg instead of μg)
3) Increase the exposure time of the experiment in order to allow for more complete volatilization into the system
4) Increase the reactor/system size in order to use poplars with greater viability and/or greater transpiration rates for overall greater plant productivity

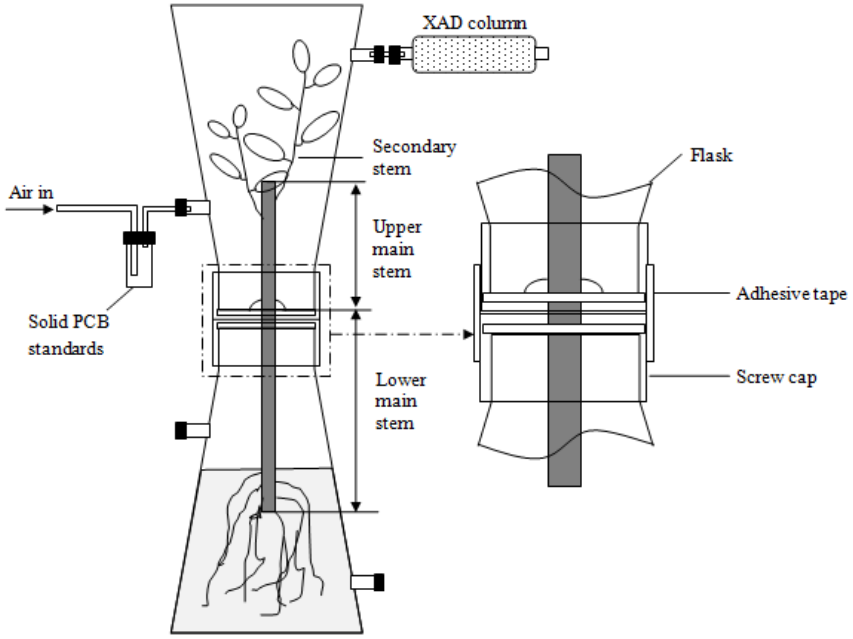

Figure 2-1. PCB Exposure Setup Schematic (Liu 2008)

Figure 2-2. Actual PCB Exposure Setup

Table 2-1. Mass balances and PCB distribution (% of mass applied) in the Exposed Whole Poplar (EWP), Dead Poplar Controls (DPC) and Unplanted Controls (UPC) after 10 days[a] for plant samples

Compound & Reactors	Solution	Leaves	Secondary stem	Upper bark	Upper wood	Lower bark	Lower wood	Roots
PCB 3 EWP	n.d.	3.4±1.8	2.4±1.2	1.9±0.7	0.40±0.12	0.021±0.022	0.018±0.044	n.d.
DPC	n.d.	6.9±3.2	1.6±0.4	5.4±0.6	n.d.	0.046±0.039	0.0033±0.0057	n.d.
UPC	n.d.							
PCB15 EWP	n.d.	51±7	10±4	11±3	1.0±0.3	n.d.	0.069±0.170	n.d.
DPC	n.d.	25±5	9.1±1.5	11±2	n.d.	0.37±0.62	0.0097±0.0168	n.d.
UPC	n.d.							
PCB28 EWP	n.d.	58±9	8.9±2.8	9.5±2.3	1.0±0.3	0.0021±0.0022	0.056±0.136	n.d.
DPC	n.d.	28±4	9.8±1.8	11±2	0.047±0.047	0.019±0.018	0.025±0.042	n.d.
UPC	n.d.							
PCB52 EWP	n.d.	68±9	6.4±2.4	6.7±2.2	0.97±0.35	0.0025±0.0025	0.033±0.082	n.d.
DPC	n.d.	28±4	9.6±1.4	7.9±1.5	n.d.	0.014±0.015	0.019±0.031	n.d.
UPC	n.d.							
PCB77 EWP	n.d.	67.4±15	16.5±18	8.4±7.1	0.87±1.13	n.d.	0.036±0.089	n.d.
DPC	n.d.	52±17	18.7±2	1.5±0.5	n.d.	n.d.	n.d.	n.d.
UPC	n.d.							

Source: Liu, Jiyan. "Phytoremediation of Airborne PCBs." *Unpublished data*, 2008.

[a] Results expressed as the percent of PCBs blowing into the reactors

[b] The summation of different compartments

[c] Mean value ± standard deviation, for exposed whole poplar and unplanted controls, n=5, for dead poplar controls, n=3

[d] Non-detectable

Table 2-2. Mass balances and PCB distribution (% of mass applied) in the Exposed Whole Poplar (EWP), Dead Poplar Controls (DPC) and Unplanted Controls (UPC) after 10 days[a] for non-plant samples

Compound & Reactors	XAD	Glass	Silicon sealant	Total PCBs recovered [b]
PCB 3 EWP	76±10 [c]	n.d. [d]	5.6±2.9	89±12
DPC	61±3	n.d.	8.1±0.7	83±5
UPC	96±13	0.025±0.050	2.0±0.8	98±13
PCB15 EWP	22±5	0.10±0.10	2.2±2.2	98±6
DPC	45±5	0.059±0.058	4.0±1.6	94±8
UPC	95±8	0.066±0.082	2.0±0.9	97±8
PCB28 EWP	23±6	0.21±0.10	2.5±2.5	103±8
DPC	40±6	0.27±0.17	4.9±2.9	94±5
UPC	96±8	0.17±0.11	2.3±0.9	98±8
PCB52 EWP	19±4	0.26±0.13	2.7±2.6	104±8
DPC	48±8	0.52±0.42	5.0±2.9	99±6
UPC	100±9	0.23±0.17	2.5±1.0	103±8
PCB77 EWP	n.d.	0.61±0.4	0.22±0.38	94±15
DPC	17±7	4.9±5.7	0.17±0.16	94±27
UPC	93±32	5.6±5.8	2.2±1.8	100±31

Source: Liu, Jiyan. "Phytoremediation of Airborne PCBs." *Unpublished data*, 2008.

[a] Results expressed as the percent of PCBs blowing into the reactors

[b] The summation of different compartments

[c] Mean value ± standard deviation, for exposed whole poplar and unplanted controls, n=5, for dead poplar controls, n=3

[d] Non-detectable

Table 2-3. PCB distribution measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for plant samples for Exposure 1

Compound & Reactors	Leaves	Secondary stem	Upper bark	Upper wood	Lower bark	Lower wood	Roots
PCB 3 EWP	40.5	2.1	25.1	3.2	0.008	0.027	n.d.
EWP-D	47.6	7.64	21.1	1.45	0.75	1.03	n.d.
DPC	14.8	-[a]	17.3	1.1	0.051	0.11	-
PCB 15 EWP	22.6	1.0	7.9	0.65	0.025	0.017	n.d.
EWP-D	5.0	1.8	4.7	0.072	0.49	0.20	n.d.
DPC	2.5	-	4.6	0.22	0.065	0.066	-
PCB 28 EWP	15.4	0.51	4.0	0.30	0.057	0.006	0.002
EWP-D	16.4	4.9	12.1	0.12	0.15	0.43	0.006
DPC	7.6	-	10.1	0.52	0.07	0.24	-
PCB 52 EWP	88.3	2.1	19.5	1.54	0.092	0.029	0.015
EWP-D	20.9	4.8	16.7	0.12	0.92	0.79	0.024
DPC	12.5	-	13.5	0.83	0.11	0.43	-
PCB 77 EWP	0.51	0.025	0.057	0.004	0.019	0.006	0.008
EWP-D	0.020	0.012	0.023	0.016	0.006	0.038	0.015
DPC	0.049	-	0.11	0.025	0.002	n.d	-
PCB 153 EWP	0.89	0.036	0.12	0.009	0.004	0.001	0.001
EWP-D	0.072	0.051	0.096	0.001	0.010	0.61	0.003
DPC	0.10	-	0.17	0.65	0.003	0.014	-

[a] No sample

Table 2-4. PCB distribution measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for non-plant samples for Exposure 1

Compound & Reactors	Input Vial	Solution	Flask	XAD
PCB 3 EWP	313.8	n.d.	n.d.	-[a]
EWP-D	2.3	n.d.	n.d.	2725.3
DPC	274.5	n.d.	-	583.9
PCB 15 EWP	1009.2	n.d.	n.d.	-
EWP-D	1382.9	n.d.	n.d.	5053.3
DPC	950.3	n.d.	-	395.6
PCB 28 EWP	268.4	n.d.	0.030	-
EWP-D	268.4	n.d.	0.007	6.9
DPC	137.0	n.d.	-	488.9
PCB 52 EWP	1073.7	n.d.	0.028	-
EWP-D	890.7	n.d.	0.008	31.8
DPC	791.5	n.d.	-	1155
PCB 77 EWP	2.5	n.d.	0.030	-
EWP-D	46.8	n.d.	0.040	32.4
DPC	33.3	n.d.	-	40.5
PCB 153 EWP	238.6	n.d.	0.015	-
EWP-D	238.6	n.d.	0.012	6.9
DPC	211.5	n.d.	-	7.9

[a] No sample

Table 2-5. PCB distribution totals measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for Exposure 1

Compound & Reactors	Mass In Vial	Mass in Plant	Mass Non-plant	Total Mass	% Recovered
PCB 3 EWP	500	70.9	0	70.9	14.2
EWP-D	400	79.6	2725.3	2804.9	701.2
DPC	500	33.3	583.9	617.2	123.4
PCB 15 EWP	300	32.2	0	32.2	10.7
EWP-D	300	12.3	5053.3	5065.6	1688.5
DPC	300	7.5	395.6	403.1	134.4
PCB 28 EWP	200	20.3	0.030	20.3	10.1
EWP-D	300	34.1	6.9	41.0	13.7
DPC	300	18.5	488.9	507.4	169.1
PCB 52 EWP	100	111.6	0.028	111.6	111.6
EWP-D	200	44.2	31.8	76.0	38.0
DPC	100	27.3	1155.0	1182.3	1182.3
PCB 77 EWP	100	0.62	0.0	0.65	0.65
EWP-D	100	0.13	32.4	32.5	32.5
DPC	200	0.19	40.5	40.7	20.3
PCB 153 EWP	100	1.1	0.015	1.1	1.1
EWP-D	100	0.85	6.9	7.7	7.7
DPC	100	0.93	7.9	8.8	8.8

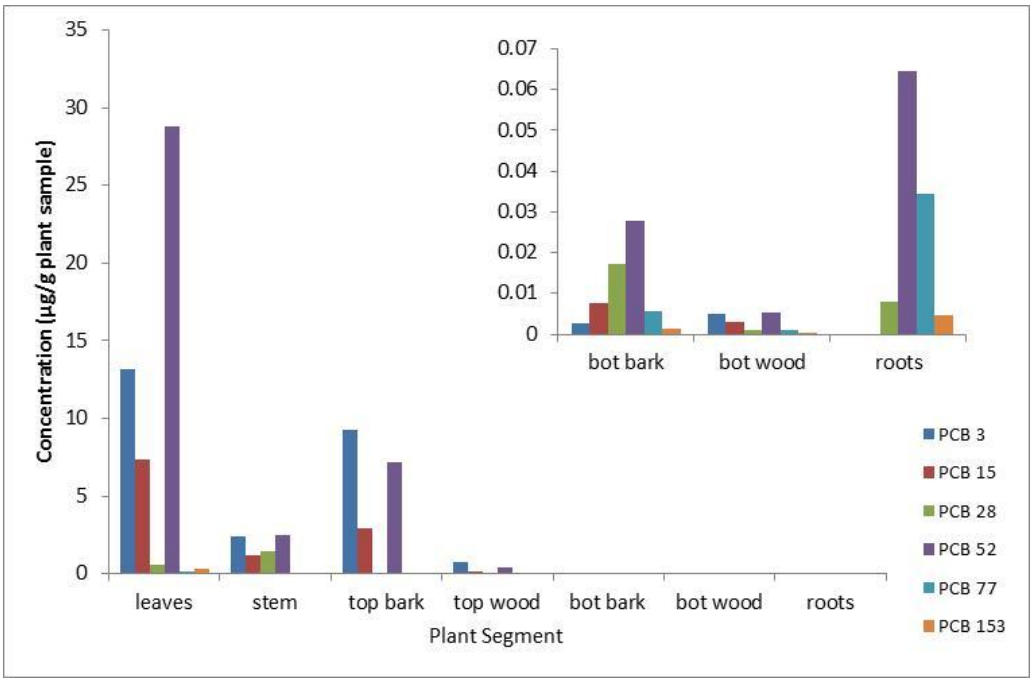

Figure 2-3. Distribution of PCBs throughout the plant in the Exposed Whole Poplar measured in µg/g of fresh plant sample for Exposure 1

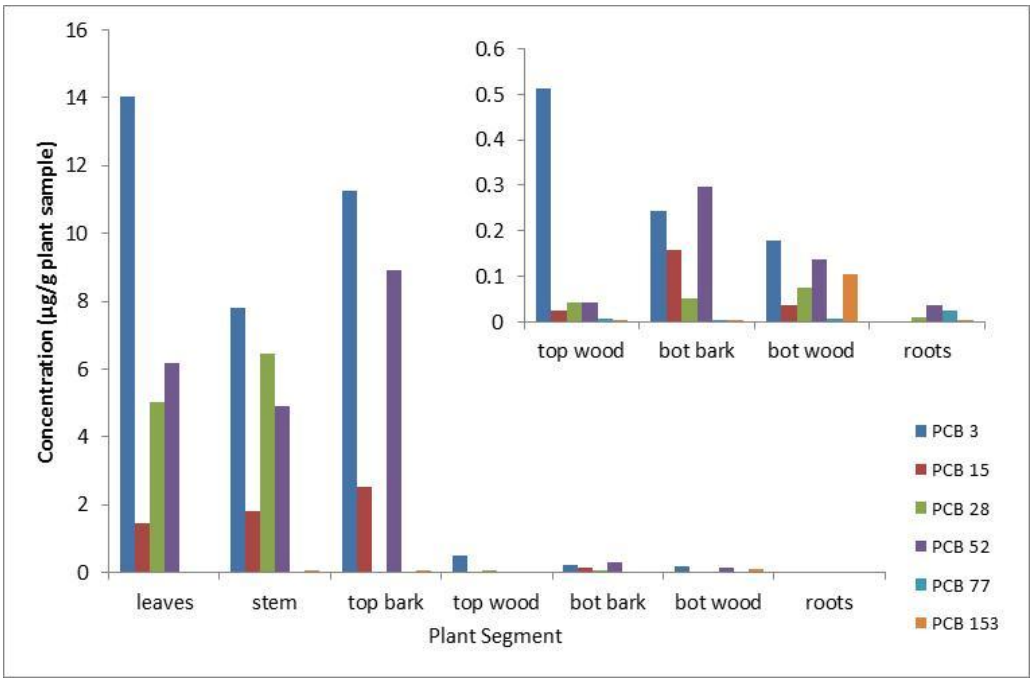

Figure 2-4. Distribution of PCBs throughout the plant in Exposed Whole Poplar-Duplicate measured in µg/g of fresh plant sample for Exposure 1

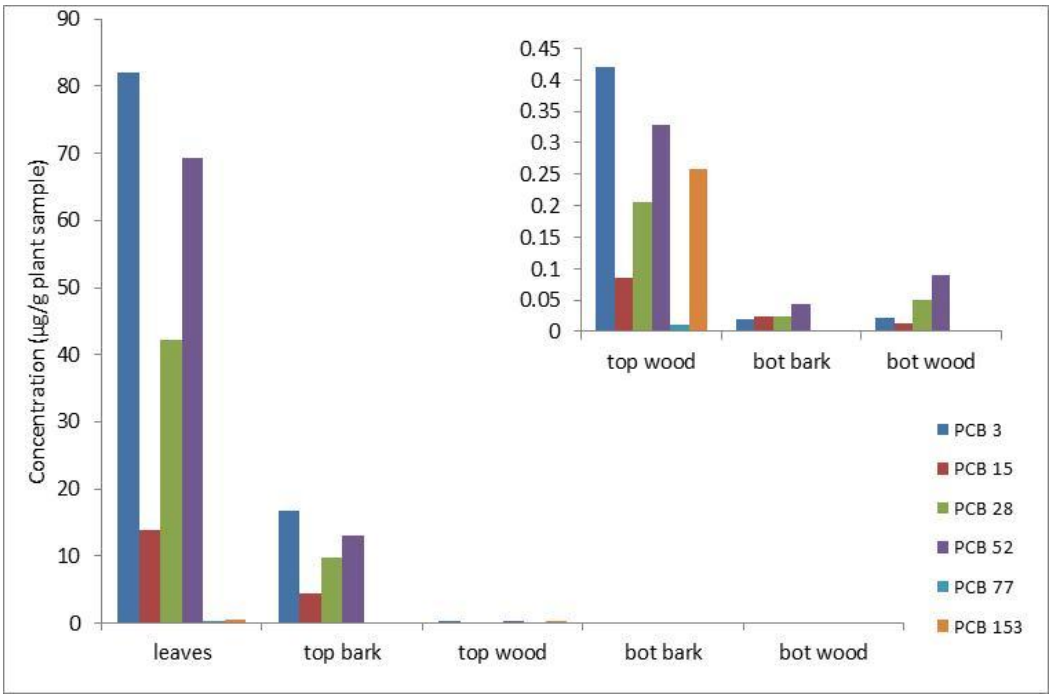

Figure 2-5. Distribution of PCBs throughout the plant in the Dead Poplar Control measured µg/g of plant sample for Exposure 1

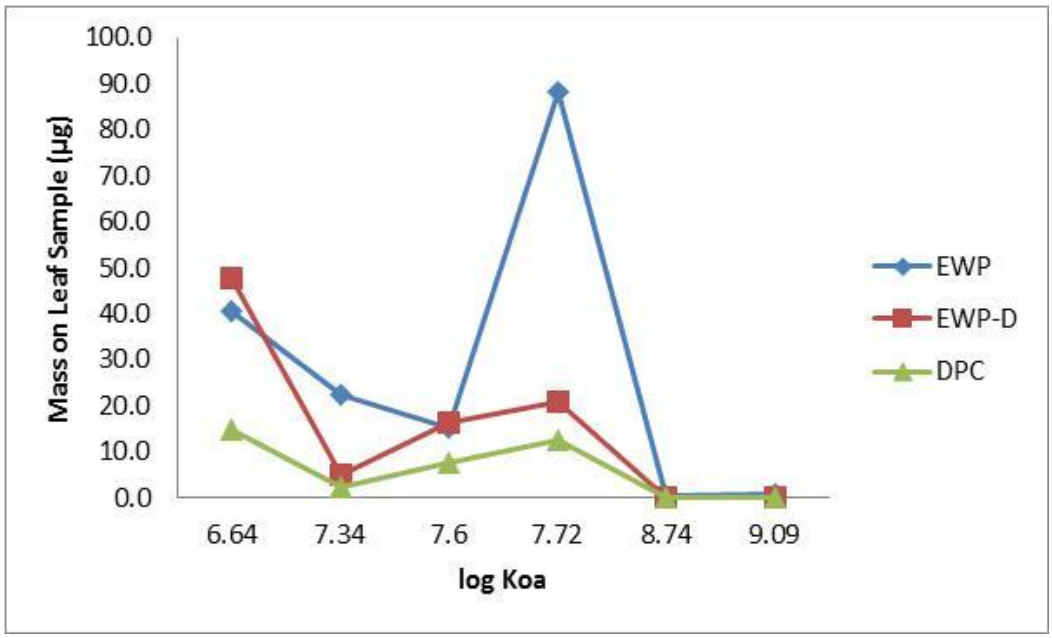

Figure 2-6. Mass of PCB congener on the leaf sample versus log K_{oa} values for each congener for Exposure 1

Table 2-6. PCB distribution measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for plant samples for Exposure 2

Compound & Reactors	Leaves	Secondary stem	Upper bark	Upper wood	Lower bark	Lower wood	Roots
PCB 3 EWP	23.3	5.4	4.3	5.6	-[a]	0.38	0.071
DPC	30.6	-	5.8	5.0	0.47	0.37	-
PCB15 EWP	31.4	3.1	5.6	3.1	-	0.049	n.d.
DPC	27.8	-	5.3	1.9	0.037	n.d.	-
PCB28 EWP	40.8	3.1	6.5	3.0	-	0.056	0.0097
DPC	17.9	-	3.3	0.98	0.017	0.011	-
PCB52 EWP	144.4	5.4	25.6	9.7	-	0.11	0.042
DPC	1.4	-	0.33	0.12	0.14	0.049	-
PCB77 EWP	1.5	0.23	0.22	0.082	-	0.066	0.020
DPC	0.30	-	0.068	n.d.	0.040	0.041	-
PCB153 EWP	0.88	0.070	0.13	0.030	-	0.019	0.013
DPC	0.11	-	0.020	0.015	0.014	0.014	-

[a] No sample

Table 2-7. PCB distribution measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for non-plant samples for Exposure 2

Compound & Reactors	Input Vial	Solution	Flask	XAD	Silicone
PCB 3 EWP	0.066	n.d.	0.14	53.9	1.6
DPC	19.9	n.d.	0.53	73.6	6.2
PCB 15 EWP	237.3	n.d.	0.14	42.9	0.19
DPC	393.5	n.d.	0.27	44.2	0.61
PCB 28 EWP	105.8	n.d.	0.042	10.4	0.17
DPC	107.3	n.d.	0.21	7.0	n.d.
PCB 52 EWP	598.1	n.d.	0.08	5.8	0.34
DPC	1.3	n.d.	0.016	6.0	0.001
PCB 77 EWP	44.8	n.d.	0.90	31.5	0.080
DPC	206.4	n.d.	0.041	32.4	0.036
PCB 153 EWP	141.7	n.d.	0.33	2.2	0.018
DPC	100.8	n.d.	0.019	2.1	0.017

Table 2-8. PCB distribution totals measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for Exposure 2

Compound & Reactors	Mass In Vial	Mass in Plant	Mass Non-plant	Total Mass	% Recovered
PCB 3 EWP	500	39.1	55.6	94.7	18.9
DPC	500	42.2	80.3	122.6	24.5
PCB 15 EWP	300	43.2	43.2	86.4	28.8
DPC	300	35.2	45.1	80.3	26.8
PCB 28 EWP	200	53.4	10.6	64.0	32.0
DPC	200	22.2	7.2	29.4	14.7
PCB 52 EWP	100	185.3	6.2	191.5	191.5
DPC	100	2.0	6.0	8.0	8.0
PCB 77 EWP	200	2.1	32.5	34.6	17.3
DPC	200	0.4	32.5	32.9	16.5
PCB 153 EWP	100	1.2	2.5	3.7	3.7
DPC	100	0.2	2.1	2.3	2.3

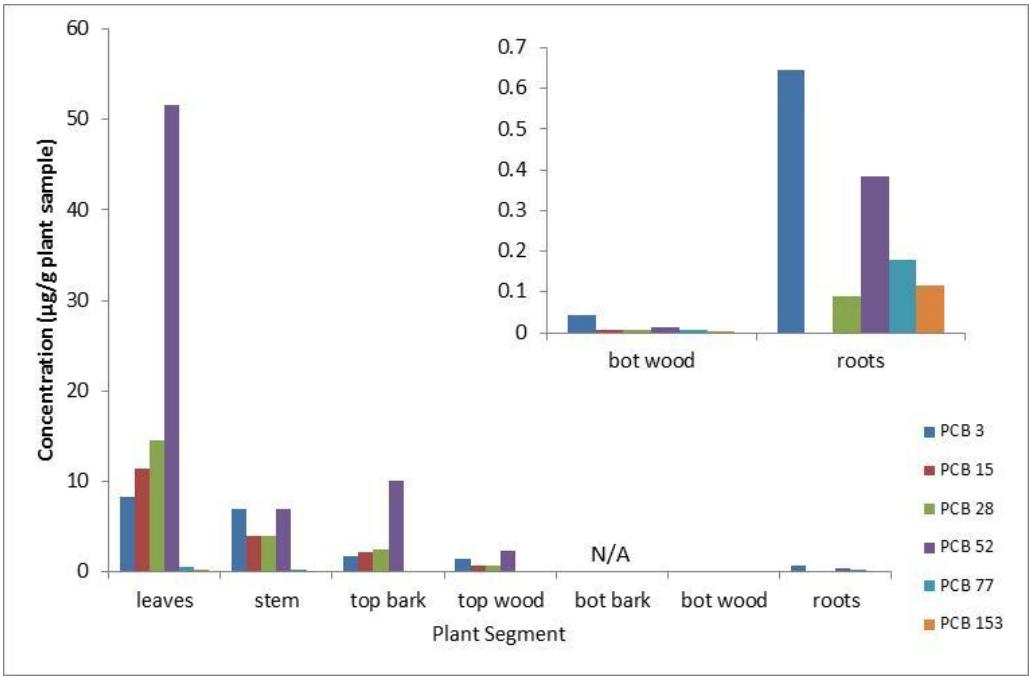

Figure 2-7. Distribution of PCBs throughout the plant in the Exposed Whole Poplar measured in µg/g of fresh plant sample for Exposure 2

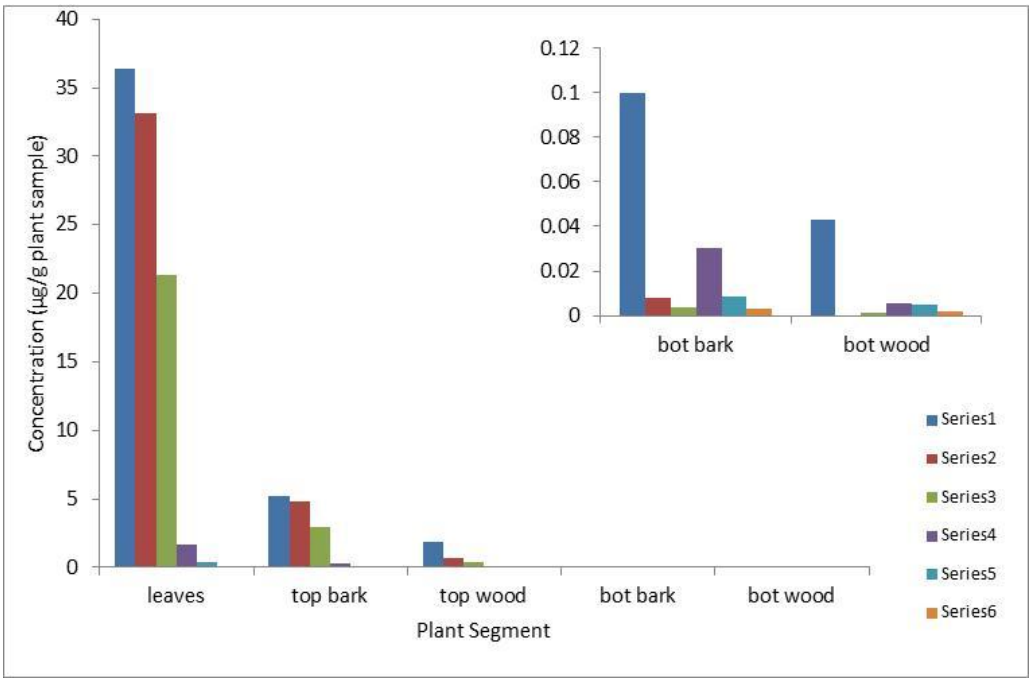

Figure 2-8. Distribution of PCBs throughout the plant in the Dead Poplar Control measured in µg/g of plant sample for Exposure 2

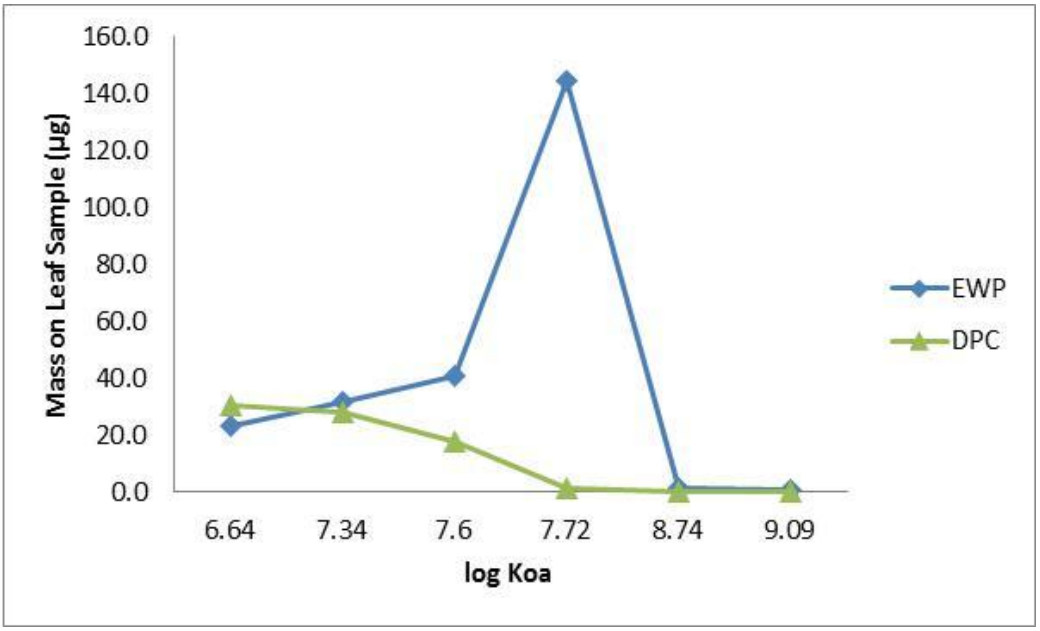

Figure 2-9. Mass of PCB congener on the leaf sample versus log K_{oa} values for each congener for Exposure 2

Table 2-9. PCB distribution measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for plant samples for Exposure 3

Compound & Reactors	Leaves	Secondary stem	Upper bark	Upper wood	Lower bark	Lower wood	Roots
PCB 3 EWP	20.9	3.4	5.8	1.10	0.45	0.22	0.044
PCB 77 EWP	10.1	0.150	0.35	0.16	0.28	0.30	0.046

Table 2-10. PCB distribution measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for non-plant samples for Exposure 3

Compound & Reactors	Input Vial	Solution	Flask	XAD	Silicone
PCB 3 EWP	16.4	n.d.	0.05	0.52	16.9
PCB 77 EWP	125.8	n.d.	11.09	0.03	0.09

Table 2-11. PCB distribution totals measured in µg in the Exposed Whole Poplar (EWP), Exposed Whole Poplar-Duplicate (EWP-D), Dead Poplar Controls (DPC) after 10 days for Exposure 3

Compound & Reactors	Mass In Vial	Mass in Plant	Mass Non-plant	Total Mass	% Recovered
PCB 3 EWP	500	31.9	17.5	49.4	9.9
PCB 77 EWP	100	11.4	11.2	22.6	22.6

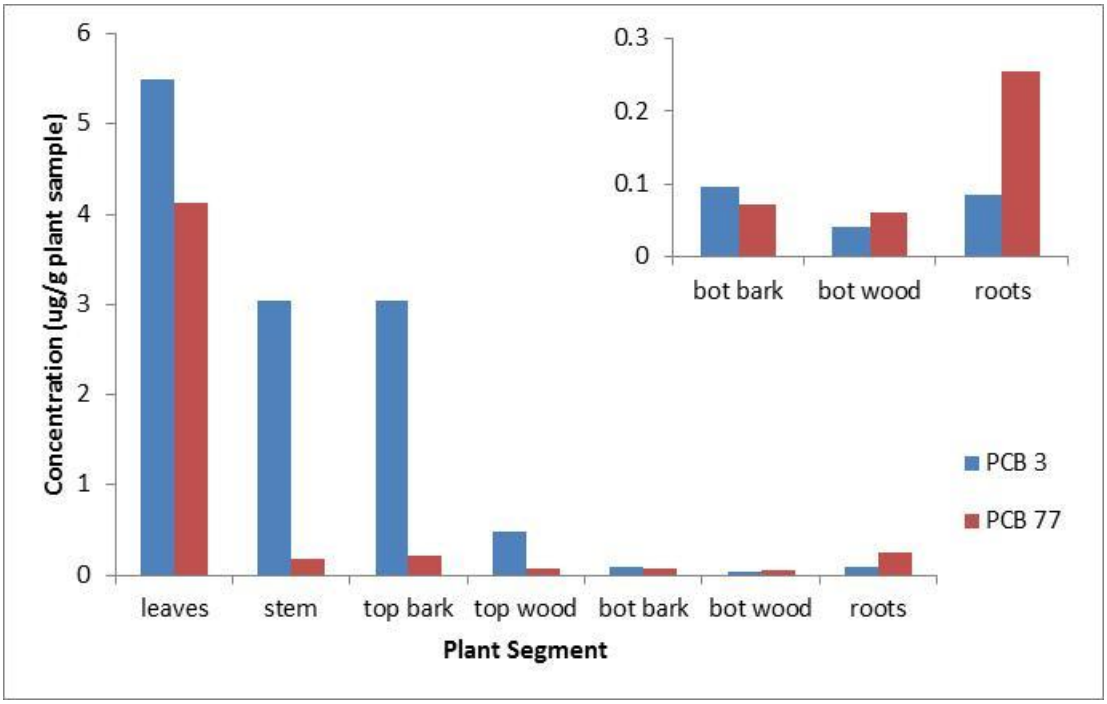

Figure 2-10. Distribution of PCB 3 and PCB 77 throughout the plant in the Exposed Whole Poplar measured in µg/g of fresh plant sample for Exposure 3

CHAPTER 3
CONCLUSIONS

The specific objectives and resulting conclusions for this research are listed below and discussed in consequent sections:

1) Determine the amount of PCBs that volatilize into an experimental exposure system of poplar plants

The amount of PCBs that were volatilized into the system could not be accurately quantified. The masses of PCBs placed in the inlet vial were measured using a balance that was not sensitive enough to accurately measure down to the μg level. As a result, GC-ECD analysis of the inlet vial following exposure resulted in higher masses than the initial mass that was recorded for some cases.

2) Determine the amount of semi-volatile PCBs that the plant can scavenge from the air onto the leaves from a specific congener mix based on a range of physical-chemical properties

For Exposure 1 the leaves of the live tree were able to capture 40.5, 22.6, 15.4, 88.3, 0.51, and 0.89 μg of PCB 3, 15, 28, 52, 77, and 153, respectively. The leaves for the duplicate sample were able to capture 47.6, 5.0, 16.4, 20.9, 0.020, and 0.072 μg of PCB 3, 15, 28, 52, 77, and 153, respectively. The dead leaves captured 14.8, 2.5, 7.6, 12.5, 0.049, and 0.10 μg of PCB 3, 15, 28, 52, 77, and 153, respectively.

For Exposure 2 the leaves of the live sample were able to capture 23.3, 31.4, 40.8, 144.4, 1.5, and 0.88 μg of PCB 3, 15, 28, 52, 77, and 153, respectively. The leaves of the dead sample contained 30.6, 27.8, 17.9, 1.4, 0.30, 0.11 μg of PCB 3, 15, 28, 52, 77, and 153, respectively.

For Exposure 3 the tree exposed to PCB 3 retained 20.9 µg on the leaves and the tree exposed to PCB 77 retained 10.1 µg on the leaves.

3) Determine if translocation occurs from the leaves into the roots

There were detections of PCBs in the roots for nearly all congeners in all three exposures. For Exposure 1 the roots were found to retain several of the higher chlorinated congeners, but no detections were found for PCB 3 or 15 in the live sample. The masses of PCB 28, 52, 77, and 153 were 0.002, 0.015, 0.008, and 0.001, respectively. There were also no detections for PCB 3 or 15 found in the live duplicate sample. There were 0.006, 0.024, 0.015, and 0.003 µg of PCB 28, 52, 77, and 153 in the roots, respectively. For Exposure 2 there were 0.071, 0.0097, 0.042, 0.020, and 0.013 µg of PCB 3, 28, 52, 77, and 153 found in the roots, respectively. For Exposure 3 there were 0.044 µg of PCB 3 and 0.046 µg of PCB 77 found in the roots. The detections of PCBs in the roots were concluded to be attributed to diffusion rather than translocation by the phloem.

4) Develop a mass balance for the entire exposure system

A mass balance was developed for the three exposure systems. Exposure 1 resulted in percent recovered values that were greater than 100%. For Exposure 2 and 3 the percent recovered values were overall much lower than 100%. The inaccuracy in the mass balances can be attributed to the balance sensitivity not being low enough to accurately measure to the µg level.

For Exposure 1 the percent recovered from the live plant system for PCB 3, 15, 28, 52, 77, and 153 was 14.2, 10.7, 10.1, 111.6, 0.65, and 1.1%, respectively. The percent recovered from the live plant duplicate system was 701.2, 1688.5, 13.7, 38.0,

32.5, and 7.7% for PCB 3, 15, 28, 52, 77, and 153, respectively. There was 123.4, 134.4, 169.1, 1182.3, 20.3, and 8.8% recovered of PCB 3, 15, 28, 52, 77, and 153 from the dead plant system, respectively.

For Exposure 2 the percent recovered from the live plant system for PCB 3, 15, 28, 52, 77, and 153 was 18.9, 28.8, 32.0, 191.5, 17.3, and 3.7%, respectively. The percent recovered from the dead plant duplicate system was 24.5, 28.8, 14.7, 8.0, 16.5, and 2.3% for PCB 3, 15, 28, 52, 77, and 153, respectively.

For Exposure 3 there was only 9.9% of the mass recovered for the PCB 3 system and 22.6% of the mass recovered for the PCB 77 system.

5) Using GC-ECD, determine if the plant produces any (unknown) metabolites from the specific congener mix of parent compounds

The additional peaks found on the chromatogram from the GC-ECD analysis cannot be confirmed as potential metabolites from the parent compounds of the specific congener mix. The chromatograms for all of the plant samples for the three exposures are provided in Appendix B. In order to more accurately determine if metabolites are present, samples would need to be analyzed using the GC-MS.

Overall, the research shows that hybrid poplar trees may be a feasible treatment candidate for scavenging airborne PCBs from nearby sources. Treatment is especially ideal for PCBs with more than one chlorine substitution. A majority of the PCBs reside on the leaves, but as a result of diffusion can be found in the roots as well. Potentially, the leaves could fall to the rhizophere in autumn, and be degraded there.

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APPENDIX A
PROTOCOLS

Table A-1. Hoagland's Solution Recipe

Stock Solution	Volume per 12 L
1 M Ca(NO3)2·4H_2O	24 mL
2 M KNO_3	18 mL
2 M $NH_4H_2PO_4$	12 mL
Micronutrients	12 mL
20 mM Fe-EDTA	12 mL
1 M $MgSO_4$·7H_2O	6 mL
1 M NaOH	to pH 6.8

Source: Epstein, Emanuel. *Mineral nutrition of plants: principles and perspectives.* New York: John Wiley & Sons, 1972.

Protocol for extraction of PCBs from solution and plant tissue

Solution:

- add 50 mL of hexane/MTBE (1:1 *v/v*) shaken overnight
    - add surrogate standard before shaking
- additional 50 mL of hexane/MTBE added and shaken for 30 minutes
- concentrate the combined 100 mL by rotary evaporation
- partitioned with 1 mL of concentrated H_2SO_4

Plant Tissue:

- 5 mL of hexane/acetone (1:1 *v/v*) g^{-1} of sample and shaken overnight
- 5 mL of hexane g^{-1} of sample shaken for 30 minutes
- Combined extract concentrated to 1 mL using the rotary evaporator
- Treated with 1-2 mL of concentrated H_2SO_4
- Centrifuge at 3000 rpm for 5 minutes
- Add an additional 1 mL of hexane and centrifuge again
- Transfer to column of 0.1 g activated silica gel and 1 g of acid silica gel
- Elute with 10 mL of hexane
- Concentrate to approximately 1 mL using the rotary evaporator
- Add internal standard

APPENDIX B

DATA

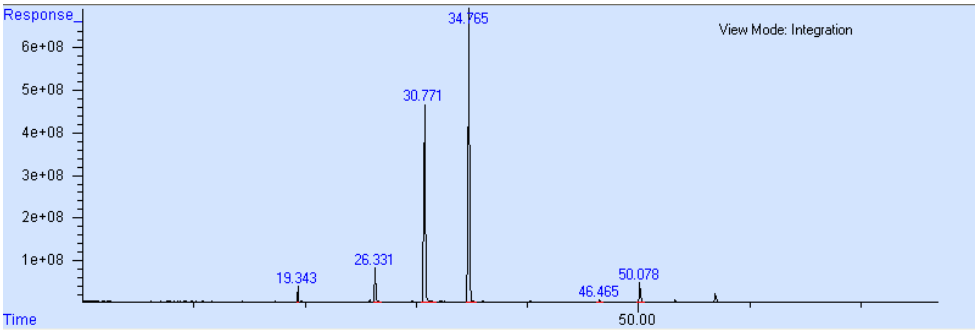

Figure B-1. GC-ECD chromatogram for select PCB congeners in the live leaf sample for Exposure 1

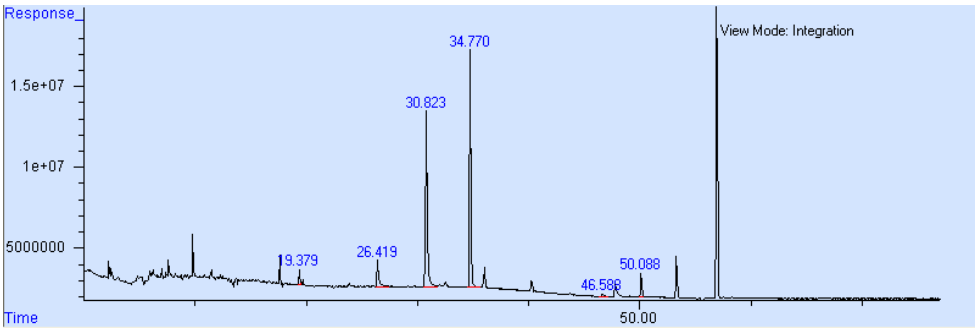

Figure B-2. GC-ECD chromatogram for select PCB congeners in the live secondary stem sample for Exposure 1

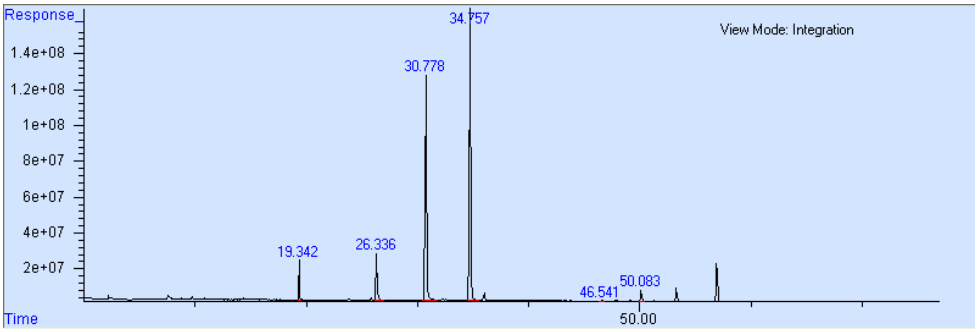

Figure B-3. GC-ECD chromatogram for select PCB congeners in the live upper bark sample for Exposure 1

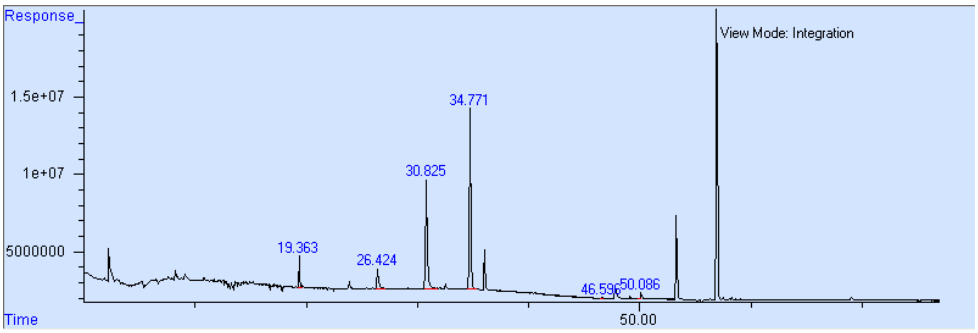

Figure B-4. GC-ECD chromatogram for select PCB congeners in the live upper wood sample for Exposure 1

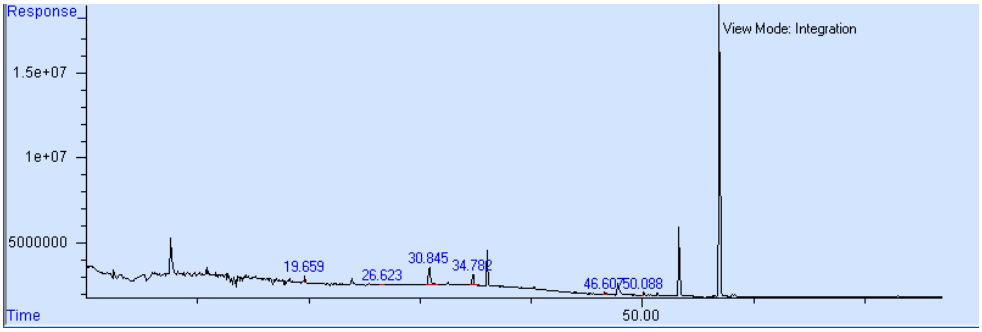

Figure B-5. GC-ECD chromatogram for select PCB congeners in the live lower bark sample for Exposure 1

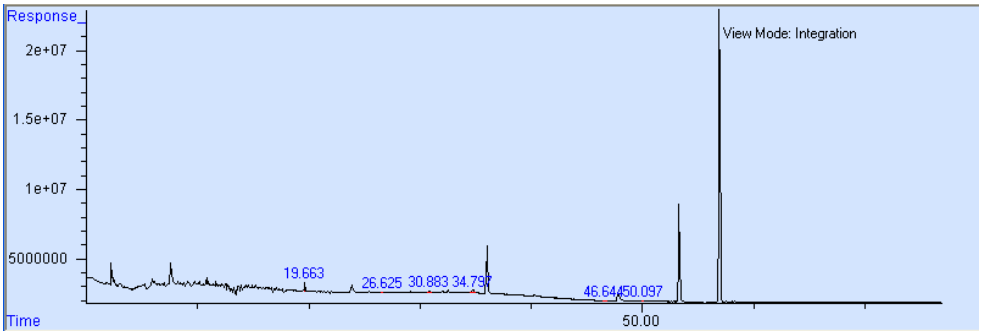

Figure B-6. GC-ECD chromatogram for select PCB congeners in the live lower wood sample for Exposure 1

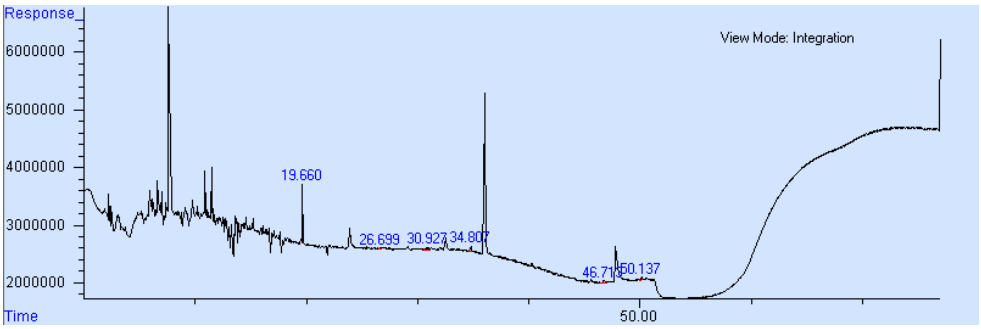

Figure B-7. GC-ECD chromatogram for select PCB congeners in the live root sample for Exposure 1

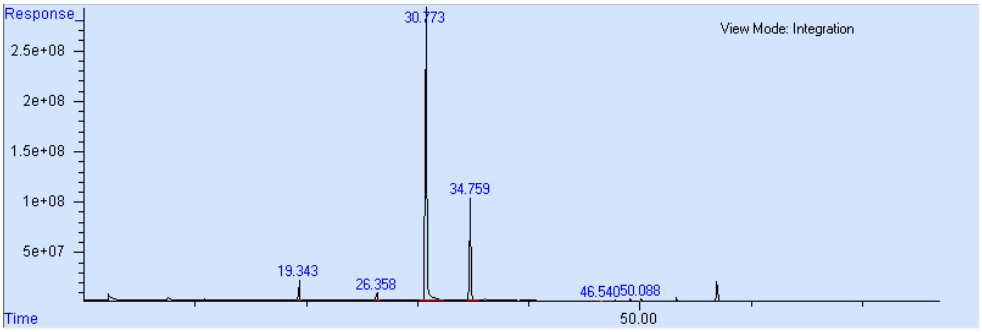

Figure B-8. GC-ECD chromatogram for select PCB congeners in the duplicate live leaf sample for Exposure 1

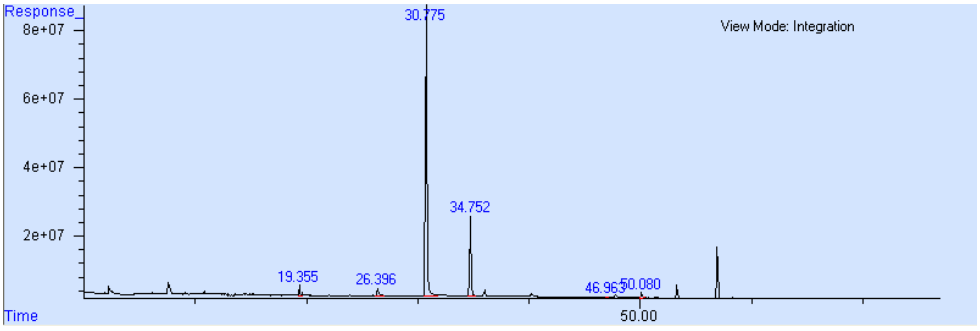

Figure B-9. GC-ECD chromatogram for select PCB congeners in the duplicate live secondary stem sample for Exposure 1

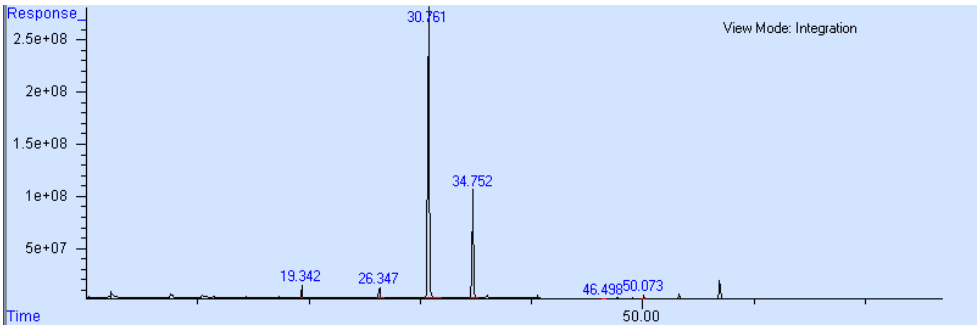

Figure B-10. GC-ECD chromatogram for select PCB congeners in the duplicate live upper bark sample for Exposure 1

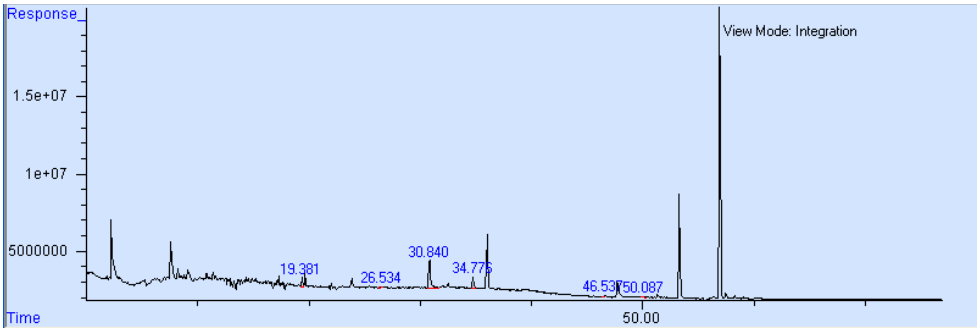

Figure B-11. GC-ECD chromatogram for select PCB congeners in the duplicate live upper wood sample for Exposure 1

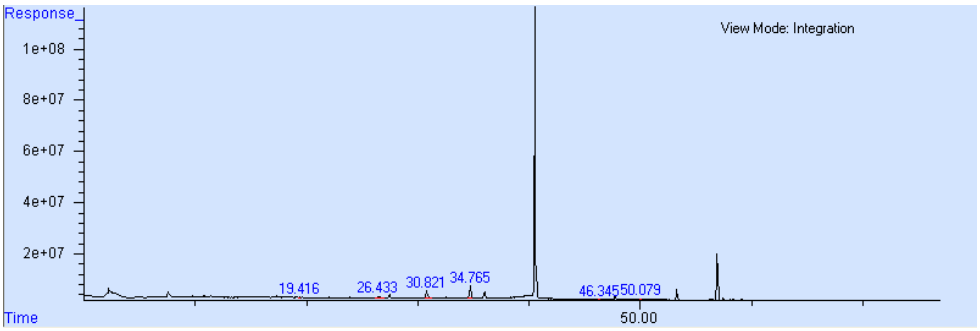

Figure B-12. GC-ECD chromatogram for select PCB congeners in the duplicate live lower bark sample for Exposure 1

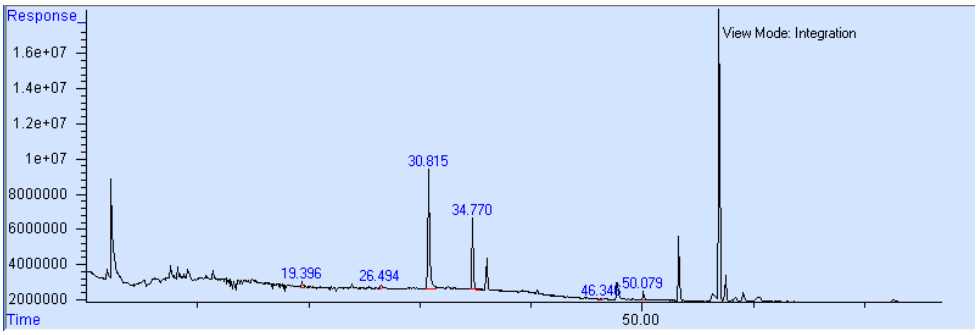

Figure B-13. GC-ECD chromatogram for select PCB congeners in the duplicate live root sample for Exposure 1

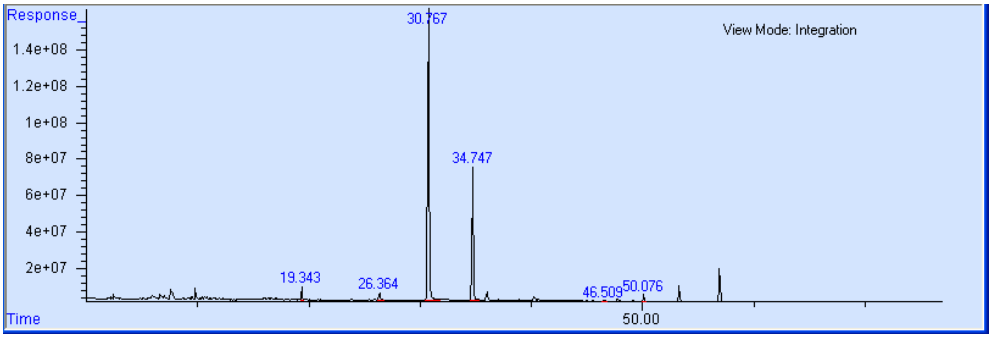

Figure B-14. GC-ECD chromatogram for select PCB congeners in the dead leaf sample for Exposure 1

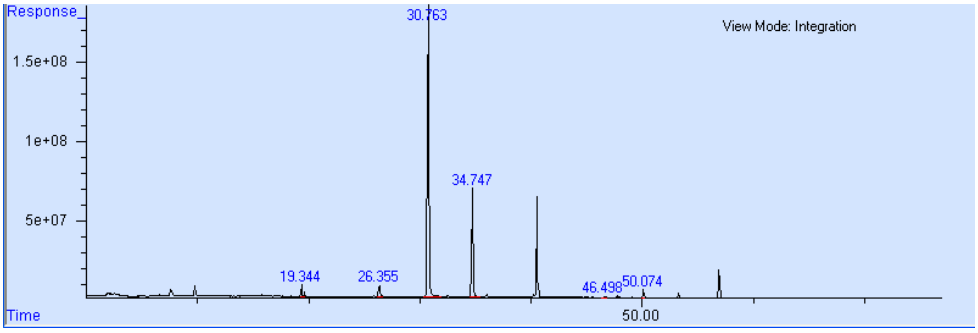

Figure B-15. GC-ECD chromatogram for select PCB congeners in the dead upper bark sample for Exposure 1

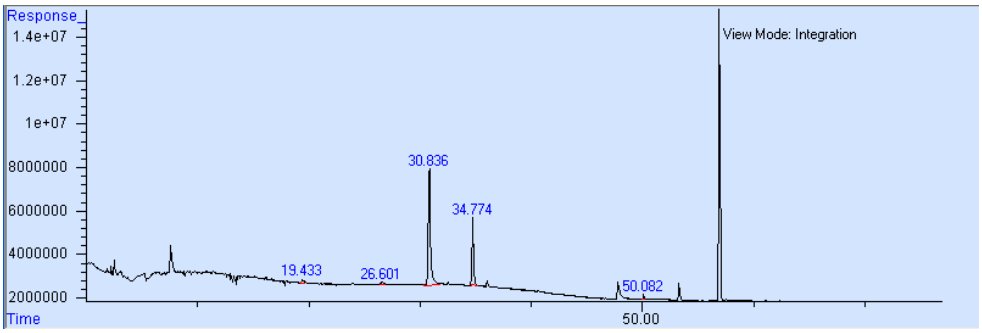

Figure B-16. GC-ECD chromatogram for select PCB congeners in the dead upper wood sample for Exposure 1

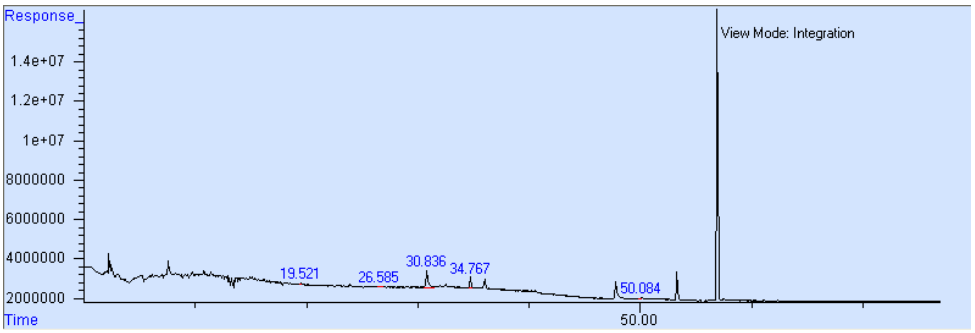

Figure B-17. GC-ECD chromatogram for select PCB congeners in the dead lower bark sample for Exposure 1

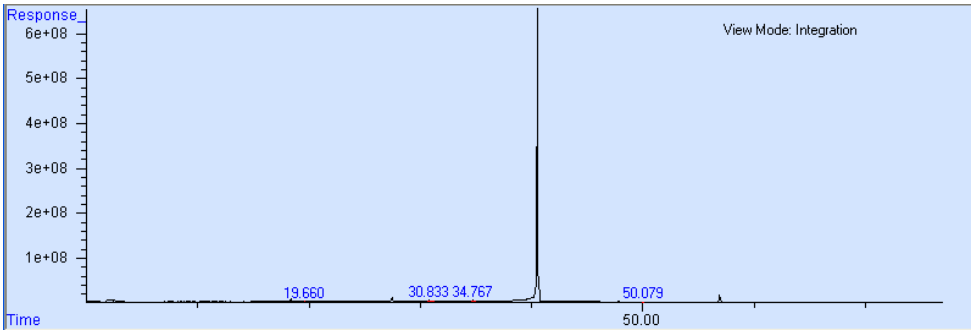

Figure B-18. GC-ECD chromatogram for select PCB congeners in the dead lower wood sample for Exposure 1

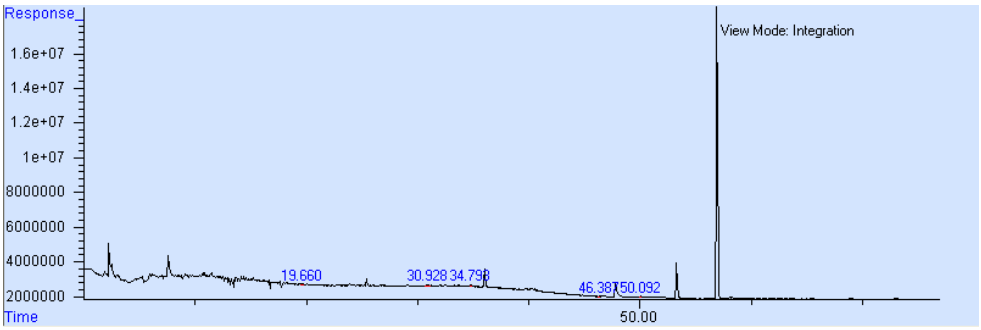

Figure B-19. GC-ECD chromatogram for select PCB congeners in the dead root sample for Exposure 1

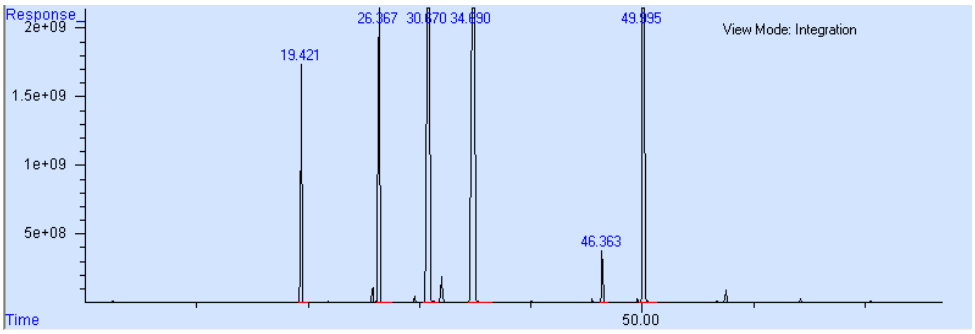

Figure B-20. GC-ECD chromatogram for select PCB congeners remaining in the inlet vial for the live plant sample for Exposure 1

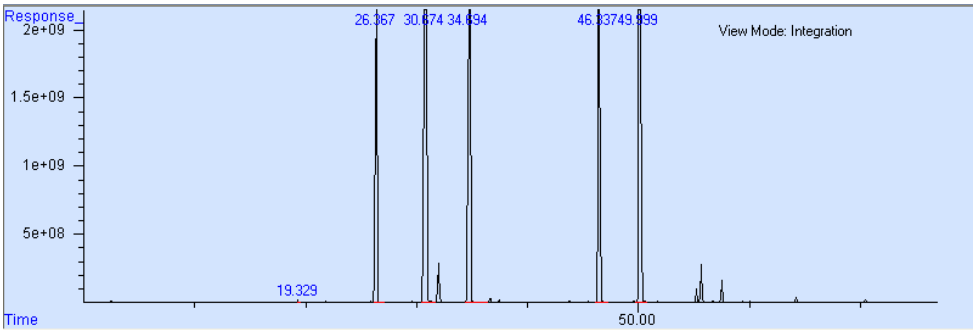

Figure B-21. GC-ECD chromatogram for select PCB congeners remaining in the inlet vial for the duplicate live plant sample for Exposure 1

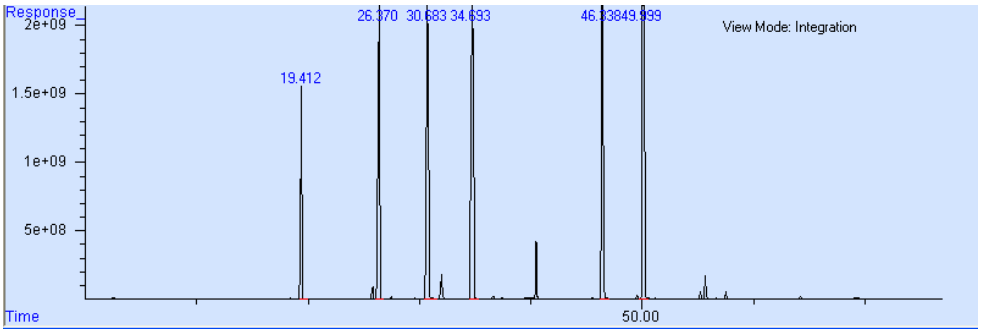

Figure B-22. GC-ECD chromatogram for select PCB congeners remaining in the inlet vial for the dead plant sample for Exposure 1

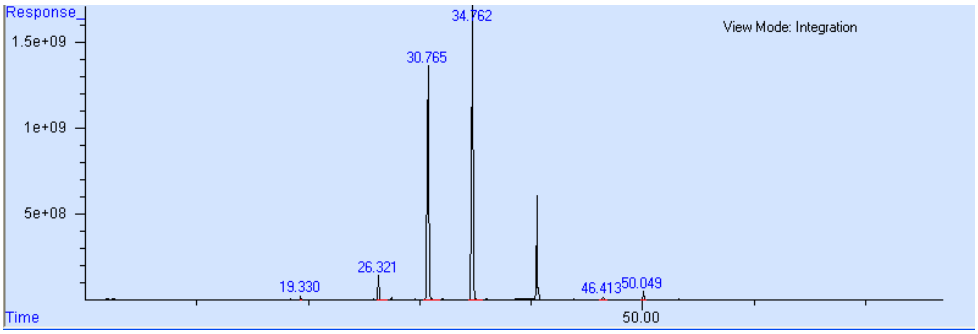

Figure B-23. GC-ECD chromatogram for select PCB congeners in the live leaf sample for Exposure 2

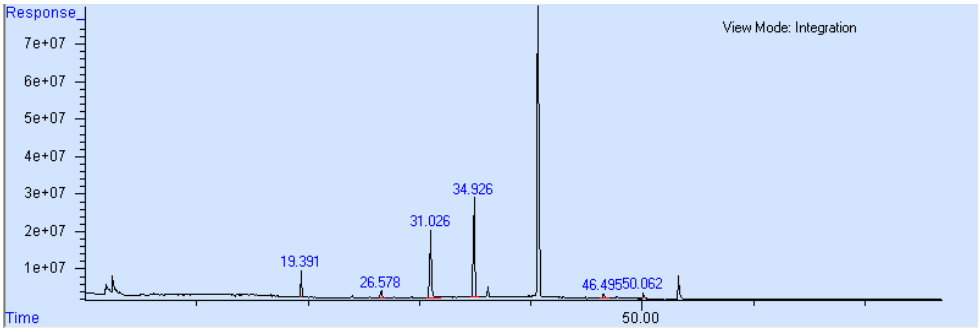

Figure B-24. GC-ECD chromatogram for select PCB congeners in the live secondary stem sample for Exposure 2

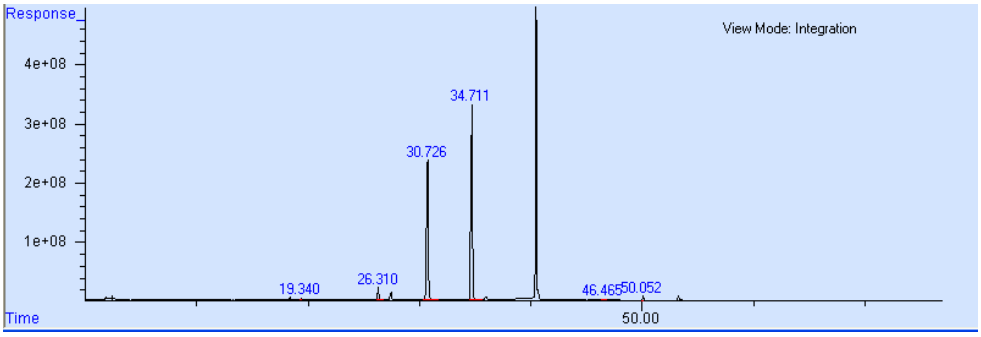

Figure B-25. GC-ECD chromatogram for select PCB congeners in the live upper bark sample for Exposure 2

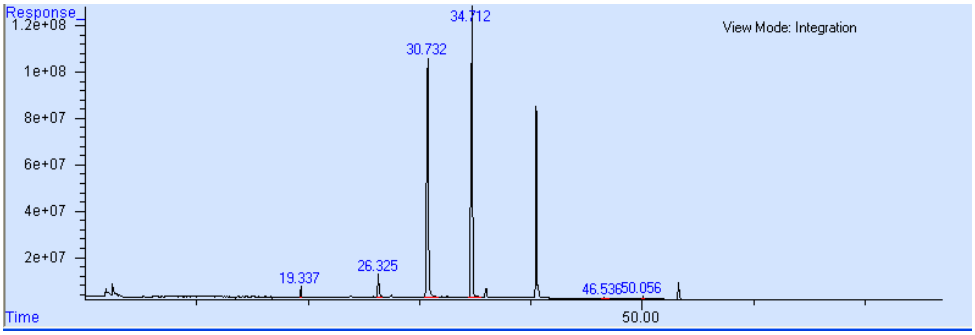

Figure B-26. GC-ECD chromatogram for select PCB congeners in the live upper wood sample for Exposure 2

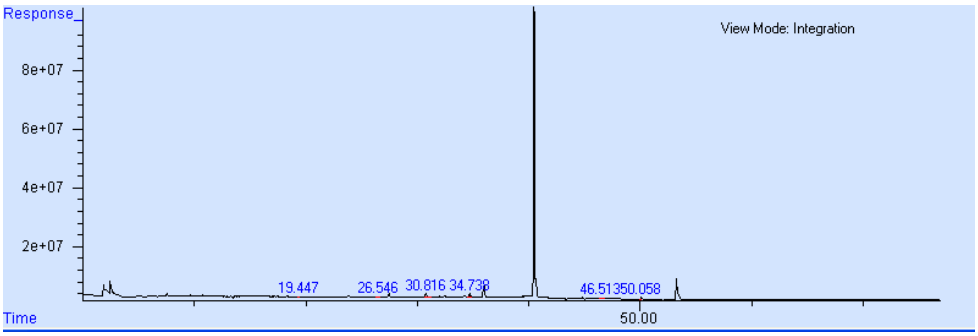

Figure B-27. GC-ECD chromatogram for select PCB congeners in the live lower wood sample for Exposure 2

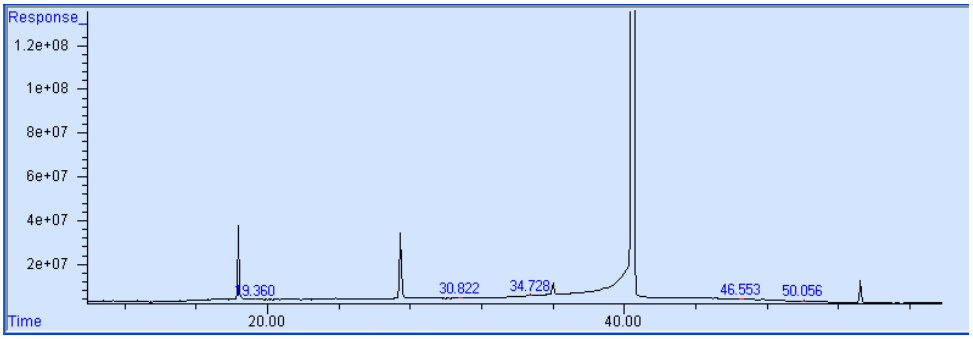

Figure B-28. GC-ECD chromatogram for select PCB congeners in the live root sample for Exposure 2

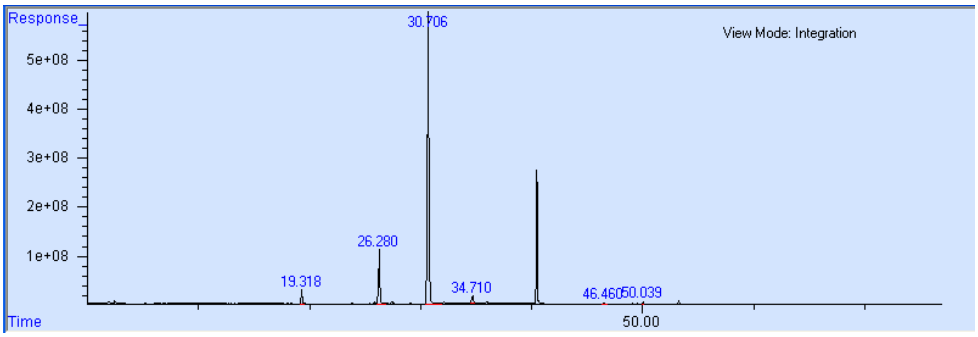

Figure B-29. GC-ECD chromatogram for select PCB congeners in the dead leaf sample for Exposure 2

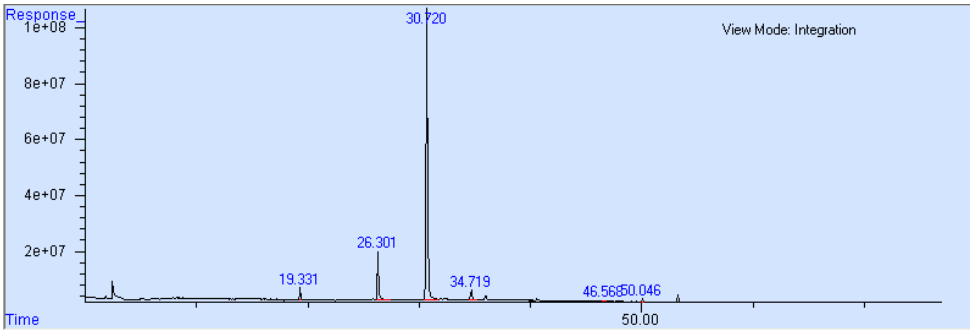

Figure B-30. GC-ECD chromatogram for select PCB congeners in the dead upper bark sample for Exposure 2

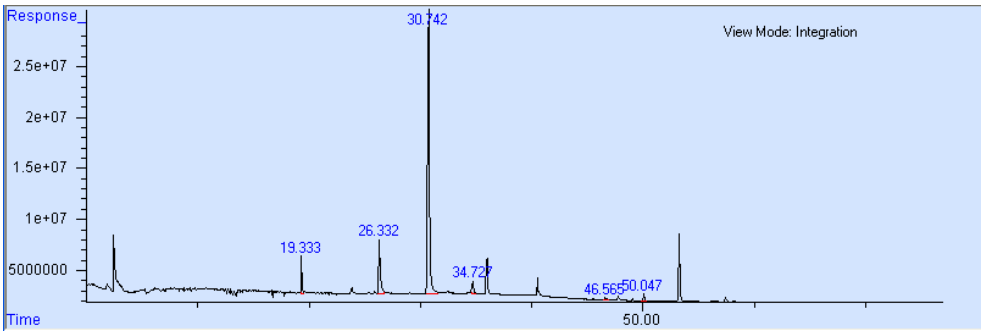

Figure B-31. GC-ECD chromatogram for select PCB congeners in the dead upper wood sample for Exposure 2

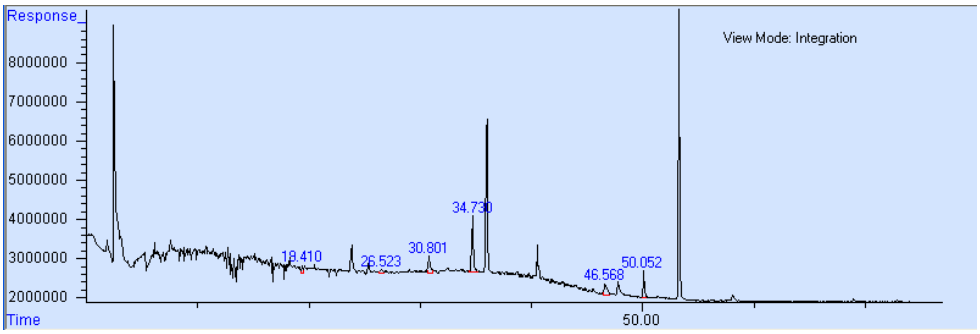

Figure B-32. GC-ECD chromatogram for select PCB congeners in the dead lower bark sample for Exposure 2

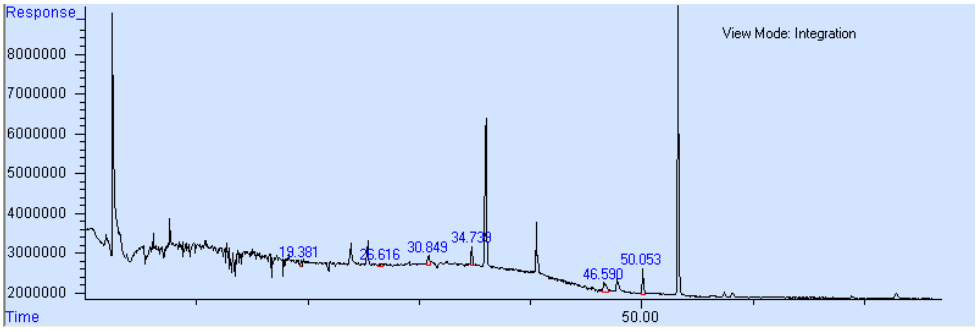

Figure B-33. GC-ECD chromatogram for select PCB congeners in the dead lower wood sample for Exposure 2

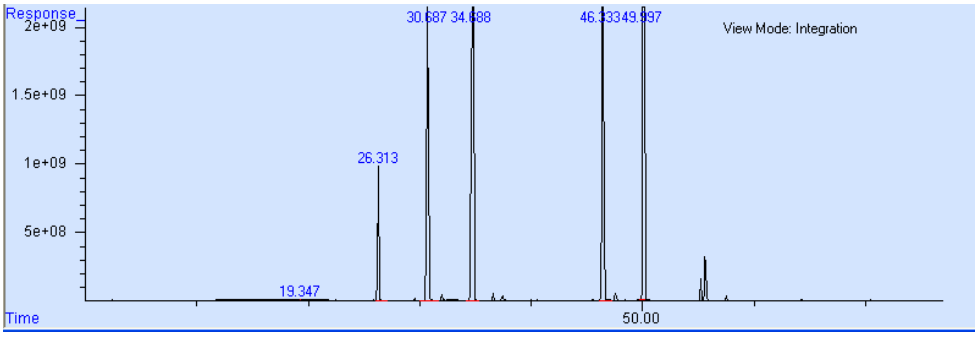

Figure B-34. GC-ECD chromatogram for select PCB congeners remaining in the inlet vial for the live plant sample for Exposure 2

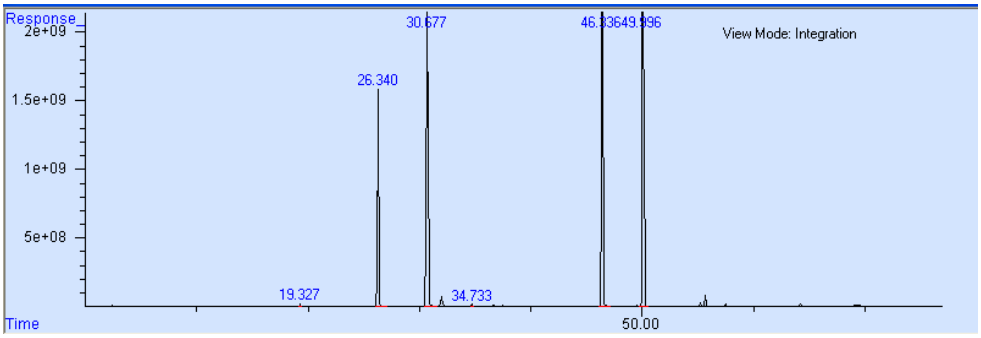

Figure B-35. GC-ECD chromatogram for select PCB congeners remaining in the inlet vial for the dead plant sample for Exposure 2

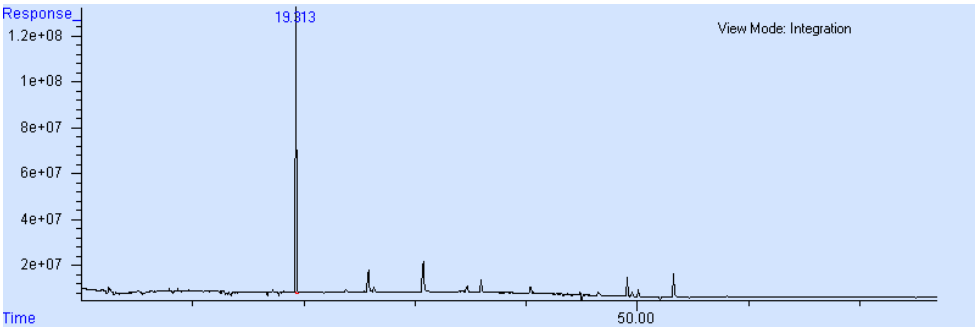

Figure B-36. GC-ECD chromatogram for PCB 3 in the leaf sample for Exposure 3

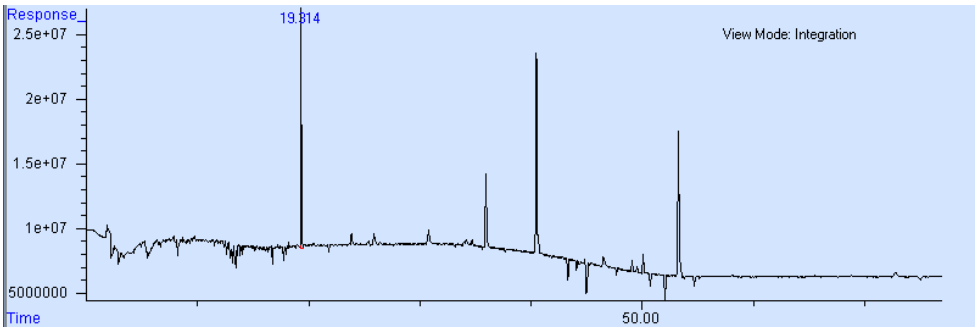

Figure B-37. GC-ECD chromatogram for PCB 3in the secondary stem sample for Exposure 3

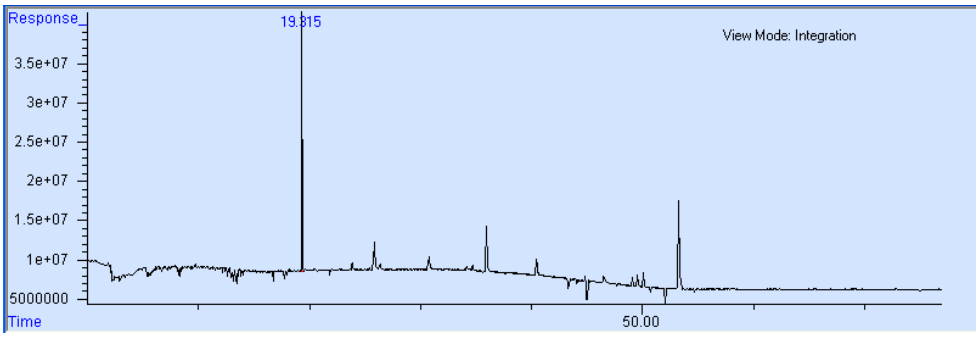

Figure B-38. GC-ECD chromatogram for PCB 3 in the upper bark sample for Exposure 3

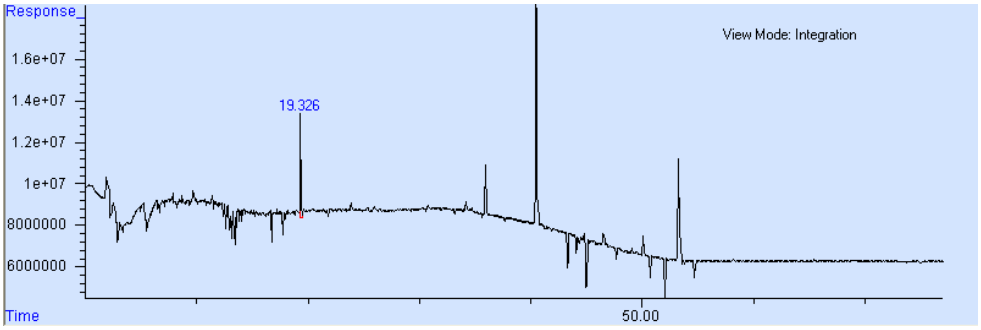

Figure B-39. GC-ECD chromatogram for PCB 3 in the upper wood sample for Exposure 3

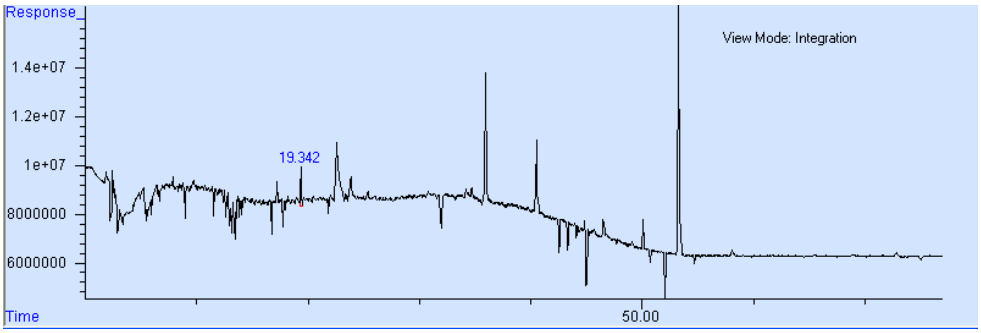

Figure B-40. GC-ECD chromatogram for PCB 3 in the lower bark sample for Exposure 3

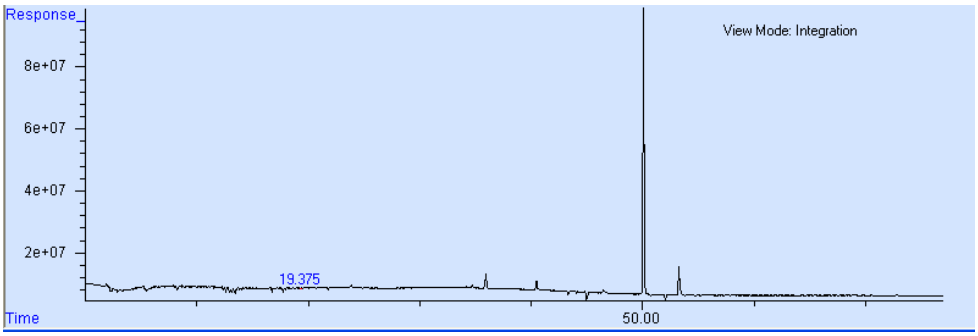

Figure B-41. GC-ECD chromatogram for PCB 3 in the lower wood sample for Exposure 3

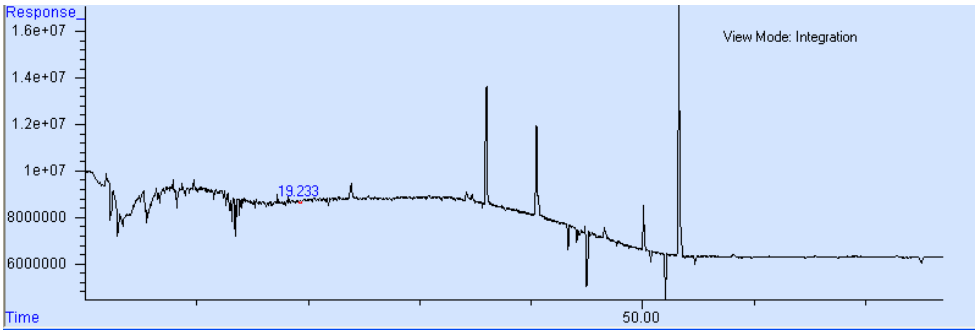

Figure B-42. GC-ECD chromatogram for PCB 3 in the root sample for Exposure 3

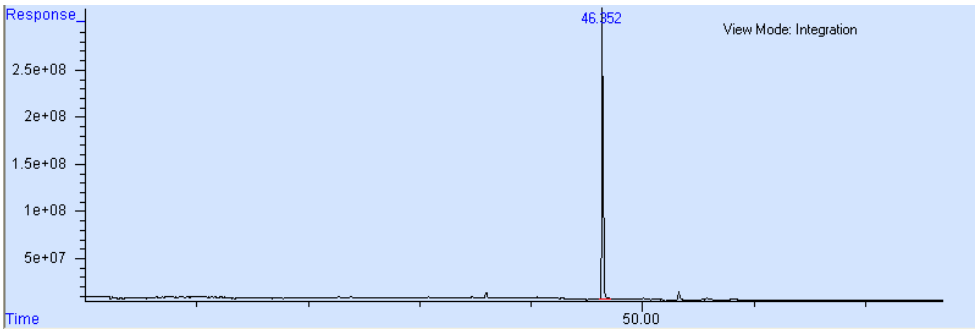

Figure B-43. GC-ECD chromatogram for PCB 77 in the leaf sample for Exposure 3

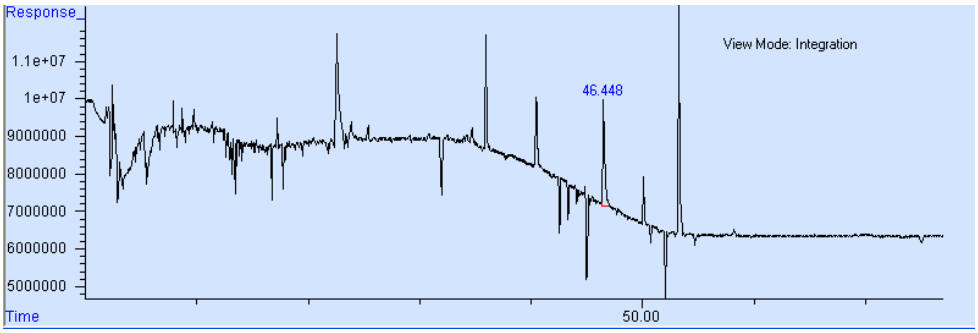

Figure B-44. GC-ECD chromatogram for PCB 77 in the secondary stem sample for Exposure 3

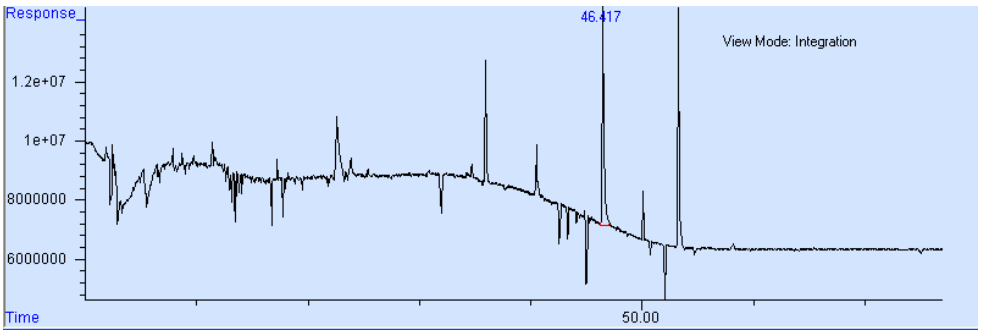

Figure B-45. GC-ECD chromatogram for PCB 77 in the upper bark sample for Exposure 3

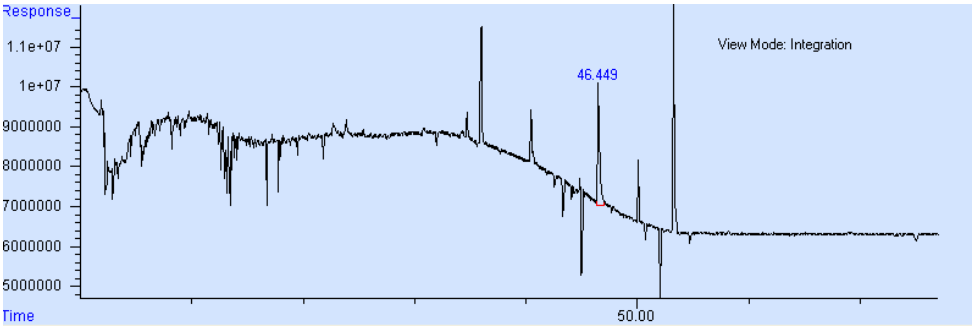

Figure B-46. GC-ECD chromatogram for PCB 77 in the upper wood sample for Exposure 3

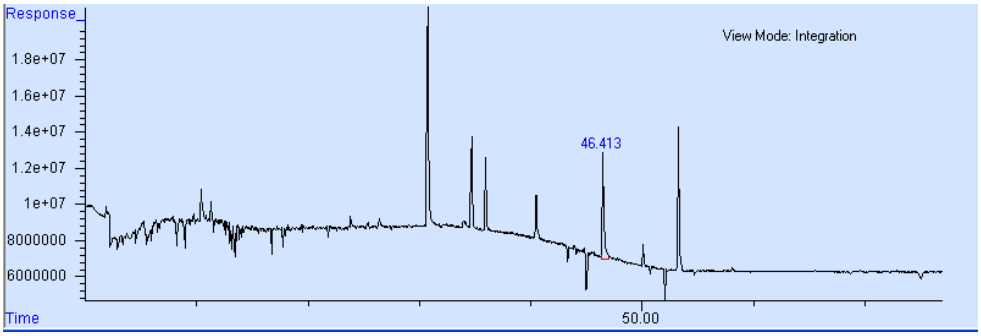

Figure B-47. GC-ECD chromatogram for PCB 77 in the lower bark sample for Exposure 3

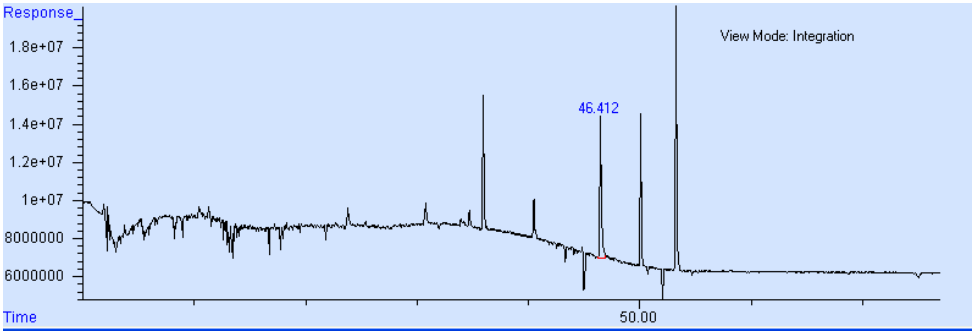

Figure B-48. GC-ECD chromatogram for PCB 77 in the lower wood sample for Exposure 3

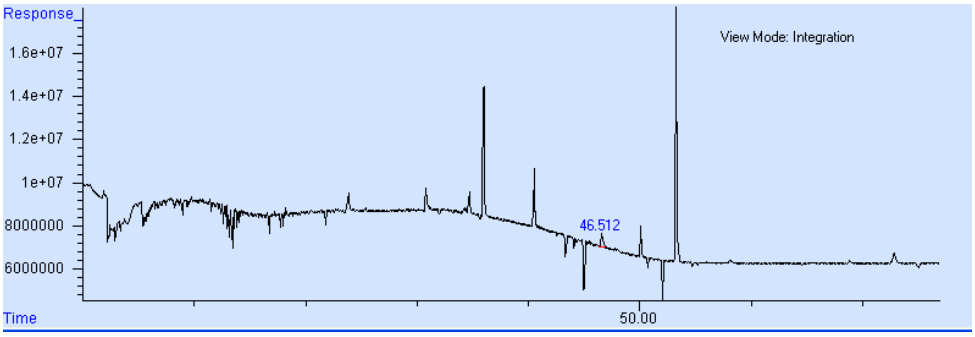

Figure B-49. GC-ECD chromatogram for PCB 77 in the root sample for Exposure 3