Spatial Distribution of Persistent Organic Pollutants in Surface Sediment Samples of Lake Huron

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LIST OF ABBREVIATIONS

ASE	Accelerated solvent extraction
ATBPE	allyl 2, 4, 6 - tribromophenyl ether
BB153	Hexabromobiphenyl
BDE	Brominated diphenyl ether
BTBPE	2, 4, 6 - tribromophenoxy ethane
COC	Chain of Custody
CB 52 L	Chlorinate biphenyls 52 labeled
CB 209 L	Chlorinated biphenyls 209 labeled
DBDPE	Decabromodiphenyl ethane
DCM	Dichloromethane (Methylene chloride)
DEC 602	Dechlorane 602
DEC 603	Dechlorane 603
DEC 604	Dechlorane 604
DP	Dechlorane Plus
ECNI	Electron captured negative ionization
EHTBB	2-ethylhexyl-2, 3, 4, 5-tetrabromo benzoate
EI	Electron ionization
EPA	Environmental Protection Agency
Field B	Field Blank
fsyn-DP	Syn fraction of Dechlorane plus
GB	Georgian Bay
GC	Gas chromatography

GLSSP	Great Lakes Sediment Surveillance Program
HBB	Hexabromobiphenyls
K_{ow}	Octanol-water partition coefficient
NC	North Channel
nXFR	Novel halogenated flame retardants
OC	Organic carbon
PB	Procedure blank
PBEB	Pentabromoethyl benzene
PBDE	Polybrominated diphenyl ether
PBT	Pentabromotoluene
PC	Principal component
PCA	Principal component analysis
PCB	Polychlorinated biphenyl
POPs	Persistent organic pollutants
RDP	Relative presence difference
QQQMS	Triple quadruple mass spectrometer
TBECH	Tetrabromoethyl cyclohexane
TCDD	2, 3, 7, 8– tetrachlorodibenzo–p–dioxin

SUMMARY

Polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and some alternative or "novel" halogenated flame retardants (nXFRs) are persistent organic pollutants found ubiquitously in various environmental matrices such as air, sediment, water, aquatic biota, and in humans. The Great Lakes of North America have been burdened with these industrial pollutants for decades. Sediments of the Great Lakes are contaminated, and may act as a reservoir and a secondary source long after these chemicals are phased out.

The purpose of this study was to determine the levels of selected PCBs, PBDEs, and nXFRs in the surface sediments of Lake Huron. To fulfill the objective, the following tasks were completed: (1) Collected surface sediment samples in Lake Huron, including the main lake, the North Channel and the Georgian Bay; (2) determined the concentrations of selected PCB congeners, PBDE congeners, and alternative halogenated flame retardants in collected samples; (3) statistically compared the measured concentrations among targeted PCBs, PBDEs, and other flame retardants, both as groups and as individual compounds; (4) statistically compared the measured concentrations of targeted chemical pollutants among the main lake, the Georgian Bay, and the North Channel, as well as individual sampling locations; and (5) identified potential sources of pollution based on the spatial distribution of the pollutant concentrations, in combination with available information obtained from the literature.

Surface sediment samples were collected from 59 locations of Lake Huron in 2012. Samples were extracted using accelerated solvent extraction (ASE). The extracts were cleaned up and fractionated with a silica gel / alumina adsorption chromatographic column. Concentrations were determined using gas chromatography (GC) coupled with a triple

SUMMARY (continued)

quadrupole mass spectrometer (QQQMS) for PCBs and PBDEs, and a single quadrupole mass spectrometer (MS) for decabromodiphenyl ether (BDE 209) and nXFRs.

Results show detectible levels of most PCBs, PBDEs, dechlorane plus (DPs), and dechlorane analogs. But lower detection rates were observed for most of the brominated non–PBDE flame retardants in Lake Huron surface sediment samples. The total PCB concentrations (Σ39PCB) were in the range of 0.05 to 91 ng/g with a median of 3.73 ng/g; and PCBs 138, 146, 153, and 110 are among the most abundant congeners. Total PBDE (Σ9BDE) concentrations varied from 0.04 ng/g to 54 ng/g; and BDE209 was the most abundant BDE congener, followed by BDE 47. The BDE 209 accounts for more than 92% of the total mass of the Σ9BDE**.** The detection rate of DP was higher than of other chlorinated flame retardants. Anti-DP was the most abundant compound in this chemical group. Other non- brominated flame retardants including 1, 2-bis (2, 4, 6-tribromophenoxy) ethane (BTBPE), hexabromobiphenyls (HBB), 2-ethylhexyl-2,3,4,5-tetrabromo benzoate (EHTBB), deca abromodiphenyl ether (DBDPE), pentabromotoluene (PBT), 2,2',4,4',5,5'-hexabromobiphenyl (BB153), allyl 2,4,6-tribromophenyl ether (ATBPE) were also detected at comparatively high levels.

Higher levels of PCBs were found in the sediments collected from Saginaw Bay than at other sampling sites, and the North Channel has the lowest PCB level. In contrast, halogenated flame retardants were found in higher concentrations in the samples collected in the North Channel. This suggests the presence of possible sources of pollution near the North Channel.

1. INTRODUCTION

1.1. <u>**Background**</u>

The Great Lakes of North America, the world's largest freshwater system, is comprised of Lakes Superior, Michigan, Huron, Ontario, and Erie along with the rivers and channels of their watersheds. The Great Lakes basin system is approximately 30,000 square miles. Lake Superior, the largest of the Great Lakes, forms the head of the water flow to Lake Huron. Lake Huron and Lake Michigan are at the same elevation. Water in Lake Huron further flows through the St. Clair River, Lake St. Clair, and the Detroit River into Lake Erie.

Lake Huron is the second largest of the Great Lakes, bound on the west by the state of Michigan (the United States) and on the north and east by the Province of Ontario (Canada). Many islands are in the northeastern part of the lake. Manitoulin Island and many others in Georgian Bay and the North Channel are examples. Georgian Bay is one of the largest bays of Lake Huron and contains thousands of islands collectively known as the "Thirty Thousand Islands." The North Channel, the northern arm of Lake Huron, is connected on the west with the St. Mary River and on the east with Georgian Bay. Many small islands lie within the channel. Saginaw Bay, the southwestern arm of Lake Huron in eastern Michigan, is popular for commercial fishing and summer recreation. A map of Lake Huron is shown in Figure 1.
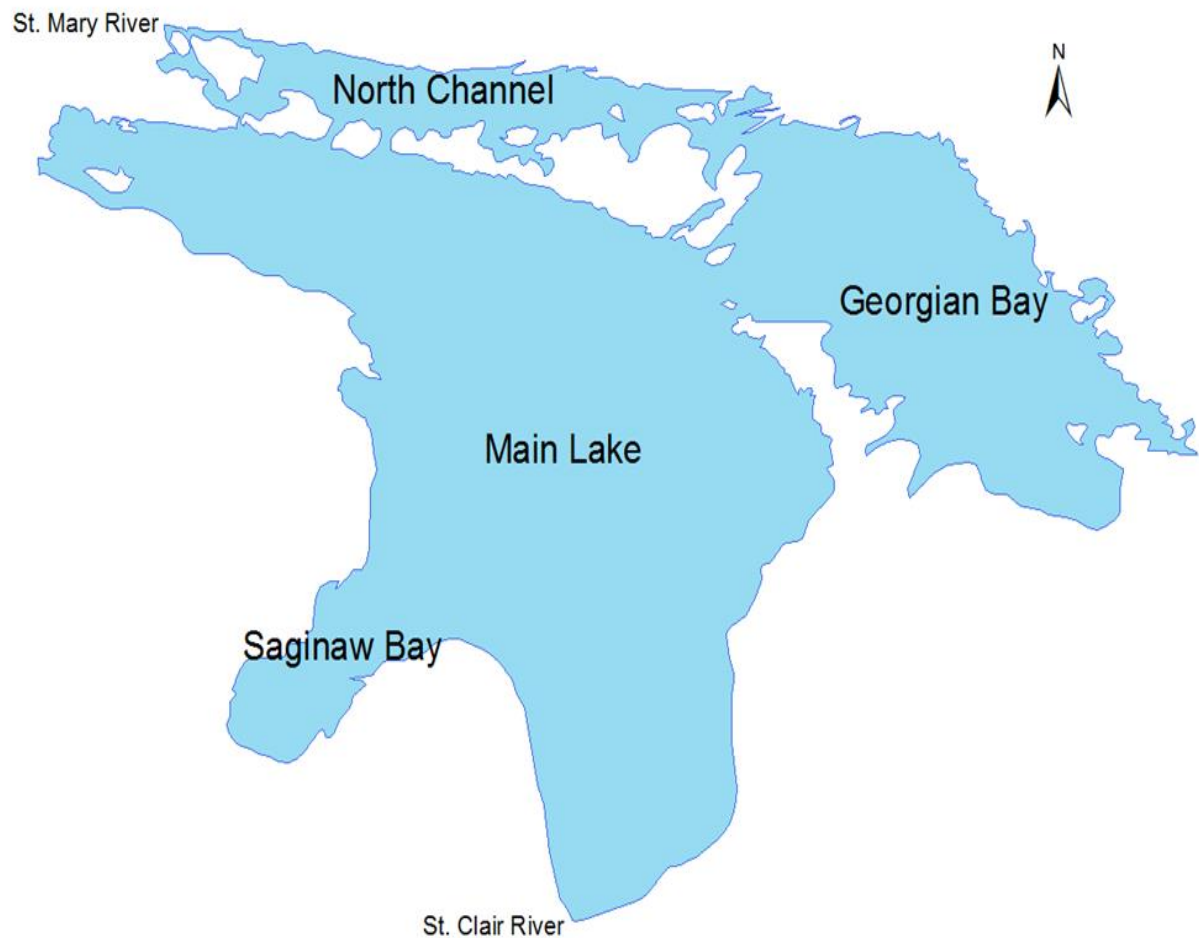
Figure 1. Map of Lake Huron.

The Great Lakes are home for more than thirty million people across the United States and Canada. The Great Lakes have been important to the economic and industrial development of the region. These developments have altered the ecosystem of the Great Lakes to some extent and in a variety of ways. Continuous loading of chemicals and nutrients have caused problems in the Great Lakes ecosystem for decades. The Great Lakes have been susceptible to the contaminant load due to their closed system, relatively long water retention time, low

sedimentation rate, low biological productivity, low suspended solid concentrations, and the heavy concentration of industries and large population centers surrounding the lakes. In addition, the large surface-area-to-volume ratio of the Great Lakes makes atmospheric deposition a major source of contaminants to the lakes' aquatic systems (Botts and Krushelnicki, 1995).

Concerns over adverse effects on contaminants were first officially addressed by the Great Lakes Water Quality Agreement of 1972, which was renewed in 1978, between the United States and Canada. Contaminated sediment and persistent toxic substances were among the topics of its annexes. In 1987, an amendment was added to the Clear Water Act (section 118 C), authorizing the US Environmental Protection Agency (EPA) to conduct five-year "project and demonstration projects" relating to treatment of toxic contaminant in sediments for the Great Lakes. The combination of performance of sewage treatment, agricultural, and industrial best management practices and the introduction of new laws prohibiting discharge of any pollutant from point source to the navigable water helped to control the pollutant levels in the Great Lakes to some extent. For an example, phosphorous burden has been notably reduced in the Great Lakes from its level in 1978 (EPA, 2012; Botts and Krushelnicki, 1995).

More than 360 chemicals have been detected in the Great Lakes (Botts and Krushelnicki, 1995); among them, persistent organic pollutants (POPs) are of high concerns. Plenty of research has been conducted over the years to investigate the contaminant levels in the Great Lakes system. Once the detected chemicals are found to cause ecological and human health problems, their manufacturing, application, and discharging are subjected to regulatory policies. Hence, there has been a decreasing trend of chemicals discharges into the Great Lakes over the last 20 years.

Persistent organic pollutants are resistant to degradation under environmental conditions and thus can remain in the ecosystem long after their productions and uses cease. Some POPs are hydrophobic, they thus accumulate in the sediments over time. When the input from primary sources such as direct discharges and atmospheric deposition is reduced, the contaminated sediment can become a reservoir and act as secondary source of contaminant. When the contaminant loading is low, sediment resuspension has been identified as a key process of introducing organic pollutants to the natural cycles (Warren et al., 2003).

A considerable amount of literature information on POPs in the Great Lake sediments is available through decades of monitoring and surveillance by various government agencies and research teams in the United States and Canada.

Since 2010, funded by a cooperative agreement with the EPA, Great Lakes National Program Office (GLNPO) under the Great Lakes Restoration Initiative (GLRI), a new project Great Lakes Sediment Surveillance Program (GLSSP) has been conducted by researchers at University of Illinois at Chicago and University of Saskatchewan (Saskatoon, Canada). The mission of this project is to identify and evaluate the presence of persistent, bioaccumulative and toxic chemicals and to reveal the spatial and temporal trends of persistent, bioaccumulative and toxic chemicals pollution in five Great Lakes by using surface and core sediment samples. Special emphasis is given to identifying the contaminants of emerging concern. The GLSSP has four basic steps including (1) collecting grab-and-core sediment samples in an approach of "one lake per year"; (2) characterizing the sediment samples for basic physicochemical parameters including solid content, bulk density, organic matter, organic carbon, soot carbon, and grain size distribution, and determining sedimentation rates for each core from the activity profiles of radioactive isotopes; (3) quantitatively analyzing selected persistent,

bioaccumulative and toxic chemicals organic compounds in the samples, and estimate the inventories, fluxes, and loads; and (4) identifying the research needs and conducting in-depth research regarding the sources, transport, and transformation of persistent, bioaccumulative and toxic chemicals.

The chemical pollutants targeted by the GLSSP include PCBs, polychlorinated dibenzo-*p*-dioxins and furans, polychlorinated naphthalenes, PBDEs, organochlorine pesticides, musk fragrance, and nXFRs.

1.2 **Specific Objective**

The objective of this project was to investigate the spatial distribution of PCBs, PBDEs, and alternative halogenated flame retardants in the surface sediments of Lake Huron. In order to accomplish this objective, the following specific tasks were performed:

1. Surface sediment samples were collected from 59 locations in Lake Huron, including the main lake, the North Channel, and Georgian Bay;

2. The concentrations of selected PCB congeners, PBDE congeners, and alternative halogenated flame retardants in collected samples were determined using a laboratory procedure previously developed;

3. Measured concentrations of targeted PCBs, PBDEs, and other flame retardants were statistically compared among chemical groups and as individual chemical compounds;

4. Measured concentrations of targeted PCBs, PBDEs, and other flame retardants were statistically compared among the main lake, Georgian Bay, and North Channel locations, and among individual sampling locations;

5. Potential sources of pollution were identified based on the spatial distribution of the pollutant concentrations, in combination with available information obtained the literature.

2. LITERATURE REVIEW

2.1   **Polychlorinated Biphenyls**

2.1.1   **Physical Properties**

Polychlorinated biphenyls (PCBs) are halogenated hydrocarbons with a biphenyl structure (two aromatic rings linked by a single carbon-carbon bond) in which some hydrogen atoms of the aromatic rings are replaced by chlorine atoms. The number of chlorine atoms range from one to ten and categorize PCBs into 10 homologs. Each homolog has a number of structural isomers with different arrangements of the chlorine atoms. Together, there are 209 congeners of PCBs. The general structure of PCBs is shown in Figure 2.
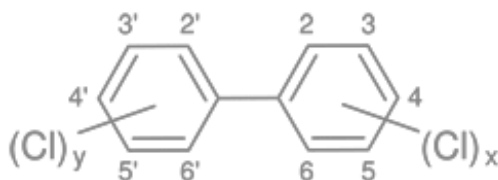
Figure 2. Chemical structure of polychlorinated biphenyls. The sum of x and y is ≤10.

Selected physicochemical parameters of PCB homologs are listed in Table I. Most PCB congeners are colorless, odorless crystals (Erickson, 2001), a few monochlorinated ones are liquids at ambient temperature. Volatility also depends on the degree of chlorination, and the vapor pressure increases as the number of chlorine atoms decreases. This affects the mobility of

PCBs in the environment, as heavily chlorinated congeners are less likely to travel far with air, and thus are more likely to be found near point sources.

All congeners of PCBs are lipophilic. Octanol-water partitioning coefficient (K_{ow}), which is the concentration ratio of a compound in solvents n-octanol and water at equilibrium, is relatively high (log K_{ow} ranging from 4.7 to 8.3) for the PCBs. High K_{ow} values indicate lipophilicity, which is related to bioaccumulation in biota and chemical affinity to organic-rich particles in soil and sediment. Higher chlorinated congeners tend to sorb more strongly to the particulate matter.

Because PCBs have low electrical conductivity and inflammability, they were used primarily as electric fluids in transformers and capacitors. Moreover, PCBs are highly resistant to chemical and thermal degradations. All these physicochemical properties are important in determining the transport and fate of PCBs in the environment.

TABLE I Source: Robertson and Hansen (2001) and Erickson (2001)

PHYSICAL AND CHEMICAL PROPERTIES OF PCB HOMOLOGS

Note: Data based on standard temperature (25°C)

Homolog group	Chemical formula	Molecular weight (g)	Number of isomers	Melting point temperature (°C)	Boiling point temperature (°C)	Vapor pressure (Pa)	Water solubility (g/m^3)	Log K_{ow}	Approximate BCF
Monochlorobiphenyl	$C_{12}H_9Cl$	188.7	3	25 –77.9	285	1.1	4	4.7	2500
Dichlorobiphenyl	$C_{12}H_8Cl_2$	223.1	12	24.4–149	312	0.24	16	5.1	6300
Trichlorobipenyl	$C_{12}H_7Cl_3$	257.6	24	28.87	337	.054	0.65	5.5	1.6×10^4
Tetrachlorobiphenyl	$C_{12}H_6Cl_4$	292.0	42	47–180	360	.012	0.26	5.9	4×10^4
Pentachlorobiphenyl	$Cl_{12}H_5Cl_5$	326.4	46	76.5–124	381	2.6×10^{-3}	.099	6.3	1×10^5
Hexachlorobiphenyl	$Cl_{12}H_4Cl_6$	360.9	24	77.150	400	5.8×10^{-4}	0.038	6.7	2.5×10^5
Heptachlorobiphenyl	$Cl_{12}H_3Cl_7$	395.3	42	122.4–149	417	1.3×10^{-4}	0.014	7.1	6.3×10^5
Octachlorobiphenyl	$Cl_{12}H_2Cl_8$	429.8	12	159–162	432	2.8×10^{-5}	5.5×10^{-3}	7.5	1.6×10^6
Nonachlorobiphenyl	$Cl_{12}H_1Cl_9$	464.2	13	182.8–206	445	6.3×10^{-6}	2.0×10^{-3}	7.9	4×10^6
Decachlorobiphenyl	$Cl_{12}H_{10}$	498.7	1	305.9	45	1×10^{-6}	7.6×10^{-4}	8.3	1.0×10^7

Physical appearances of pure PCB congeners vary from solid to liquid state. Chemical stability, dielectric properties, inflammability, and miscibility with organic solvents are some of the properties that lead to widespread utilization of PCBs in industries. They have been used as heat transfer fluids, hydraulic lubricants, dielectric fluids for transformers, capacitors, plasticizers, wax extenders, adhesives, organic diluents, deducting agents, pesticide extenders, cutting oils, carbonless reproducing papers and flame retardants (ATSDR, 2000; Jacobson et al., 1990, Erickson, 2001). Due to the high stability of the highly chlorinated PCBs and bioaccumulative properties, PCBs are widely distributed and transported in the environment, and residues will be found in air, water, aquatic sediments, fish and wild life, human adipose tissue, serum, and milk (Safe, 1983; Erickson, 2001). Hence, PCBs have become a continuing topic of concern and controversy, even though their production has been banned in 1977.

2.1.2 **Industrial Legacy and Regulations**

Although PCBs were first synthesized in 1881 (Djebbar et al., 2010), their commercial production did not start until 1929, when they were first manufactured commercially by the Anniston Ordnance Company, and later manufactured by the Monsanto Chemical Cooperation (Risebrough et al., 1970; USEPA, 1979; Cairns et al., 1981). The Monsanto PCB mixtures were sold under the trade name of Aroclor. These were complicated mixtures; each spanning several homologs and having unique congener compositions (Solla and Martin, 2008; Erickson, 2001). The production of PCB was estimated to be more than 1 million tons, of which 60% was Aroclor (Robertson and Hanson, 2001). The second manufacturer in United States was the General Electric Company, which marketed their products under the trade name of Pyranol (ATSDR, 2000). Those PCBs manufactured in other countries were called Clophen (Germany),

Fenclor (Italy), Kanechlor (Japan), and Phenoclor (France) (Erickson, 2001). Table II shows the common commercial mixtures, manufacturing countries, and their equivalencies among the formula.

In the United States, PCB production peaked in the 1960s. Due to the toxic potential of PCBs, manufacturing was halted in 1977 in the United Sates (EPA, 1979). Regulation of PCBs started in 1976 with the Toxic Substances Control Act, which gave the EPA authority to monitor the manufacture, use, disposal, and chemical use of PCBs in the United States. A number of regulatory bodies have been involved in monitoring PCBs globally. Table III presents the regulatory laws of PCBs in the United States. Levels of PCBs are declining globally due to cessation of production and the regulatory measures on emission and disposal.

TABLE II

COMMERCIAL MIXTURE OF PCBs

Aroclor	Cophen	Phenclor	Pyralene	Kenechlor	Fenclor	Delor	Average number of chlorine molecule	chlorine content % by weight	Approximate molecular weight (g/mole)
1221							1.15	21	93.1
1232			2000	200			2	32–33	223
							2.5	38	240.3
1242,1061	A 30	CP 3	1500	300	42	2	3	40–42	275.5
1248	A 40	DP 4	3000	400		3	4	48	291.9
1254	A 50	DP 5		500	54	4;5	5	52–54	326.4
1260	A 60	DP 6		500			6-6.3	60	366
1262				600	64		6.8	62	388.4
							7.7	65	419.4
1268					70		8.7	68	453.8
							9.5	70	481.7
1270					DK		10	71	498.6

Source: Erickson, 2001

Note that any producers made equivalent products, such as: Arochlor 1232, Pyralene 2000 and Kenachlor 200.

2.1.3 **Environmental Discharge and Transport**

One of the most ubiquitous organic pollutants, PCBs have been found in air, water, soil, and sediment (Covaci et al., 2004; Risebrough et al., 1976; Fein et al., 1984). They enter the environment during the process of manufacturing, use, and disposal. Since PCBs are highly lipophilic substances, more than 99% of them are found in the soil (Erickson, 2001). However, volatilization of PCBs from the landfills, spills, oils, contaminated soils, and other sources may contribute to measurable amounts in the atmosphere.

Once the PCBs are released to the environment, they are not readily degradable and will remain in the environment for a long time cycling through the air, water, and sediment. The mode of transport in the environment is complex. Vaporized PCBs are particularly adsorbed on particulates and transported with wind, and may deposit on land or water by gravitational setting or rainout. Eisenreich (1987) revealed that the atmospheric pathway contributes to 60%−90% of the PCB load to the Great Lakes. They have been found in places far away from points of release, such as the polar regions (Hansen, 2009; Li et al., 2010). Environmental transport has caused uniform distribution of PCBs in Northern and Southern Hemispheres. Several heavily contaminated areas, such as New Bedford Harbor, Massachusetts; Hudson River in New York State; and Yusho, Japan, had point sources with intensive emissions. In contrast, nonpoint sources have been identified to dominate the input of PCBs into the Great Lakes (Samara et al., 2006).

The PCBs in water are sorbed by waterborne particles or benthos, and deposit to the bottom sediments. The PCBs in sediments may redissolve into the water or be taken up by benthic organisms, thus entering food chains and cycling among environmental matrices. The

PCBs in sediments may also diffuse into deeper sediments and buried. Less research has been conducted regarding PCB levels in macrophytes, though rooted macrophytes can absorb PCBs from the lower sediment layer. Lower chlorinated congeners will be readily absorbed by the plants and also enter the food chains (Hansen, 1999).

2.1.4 **Environmental Degradation of Polychlorinated Biphenyls**

Although PCBs are very stable, they are subjected to chemical, photochemical, and biological transformation processes. The atmospheric half-life for the photodegradation depends on the number of chlorine atoms present in the molecule. Tri-CBs have a half-life of about three days while hepta-CBs have a half-life of 500 days. The other homologs are in between these two extremes. In practice, PCBs have 10 to 20 years of half-life in the environment. According to Erickson (2001), tri-CBs have a half-life of three years and hepta-CB 38 years in soil and sediment.

Dechlorination is an important process of creating lower chlorobiphenyls from more heavily chlorinated congeners. Anaerobic degradation due to microbial activity is a major dechlorination process taking place in deep sediments. Microorganisms partially dechlorinate the higher chlorinated congeners to the lower chlorinated congeners. In natural conditions, microbial degradation is very slow and incomplete. Under aerobic conditions, however, the lower chlorinated congeners are fully degraded to carbon dioxide and water (Erickson, 2001).

TABLE III

ENVIRONMENTAL REGULATIONS OF PCB IN USA

Law	Agency	Topic	Key Features
Toxic Substances Control Act	United States Congress	New and legacy toxic substances in the environment	Gave the authority to EPA to administer the production, use, and disposal of PCBs.
Occupational Safety and Health Act	OSHA	Worker exposures to PCBs	Permissible Exposure Limit for Aroclor 1242 is 1 mg/m^3 (42% chlorine) and 0.5 mg/m^3 (54% chlorine) as an 8-hour time-weighted average, with skin notation.
Clean Water Act	EPA	Discharge limits for actions that affect surface water	Discharge of more than 10 pounds of PCB s within a 24-hour period must be reported. The water quality criterion for chronic exposure through drinking water and fish ingestion is 80 pg/L (0.00008 ppb) based on an excess cancer risk of 10^{-6}.
CERCLA and SARA	EPA	Cleanup of toxic or hazardous waters at closed or abandoned dumpsites	Cleanup to be approached on–site. A remedial investigation/feasibility study will design the remedy based on cleanup levels needed and available alternatives.
RCRA	EPA	Handling storage and disposal of hazardous waste.	PCBs and PCB-contaminated materials (e.g., mineral oils) can be classified by EPA as hazardous wastes. The RCRA also requires a response to imminent hazards created by the handling, storage, transport, treatment, or disposal of any solid waste.
Food, Drug, and Cosmetic Act	EPA	Poisonous and deleterious substances, including environmental contaminants in the food supply.	Milk, eggs, other dairy products; poultry, fat fish, shell fish, and infant food cannot contain more than 0, 2–3 ppm of PCB s (lipid basis) to protect from noncancer harmful effects.
Safe Drinking Water Act	EPA	Maximum contaminant level and maximum contaminant level goals are established	For PCBs the MCL of 0.5 ppb was proposed in May 1989.
Clean Air Act	EPA	Air emission from mobile and stationary sources	Contaminants are designated and regulated by defining a list of 189 hazardous air pollutants, one of which is polychlorinated biphenyls "Aroclors."

Source: Erickson, 2001; www.cdc.gov

2.1.5 **Exposure and Toxicity of Polychlorinated Biphenyls on Humans**

Humans are exposed to PCBs in various ways. Consumption of contaminated fish and other food is the main exposure pathway (Alock, 1998). Children can be exposed to PCBs prenatally across the placenta and postnatally via lactation (ATSDR, 2000; Jacobson et al., 1990; Carpenter et al., 2006; Gasull et al., 2011). However, lactation will reduce the body burden of the mother but increase exposure of the child to PCBs.

The toxicology of PCBs has been extensively studied using animal models as well as in the epidemiological studies (Erickson, 2001; ATDSR, 2000). Acute and chronic toxicity can be exerted by PCBs, and the toxic effect differs among congeners, depending on chemical structure. Coplanar PCBs have no more than one chlorine at the ortho (2) positions, and thus can get closer to being a "flat" molecule. Among coplanar PCBs, 12 have chlorines at both para (4, 4') positions and 2 to 4 chlorines at meta (3, 5, 3', and 5') positions for a total of at least 4 chlorines in the molecule. They therefore resemble 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (TCDD) in molecular shape, and thus are commonly known as dioxin-like PCBs. The PCB toxicity is described by the Toxicity Equivalence Factor (TEF), which normalizes the toxicity of dioxin-like PCBs to the toxicity of 2,3,7,8-TCDD. The TEF value therefore indicates the relative magnitude of toxicity. The total toxic equivalent, is the product of the mass of compound ingested and the TEF value, and may be summed across multiple congeners.

Animal studies to investigate the health effects of PCBs suggest as possible effects immune suppression, low birth weight, birth defects, and kidney and liver carcinogenicity in most of the rats, mice, and rabbits (Cogliano, 1998). Exposure to PCB also can increase the risk of liver, cardiovascular and diabetics. An epidemiological study carried out with capacitor manufacturing workers revealed that the mortality of liver, gallbladder, and biliary cancers; gastrointestinal cancer and malignant cancer had been increased (Cogliano, 1998). Initial evidence of teratogenicity comes from the studies of the Japanese and Taiwanese pregnant woman who accidently ingested PCB-contaminated oil (Jacobson et al., 1990; Huang et al., 2007).

Exposure to PCB during fetal and early life leads to reduced IQ, low birth weight, sluggishness, clumsy and jerky movements and altered behavior through alteration of the immune system (Fein et al., l984). Chronic exposure of children in utero to PCBs brings about detrimental health consequences, such as neurodevelopment deficiencies. That may result in reduced reflexes and muscle tone, rather than poor memory (Wigle et al., 2007; Jacobson et al., 1990).

The EPA has listed PCBs as probable carcinogens, since there are incidences of cancer risk in animals as well as humans who are exposed to PCBs in occupational settings (USEPA, 2012), and recently developed a cancer slope factor for PCBs. In 2013, the International Agency for Research on Cancer reassessed the carcinogenicity of PCBs, and classified them as carcinogenic (Group 1) to humans (Lauby-Secretan et al., 2013).

2.1.6 **Exposure and Toxicity of Polychlorinated Biphenyls on Wildlife**

Aquatic organisms accumulate PCBs by way of the water column, from interstitial sediment waters, and by consumption of contaminated diet. Marine mammals are the most susceptible organisms for PCBs. Adverse effects on reproduction of aquatic organisms may occur at PCB concentrations of 5 µg/L or less (Mayer and Stallinng, 1974). Exposure to PCBs causes direct effects on breeding and developmental effects on embryos. The effects on embryos include mortality or reduced hatchability, wasting syndrome, and teratological effects and impaired differentiation of the reproductive and nervous systems through mechanisms of hormonal mimicking of estrogens (Fry, 1995).

Leg abnormalities were observed in 19% of colonial birds of the lower Great Lakes. Subcutaneous edema in cormorants and gastroschisis in terns were the most common abnormalities in eggs (Gilbertson et al., 1973). In addition, one study observed high mortality rates of Atlantic salmon embryos in hatcheries exposed to higher PCB levels (Jensen et al., 1970).

2.1.7 **Sediment Loads of Polychlorinated Biphenyls in the Great Lakes**

Since PCBs were banned in the 1970s, unintentional environmental release has continued, but declined. Contaminated sediment is now considered a secondary source of environmental release of PCBs. In 1968, PCBs were first found in the Great Lakes (Li et al., 2008) and it was estimated that 58%−97% of the total PCB burden in the Great Lakes in the 1980s was in sediments (Eisenreich, 1981). Table IV shows the PCB levels in the sediment samples of the United States.

TABLE IV

PCB LEVELS IN SEDIMENTS OF UNITED STATES

Location	Mean PCB concentration (ppb)	Year	Reference
Lake Ontario	57	1974	Frank et al., 1976
Houston ship channel	4.18–460		Howell, 2008
	136	1971	
Lake Erie	43	1997	Painter, 2001
	19	1970	
Lake St. Clair	10	1974	Frank et al., 1977
Lake Huron	13		Frank et al., 1979

There is a decreasing trend of PCBs in sediments with time across the Great Lakes.

Hickey et al. (2005) showed that average concentrations decreased from 23,000 ng/g in 1975 to

1800 ng/g in 1998. According to Marvin (2003), average sediment PCB levels of Lake Erie

were found to have decreased roughly 70% from 136 ng/g in 1971 to 43 ng/g in 1997. In

addition, more than 30% of total PCB reduction has been observed in the Great Lakes since

1980s (Li et al., 2009).

2.2 **Chlorinated Flame Retardants**

The idea of flame retardants runs back to about 450 BC, where the Egyptians used alum

to reduce the flammability of wood. The Romans (about 200 BC) used a mixture of alum and

vinegar to reduce the combustibility of wood (Alaee et al., 2003).

Today, there are 175 synthetic flame retardants that can be classified as (1) halogenated

organics (brominated or chlorinated), (2) phosphorous containing, (3) nitrogen containing, and

(4) inorganic flame retardants (Birnbaum and Staskal, 2004; Alaee, 2003). In the present study

we focus on few of those halogenated organic flame retardants.

2.2.1 **Dechlorane Plus**

Dechlorane Plus (DP) is a highly chlorinated cycloaliphatic flame retardant (Kang et al.,

2010; Gauthier and Letcher, 2009). It was manufactured in the mid-1960s as a substitute for the

flame retardant dechlorane, which is the same chemical as the pesticide Mirex, and was

produced by the Diesels Alder condensation of hexachlorocyclopentadiene and 1, 5-

cyclooctadiene in a 2:1 molar ratio. This reaction yields syn- and anti- DP at a 1:3 isomer ratio.

Figure 3 shows the molecular structures of syn-DP and anti-DP. An additive flame retardant,

DP can be found in electric wires, cable coatings, computer connectors, and plastic roofing

materials. Annual production exceeds 10 million pounds and DP has been sold throughout the

world (Gauthier and Letcher, 2009; Kang et al., 2010; Feo et al., 2012; Sverko et al., 2009).
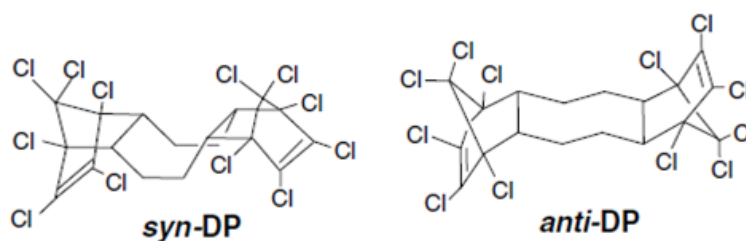
Figure 3. Syn and anti-isomers of DP. Hydrogen atoms are omitted for the clarity of the
diagram.

Dechlorane plus is a white, crystalline, odorless, powder, with a molecular weight of 654 daltons. There is a lack of measured physicochemical property data for DP and its analogs. Therefore, quantitative structure-activity relationship models were used to determine water solubilities, vapor pressure, and octanol water partitioning coefficient (Feo et al., 2012; Sverko et al., 2011). Due to its thermal stability, photochemical stability, lower density, and lower cost, DP is more advantageous than other brominated flame retardants (Feo et al., 2012). Physicochemical parameters of DP are shown in Table V.

TABLE V

PHYSICOCHEMICAL PARAMETERS OF DP

Property	DP
Chemical formula	$C_{18}H_{12}Cl_{12}$
Molecular mass	653.7
Melting point(^{0}C)	206
Vapor pressure (Pa)	4.71×10^{-8}
Density (g/cm^3)	1.8
Water solubility (ng/L)	0.04
Log K_{ow}	9.0
Log K_{aw}	-3.24
Log K_{oa}	12.26

Source: Feo et al., 2012

Attention to DP has been increasing after it was detected in the sediments of the Great Lakes (Hoh et al., 2006). It has been found in all the environmental matrices such as air, sediment, fish, and aquatic birds especially in the Great Lakes area and in China (Kang et al., 2010; Qiu et al., 2007; Sverko et al., 2008; Hoh et al., 2005). In a few studies, DP was also

detected in Spain and the Atlantic, and was also detected in air samples from Greenland to

Antarctic. These studies suggest that DP is a global contaminant (Moller et al., 2010).

2.2.1.1   **Sediment Load of Dechlorane Plus**

Studies of DP in sediment and aquatic and terrestrial biota have concentrated on

the Great Lakes or the urban areas of China.

Dechlorane Plus has been detected in the Great Lakes sediment samples (Yang et al.,

2011; Hoh et al., 2006; Sverko et al., 2007; Qiu et al., 2007; Sverko et al., 2009; Tomy et al.,

2007; Shen et al., 2009; Sverko et al., 2011; Li et al., 2008). Among the Great Lakes, DP levels

are highest in Lake Ontario (Sverko et al., 2007; Qiu et al., 2007), which may be due to the

presence of a DP manufacturing plant in Niagara Falls, New York (Hoh et al., 2006). It was

also detected in studies conducted in most of the other areas of the world including China (Qi et

al., 2010; Zhao et al., 2011; Chen et al., 2011). High levels of DP in the sediment were found in

samples collected near manufacturing facilities in China (Wang et al., 2010; Feo et al., 2012).

2.2.1.2   **Bioaccumulation of Dechlorane Plus**

Bioaccumulation factor and biota sediment accumulation factor are commonly

used to measures bioaccumulative properties of organic contaminants in aquatic organisms.

Bioaccumulation of DP depends on species and location. One study suggested that DP levels of

lake trout collected from Lake Ontario were lower than 1 ng/g lipid while those from Lake Erie

had DP levels ranging from 0.1 ng/g to 1.0 ng/g lipid. The levels of DP in aquatic organisms

collected from some places in Asia are much higher than in the fish from the Great Lakes.

Terrestrial birds and their eggs have been studied for years to investigate the contamination of

the terrestrial food webs (Sverko et al., 2011). Levels of DP in these falcon eggs from Spain and Canada were 0.8–25 ng/g lipid and 38–65 ng/g, respectively (Guerra et al., 2010).

Different isomers of DP have different levels of biomagnification potentials in the aquatic food webs (Feo et al., 2012). It was found that the anti-DP isomer dominated in the higher trophic levels and syn-DP dominated in the lower trophic levels (Tomy et al., 2007).

2.2.1.3 **Dechlorane Plus on Humans**

Studies on DP levels in humans are scarce. Ren et al. (2009) presented serum concentration levels of DP in two cohorts of electronic waste recycling workers in the Southern China and their fishing community that is 50 km away from the electronic waste recycling plant. The mean DP concentration was 39.8 ng/g lipid weight (lw) for the workers and 11.9 ng/g (lw) for the fishing community. Moreover, human hair samples were studied in urban and rural areas of southern China for DP levels. The levels were 15 folds higher concentration in urban workers hair than the rural ranging 1.46 -58.3 ng/g lw and 0.09- 8.38 ng/g (lw) respectively. Further, DP was reported in breast milk in two Canadian cities, with a mean 0.98 ng/g (lw) and a range from the detection limit to 8.0 ng/g lw with a mean value of 0.98 ng/g (lw) (Feo et al., 2012; Zheng et al., 2010).

There is very limited information about the toxicity of DP on aquatic and terrestrial organisms. However, low toxicity was documented for fish as well as rats. There is no observed cytotoxicity or embryonic vitality in domestic chickens at concentrations 10 times higher than was detected in the herring gulls of the Great Lakes (Feo et al., 2012).

2.2.2. **Dechlorane Plus Analogs**

Dechlorane analogs have a similar chemical structure to DP and were developed to improve the fire retardant properties of polymers in the late 1960s and 1970s. Very little information is available on the production and application of these compounds. The formation of the dechlorane analogs is shown in Figure 4. However, DEC 602 and DEC 604 was used in fiber glass-reinforced Nylon-6 at 18% and Molykote AS 810 silicone grease, respectively. There is no information on application of DEC 603 (Feo et al., 2012; Shen eta al., 2011).

There is little information on the physicochemical parameters of dechlorane analogs. Table VI shows the physicochemical parameters of the dechlorane plus analogs.

Table VI

PHYSICOCHEMICAL PROPERTIES OF DECHLORANE PLUS ANALOGS

Property	DEC 602	DEC 603	DEC 604
Chemical formula	$C_{14}H_4Cl_2O$	$C_{17}H_8Cl_{12}$	$C_{13}H_4Br_4Cl_6$
Molecular mass	613.6	637.7	692.5
Melting point (°C)	190	198	203
Vapor pressure (Pa)	5.53×10^{-8}	1.59×10^{-7}	8.47×10^{-8}
Density (g/cm3)	Not found	Not found	Not found
Water solubility (ng/L)	8.49	0.30	2.21
Log K_{ow}	7.1	8.5	8.5
Log K_{aw}	-5.21	-3.37	-4.70
Log K_{oa}	12.27	11.83	13.22

Source: Feo et al., 2012
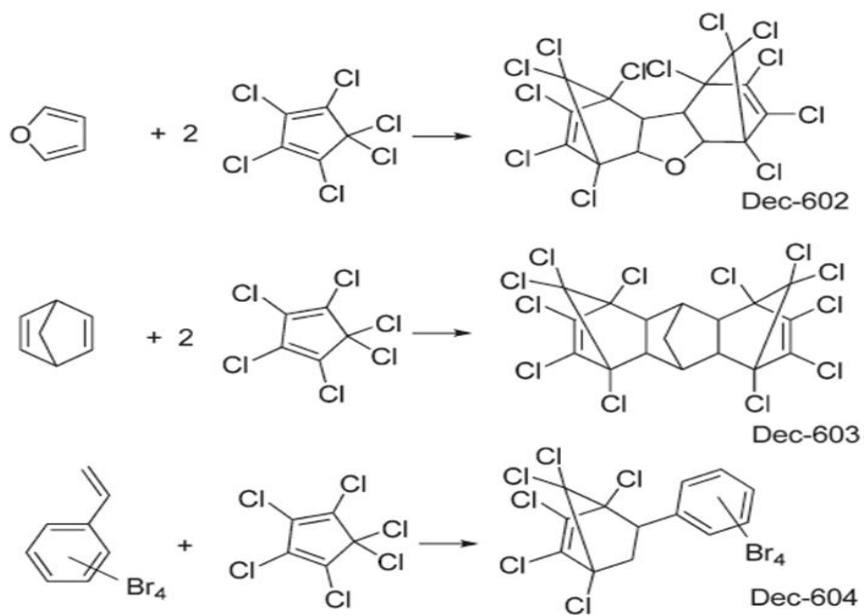
Figure 4. Formation of DEC 602, DEC 603, and DEC 604

(Figure Source: Sverko et al., 2011).

There are limited publications reporting the concentrations of DP analogs in the aquatic and terrestrial organisms. Results are summarized in Table VII.

Table VII

DEC 602, DEC 603, DEC 604 LEVELS OF AQUATIC AND TERRESTRIAL ORGANISMS
(unit ng/g lw)

Species		Area	DEC 602 Mean (range)	DEC 603 Mean (range)	DEC 604 Mean (range)
Aquatic Biota	Lake Trout	Great Lakes	0.47-34	0.014–0.55	(0.063–1.3)
	Oyster	Northern China	0.21	0.12	-
	Franciscan dolphin	Southeastern and	0.38 (0.12–0.94)	0.75(0.25–1.99)	-
	Peregrine falcon (eggs) terrestrial	Canada	89.2 (44–211)	43.9 (12–220)	3.70 (1.4–9.8)
		Spain	9.78 (nd-–15)	2.33 (1.5–6.2)	0.33 (ND–0.35)
Terrestrial biota	Peregrine falcon (eggs) (aquatic)	Canada	27.4 (7.2–104)	12.4 (5.3–29)	2.13 (1.3– 3.5)
		Spain	13.3 (ND–-25)	4.91 (3.0–7.5)	0.18 (ND–0.32)

Source: Feo et al., 2012

Note: ND non detected—no information available.

2. 3 **Brominated Flame Retardants**

2. 3. 1 **Polybrominated Diphenyl Ethers**

2. 3.1.1 **Physical and Chemical Properties**

One of the most widely distributed flame retardants, PBDEs have both domestic and industrial applications. At present, PBDEs are ubiquitous and found in both abiotic and biotic environment (Alaee et al., 2003).

Polybrominated diphenyl ethers were produced by bromination of diphenyl ether in the presence of a Friedel–Craft catalyst in the presence of dibromomethane (Alaee et al., 2003). Structurally, PBDEs bear some similarities to PCBs. However, the two aromatic rings are bridged by an ether oxygen atom. Ten homologous and 209 congeners differ by the number and

the arrangement of the bromine atoms. Physical and chemical properties of PBDEs (Table VIII) depends on the presence of the Bromium atom in ortho, para, or meta position; they are not planar since two phenyl rings can rotate at the oxygen atom and are twisted approximately perpendicularly (Wang et al., 2005). The general structure of PBDEs is shown in Figure 5.
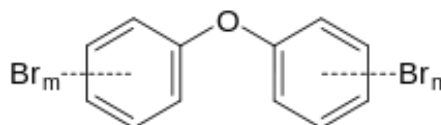
Figure 5. General structure of PBDEs

Table VIII

PHYSICOCHEMICAL PROPERTIES OF SELECTED PBDE CONGENERS

Congeners	No. of Br atoms	Molecular Weight (g)	Melting point (^{O}C)	Water solubility (mg/L)	Log K_{OA}	Log K_{ow}	Vapor pressure (Pa)
BDE 28	3	406.9	64	7×10^{-1}	9.46	5.94	2.19×10^{-3}
BDE 47	4	485.8	84	1.5×10^{-2}	10.53	6.81	1.86×10^{-4}
BDE 66	4	485.8	N/A	N/A	N/A	6.90	N/A
BDE 85	5	564.7	123	7.86×10^{-5}	11.66	7.37	5.11×10^{-5}
BDE 99	5	564.7	92	9.4×10^{-3}	11.32	7.32	1.76×10^{-5}
BDE 100	5	564.7	100	4×10^{-2}	11.18	7.24	2.09×10^{-6}
BDE 153	6	643.6	162	8.7×10^{-4}	11.86	7.90	2.09×10^{-6}
BDE 154	6	643.6	132	8.7×10^{-4}	11.93	7.82	$3.80 \times 10\text{-}6$
BDE 183	7	722.5	172	1.5×10^{-3}	11.96	8.27	4.68×10^{-7}
BDE 209	10	959.2	~300	1.3×10^{-8}	N/A	8.70	5.42×10^{-11}

[a]Tittlemier et al., 2002; Chen et al., 2003; Wania and Dugani, 2003; Guan et al., 2009.
[b]K_{oa} = n-Octanol-air partition coefficient at 25 °C.
[c]K_{ow} = Octanol-water partition coefficient at 25 °C.

2.3.1.2   **Industrial Legacy and Application**

In 1970, industrial use of PBDEs started as a flame retardant. Production and use of PBDEs had increased over time and peaked in the late 1990s. The global demand for PBDEs was approximately 40,000 tons and 70,000 tons in years 1992 and 1999, respectively (Sjodini et al., 2003; BSEF, 2000). Table IX shows the world market demand for some of the three major commercial mixtures of PBDEs.

Table IX

WORLD MARKET FOR THE THREE MAIN COMMERCIAL PBDE MIXTURES

(unit tons)

Compound	America	Europe	Asia	Total
Deca BDE	24,300	7500	23,000	54,800
Octa BDE	1,375	450	2,000	3,825
Penta BDE	8,290	210	-	8,500

Source: www.BSEF.com: All data are in metric tons

Three commercial mixtures are manufactured: a penta BDE mixture, an octa BDE mixture, and a deca BDE mixture. Trade names for penta BDE mixture are DE-60F, DE-61, DE-62, and DE-71. The trade name DE-79 was for the Octa BDE mixture and the trade names DE 83R, Saytex 102E for DEC a BDE mixture. The Albermale Cooperation and Chemtura

Cooperation marketed PBDEs in the United States. In year 2004, Penta-BDE and Octa-BDE were voluntarily withdrawn from the US marketplace by the manufacturers due to their possible environmental and health consequences.

Some PBDEs were used in wide variety of products like furniture, upholstery, electrical equipment, electronic devices, textiles, and other household products (ATSDR, 2004; EPA 2012; EPA OPPT 2010). Since PBDEs are additive flame retardants, they can be easily emitted during the lifetime of the products containing them. Major sources of PBDEs to the environment include effluents and emissions of PBDE production, as well as textile industries and electrical appliance manufacturing. They have been found in household dust (Wei et al., 2009; Watanabe and Sakai, 2003). Further, recycling, land filling, and incineration of products that contain PBDEs introduce PBDEs to the environment.

2.3.1.3   **Polybrominated Diphenyl Ethers in Environment**

There are plenty of studies of sediment levels of PBDEs in various water bodies around the world. Many studies reported that BDE209 accounted for greater than 90% of the total PBDEs in sediments, including those in the Great Lakes (Song et al., 2004, 2005a, 2005b; Li et al., 2006a, 2006b; Zhu et al., 2005).

In addition, PBDEs have been reported in algae, invertebrates, and in fish (Darnerud, 2003). In the bass collected from the Detroit River, BDE 47 accounted for 76% of the total PBDE mass and the other congeners like BDE 99, BDE 100, BDE 153, and BDE 154 were also found. In contrast, carp from the Des Plaines River near Chicago showed the hepta congeners (BDE 181, BDE 183, and BDE 190). In addition, BDE 47 represented approximately 50% of the total PBDE in Northern California followed by 30% of the BDE 100, and 10% of each of

the following BDE congeners BDE 99 and BDE 154 and traces of BDE 153 (Birnbaum and

Staskal, 2003).

Congener patterns of PBDEs differ among environmental matrices such as air, soil,

sediment, and sludge (Birnbaum and Staskal, 2003). According to Dewit (2002), lower

brominated congeners are more bioaccumulative than the higher brominated compounds.

However, higher brominated compounds are not transported long distances due to their low

water solubility and vapor pressure. Due to their high hydrophobicity, higher PBDEs in natural

waters tend to accumulate in the sediment, especially at locations near point sources (Watanabe

et al., 2003; Wong et al., 2001). It is reported that higher levels of lower brominated congeners

are more likely to be found in biota while the higher brominated congeners are in the sediment.

2.3.1.4 **<u>Human Exposure to Polybrominated Diphenyl Ethers</u>**

Humans are exposed to PBDEs via dietary intake, dust inhalation, (Wei et al.,

2009) and skin contact. Dietary intake accounts for a significant part of the total exposure and

most comes from meat, fish, and dairy products. Inhalation of PBDE-contaminated dust is also

a significant source of exposure, and could outweigh dietary intake.

The levels of PBDE in the serum of the US population are monitored by the Centers for

Disease Control, and the results are published in the National Health and Nutrition Examination

Survey. The continuous production of PBDE in North America caused widespread

contamination of the environment, thereby increasing human exposure. Occupational exposure

to PBDEs has been reported for those working in PBDE production, or recycling or disposal of

PBDE-containing products. Levels of PBDEs were significantly higher in workers in such jobs

as computer dismantling and rubber manufacturing as well as in computer technicians

(Darnerud, 2003).

In several studies, PBDEs have been found in breast milk from mothers representing the

general population (Schecter et al., 2004). The concentration of PBDEs in human breast milk

was 34 ppb in Texas in 2002 and median values for BDE 47 and BDE 99 were 18 ppb and 6

ppb respectively (Birnbaum and Staskal, 2003). There is a tendency for PBDE to transfer via

the placenta and breast milk from mother to children.

2.3.1.5 **Toxicity of Polybrominated Diphenyl Ethers**

There are observed effects of PBDEs on the endocrine system, the nervous

system, sexual maturation and function, metabolism, and overall homeostasis since PBDE is

structurally similar to the natural hormones and will easily bind to the endocrine

EDC/receptors. The major impact of PBDEs is on thyroid glands. The chemicals alter

thyroglobulin antibodies and the thyroid hormone thyroxin. By altering thyroid function,

PBDEs affect liver function. Specifically, penta BDE will affect sexual development and sexual

dimorphic behavior by delaying puberty in males and decreasing follicle formation in females.

In vivo experiments suggested that PBDE exposure can lead to cytotoxic effects that increase

apoptosis by arresting P53, and the necrosis of tissues. It is expected that congeners with lower

bromination are expected are relatively carcinogenic.

There is a great impact on prenatal exposure of PBDEs on the nervous system, creating

issues with memory and learning. Research on animal models suggests that BDE 209 can cross

the placenta. A strong correlation between elevated PBDE levels in breast milk and

cryptorchidism in newborns has also been observed (Main et al., 2007).

2.3.2 **Polybrominated Biphenyls**

Polybrominated biphenyls (PBBs) are identical in molecular structure to their

chlorinated counterpart, PCBs, except that the Chlorine atoms in PCBs are replaced by

Bromine atoms. The general structure of PBBs is shown in Figure 6. In the early 1970s, PBBs

were introduced as a flame retardant and marketed under the trade name "Fire Master BP-6"

(Kay, 1977), in which 2,2',4,4',5,5'-hexabromobiphenyl (BB 153) was the major component.

Attention of PBB was drawn due to the incidence of unintentional mixing of Fire Master BP-6

into the cattle feed in Michigan (Di Carlo et al., 1978; Hardy, 2002; Kay, 1977). Even though

this led to banning the hexabromobiphenyl (HBB), octa and deca bromobiphenyls were

continued to be produced until 1979 in the United States. A mixture of PBBs was produced in

Germany until 1985 and in France until 2000.
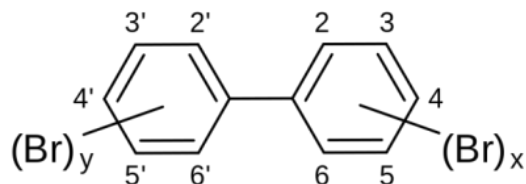
Figure 6. General structure of PBB.

In the Great Lakes region, the major PBB manufacturer was Velsicol Chemical

Corporation in St. Louis, Michigan. HBB has heavily contaminated the sediments of the Pine

River, which bordered the Velsicol plant and flows into the Saginaw Bay of Lake Huron

(USEPA, 1997). This could be a significant point source of PBB contamination to the Great

Lakes, particularly Lake Huron. Yang et al. (2012) found location HU-12 had HBB concentrations and inventory an order of magnitude higher than all the other 15 sites they sampled across the Great Lakes.

Studies have been conducted on the sediment and aquatic biota of the Great Lakes for PBB levels. One such study reported that the concentration of PBB in water fowl found in Green Bay, Michigan was 50 ng/g wet weight. This concentration is similar to some of the concentrations found in the fish of Saginaw Bay, but higher than concentrations found in lake trout sampled from the Lake Huron (Hites, 2005). However, there is no increasing or decreasing trend observed in herring gull colonies of Lake Huron from the peaks observed in year 2005 (Gauthier and Letcher, 2009).

2.3.2 **Toxicity of Polybrominated Biphenyls**

Similar to PCBs, co-planar PBBs are more toxic than other PBBs. Toxicity of PBB has been studied using rat, mice, and rabbit models. The PBBs interact with thyroid hormone and decrease the serum T3 and T4 (Darnerud, 2003). They also alter the levels of steroid hormone and vitamin A. There is a significant effect on liver cells: liver enlargement, hepatocyte swelling and vacuolation, and single-cell necrosis; hepatocarcinoma has often been observed as well. With respect to wildlife, one study reported that egg production and hatchability were affected at 30 mg PBB/kg feed in hens (Darnerud, 2003). One other study conducted using the same species suggested that exposure to PBBs would increase mortality, reduce growth rates, and cause embryonic death. Low levels of HBB have been observed in herring gull eggs across the Great Lakes (Gauthier and Letcher, 2009). These results would be interpreted either as

evidence of low bioaccumulation of the chemical due to high molecular weight, or low permeability of the chemical across the egg membrane.

There are two epidemiological studies of the effects of PBBs on humans (Darnerud, 2003; IPCS, 1994). No specific relationship was observed between abnormalities, disease frequencies, and the level of exposure to the chemical in the Michigan incident (Darnerud, 2003). In contrast, a Wisconsin study showed increased incidence in neurological and musculoskeletal symptoms with PBB exposure (Darnerud, 2003). Neither studies showed dose response with the serum PBB levels and the prevalence of the symptoms.

2.3.3 <u>**Decabromodiphenyl Ethane**</u>

Introduced in the early 1990s (Wu et al., 2012; Kierkegaard et al., 2004; Ricklund et al., 2008), DBDPE is a high production volume flame retardant (Gauthier and Letcher, 2009a, 2009b) that is marketed as a replacement and alternative to the decaBDE commercial mixture (Hu et al., 2010; Kierkegaard et al., 2004). It is highly brominated, highly hydrophobic, and thermally labile (Gautheir, 2009). The structure of the DBDPE is shown in Figure 7.
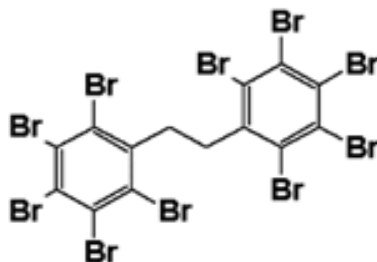
Figure 7. Structure of DBDPE.

There is limited information about DBDPE in the environment compared to other flame retardants. However, DBDPE was recently reported in abiotic environments such as sediment, air, and dust samples from an electronic recycling facility, tree bark collected in Arkansas, and house dust samples (Venier and Hites, 2008; Li et al., 2008; Kierkegaard et al., 2004; Ricklund et al., 2008; Hu et al., 2010; Zhu and Hites et al., 2004; Stapleton et al., 2008; Wu et al., 2011). Regarding the bioaccumulation of DBDPE, there have been no observed levels in planktons or mussels, but surprisingly it was detected in predator fish such as walleyes.

Toxicity data on DBDPE are limited. However, oral toxicity of DBDPE in rats is low because of the poor bioavailability, large molecular weight, and log P_{ow} (Hardy et al., 2002; Hu et al., 2010).

2.3.4 **1, 2-Bis (2, 4, 6-tribromophenoxy) Ethane**

An additive flame retardant, BTBPE has been used widely as a substitute for octa BDE. It is marketed as FF-680 by Chemtura Corporation in Arkansas, USA (Covaci et al., 2011). The structure of BTBPE is shown in Figure 8. Its major application is on thermoplastic and thermoset systems (WHO 1997; Covaci et al., 2011).
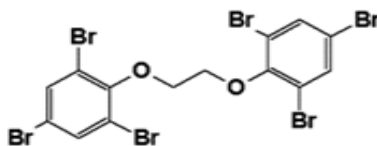
Figure 8. Structure of BTBPE

In addition, BTBPE has been found in various abiotic and biotic matrices such as sediment, household dust, and gull eggs. The presence of BTBPE in herring gull eggs reflects dietary

exposure via fish. The potential uptake of BTBPE via the aquatic food web was studied using juvenile rainbow trout. There is evidence of rapid degradation/depuration of BTBPE. Another study, conducted by Lewis (2009) using the herring gull population in Lake Huron, shows that the presence of the chemical in herring gulls started in 2002 suggesting it is a relatively recently produced flame retardant compared with PBDE.

3. MATERIALS AND METHODS

3.1   __Method Background__

3.1.1   __Sediment Sampling__

Lake Huron sediment sampling was conducted in 2012 with two separate trips on the EPA research vessel *Lake Guardian*. A total of 59 surface sediment samples were collected at 59 locations in Lake Huron, including the main lake, Georgian Bay, and the North Channel (Figure 9). The selected sampling locations included 10 regularly used EPA stations. Additional stations were selected to provide relatively even geographical distribution. Both near-shore and open-water sites were included.

The main basin of Lake Huron was sampled from September 14–19, 2012. A total of 30 locations were planned before the trip. Three other locations (SOTXD, SOTXM, and SOTXS) were added while onboard. Six planned Ponar grab stations (H105, H116, H117, H120, H121, and H122) were not sampled due to weather conditions. Surface sediments were collected at 27 sites (Figure 9 green circles and red squares). Table X summarizes the basic sampling information.

Another trip was made from October 4–7, 2012, to collect the surface sediment samples in Georgian Bay (GB), the North Channel (NC) and Thunder Bay (TB). A total of 15 locations were selected before the trip, including eight in GB and four in NC, as well as three sites missed in the September trip (H116, H117, and H121). With 23 sites being added during the trip and four planned sites dropped due to weather conditions, a total of 32 Ponar grab samples were successfully collected at the locations marked in Figure 9 (green triangles) and are summarized in Table XI.
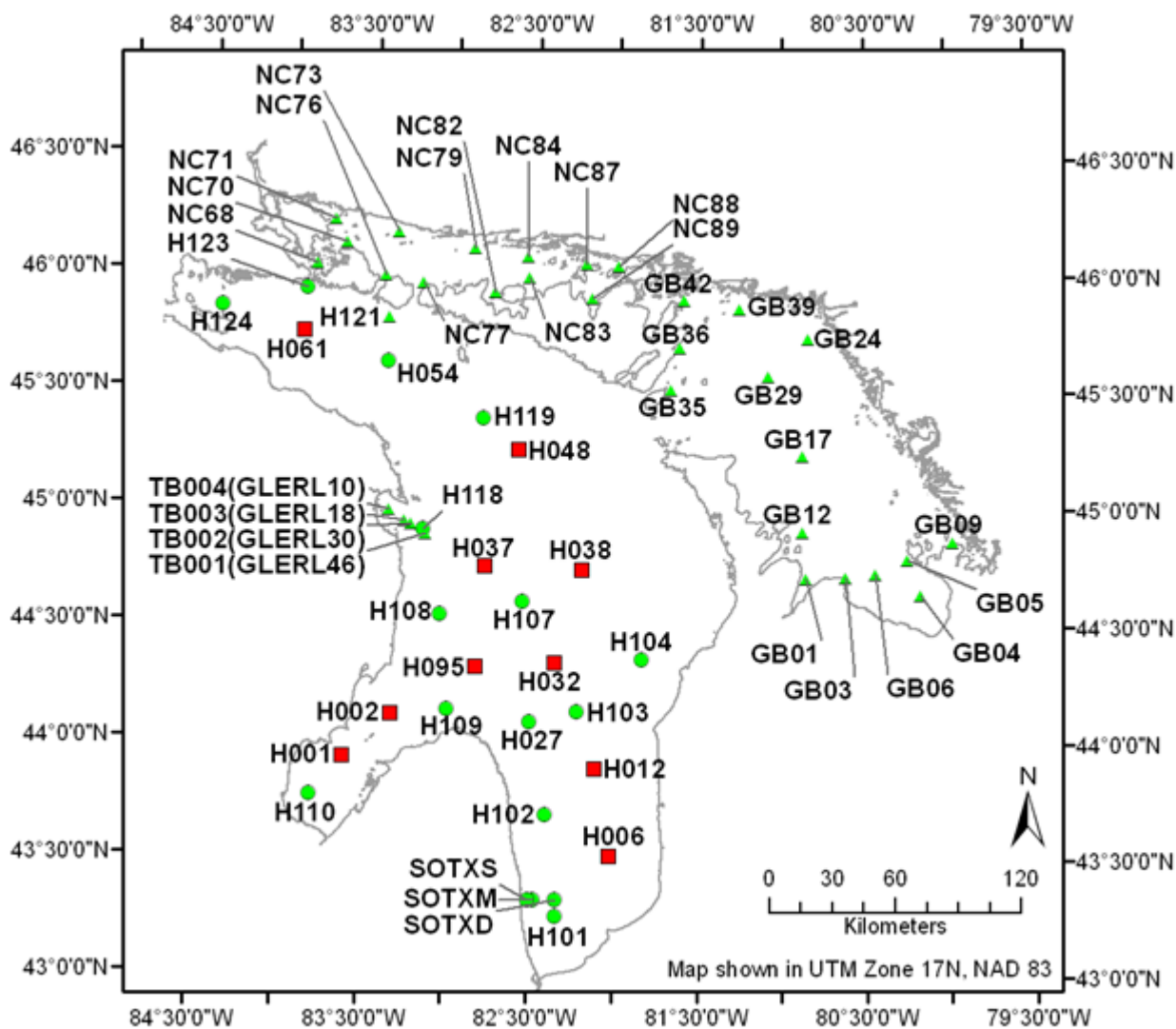
Figure 9. Lake Huron sediment sampling locations. Green dots and triangles: only Ponar surface grab samples were collected. Red squares: both Ponar grab surface samples and cores were collected. The map was created by Mr. Colin Smalley of the UIC Department of Earth and Environmental Sciences.

Table X

SAMPLING INFORMATION FOR THE MAIN BASIN OF LAKE (SEPTEMBER 14–19, 2012)

Location	Sample	Date Time CDT [1]	Latitude[2]	Longitude[2]	Depth(m) [3]
H101	PG	9/15/2012 14:14	43.2690	- 82.3349	31
SOTXD	PG	9/15/2012 14:45	43.3399	- 82.3335	37
SOTXM	PG	9/15/2012 16:09	43.3398	- 82.4668	19.6
SOTXS	PG	9/15/2012 16:57	43.3397	- 82.4991	12.1
H006	PG, MC	9/15/2012 19:40	43.5265	- 82.0185	62
H102	PG	9/15/2012 22:59	43.7059	- 82.4039	53
H012	PG, MC	9/16/2012 0:40	43.9007	- 82.1130	99
H103	PG	9/16/2012 3:03	44.1449	- 82.2209	99
H104	PG	9/16/2012 5:06	44.3720	- 81.8380	132
H032	PG, MC	9/16/2012 7:17	44.3542	- 82.3596	94
H027	PG	9/16/2012 9:42	44.0999	- 82.5025	65
H095	PG, MC	9/16/2012 11:43	44.3328	- 82.8326	70
H109	PG	9/16/2012 13:53	44.1502	- 83.0000	35
H002*	PG, MC	9/16/2012 15:17	44.1249	- 83.3324	18.8
H001	PG, MC	9/16/2012 17:29	43.9374	- 83.6142	12.7
H110	PG	9/16/2012 19:18	43.7723	- 83.8037	6.72
H108	PG	9/17/2012 0:42	44.5574	- 83.0502	55
H118	PG	9/17/2012 2:48	44.9168	- 83.1660	46
H037	PG, MC	9/17/2012 4:37	44.7619	- 82.7836	76
H107	PG	9/17/2012 7:12	44.6154	- 82.5541	66
H038	PG, MC	9/17/2012 8:49	44.7507	- 82.2024	166
H048cast2	PG, MC	9/17/2012 13:47	45.2614	- 82.5912	183
H048cast1#	PG, MC	9/17/2012 13:47	45.2614	- 82.5912	183
H119	PG	9/17/2012 16:49	45.3977	- 82.8107	135
H054*	PG, MC	9/17/2012 19:31	45.6338	- 83.4028	142
H061	PG, MC	9/18/2012 0:58	45.7498	- 83.9164	122
H123	PG	9/18/2012 3:02	45.9365	- 83.9059	30
H124	PG	9/18/2012 5:13	45.8512	- 84.4216	57

Notes :

(1) Date Time CDT = "On Station" Date Time GMT (from *Lake Guardian*'s bridge record) minus five hours.

(2) Latitude and Longitude data are calculated from the "On Station" entries of the *Lake Guardian*'s bridge record. Reading in degree and minute was converted to degree.

(3) Water depth data are from the "On Station" entries of *Lake Guardian*'s bridge record.

Table XI

SAMPLING INFORMATION FOR GEORGIAN BAY (GB), THE NORTH CHANNEL (NC), AND
THUNDER BAY (TB) OF LAKE HURON (OCTOBER 4–7, 2012)

Location	Sample	Date Time CDT [1]	Latitude[2]	Longitude[2]	Depth(m) [3]
H121	PG	10/4/2012 13:49	45.8189	83.4039	45
NC68	PG	10/4/2012 16:23	46.0413	83.8536	16.4
NC70	PG	10/4/2012 17:38	46.1365	83.6720	21.7
NC71	PG	10/4/2012 18:39	46.2335	83.7462	36
NC73	PG	10/4/2012 20:25	46.1869	83.3552	19.2
NC76	PG	10/4/2012 21:44	46.0003	83.4329	60
NC77	PG	10/4/2012 22:55	45.9704	83.1977	80
NC79	PG	10/5/2012 0:50	46.1230	82.8867	26.2
NC82	PG	10/5/2012 2:17	45.9369	82.7588	28.4
NC84	PG	10/5/2012 3:40	46.0917	82.5564	36
NC83	PG	10/5/2012 4:52	46.0000	82.5497	31
NC87	PG	10/5/2012 6:28	46.0611	82.1971	41
NC89	PG	10/5/2012 7:36	45.9165	82.1617	39
NC88	PG	10/5/2012 8:57	46.0553	81.9998	37
GB42	PG	10/5/2012 11:32	45.9125	81.5954	26
GB39	PG	10/5/2012 13:09	45.8729	81.2584	26.9
GB36	PG	10/5/2012 15:04	45.7082	81.6201	54
GB35	PG	10/5/2012 16:22	45.5257	81.6705	37
GB29	PG	10/5/2012 18:55	45.5836	81.0830	44
GB26*	PG	10/5/2012 20:41	45.8335	80.9000	21.3
GB24	PG	10/5/2012 21:22	45.7457	80.8394	31
GB17	PG	10/6/2012 0:11	45.2449	80.8742	80
GB12	PG	10/6/2012 2:36	44.9202	80.8748	91
GB01	PG	10/6/2012 4:03	44.7178	80.8564	93
GB03	PG	10/6/2012 5:29	44.7253	80.6170	34
GB06	PG	10/6/2012 6:34	44.7382	80.4360	88
GB04	PG	10/6/2012 8:08	44.6457	80.1673	59
GB05	PG	10/6/2012 9:20	44.7969	80.2431	60
GB09	PG	10/6/2012 11:53	44.8716	79.9675	29.9
GB08*	PG	10/6/2012 13:08	44.9527	80.1484	52
TB01	PG	10/7/2012 3:38	44.8996	83.1496	50
TB02	PG	10/7/2012 4:28	44.9387	83.2405	31
TB03	PG	10/7/2012 5:07	44.9552	83.2770	18.6
TB04	PG	10/7/2012 5:46	44.9997	83.3742	10.3

Notes: **Bold** font indicates planned stations for laboratory work. Samples from other stations were
   collected for archive purpose.
(1)–(3): See footnotes of Table 1.*GB26: no sediment was collected due most likely to the hard rock.
   GB08: no sediment was collected after three tries with bad weather conditions. Planned sites GB11,
   GB20, H116, and H117 were skipped due to bad weather.

For surface sediment collection, a Ponar grab sampler was deployed to the lake bottom and took a scoop of sediment. Upon retrieving the Ponar sampler onto the deck, the water was completely drained from the Ponar. Next, the sediment was dumped into a stainless steel tray. The tray with the sediment was then brought into the ship's general laboratory, where a photo image was taken. The sediment was then transferred from the tray to a bucket and homogenized using a drill-driven metal (September trip) or stainless steel (October trip) paint mixer. The well-mixed Ponar grab sample was subsampled into two 125 mL amber glass jars for chemical analysis; two 500 mL clear glass jars for archive; one 50 mL Falcon tube and one 15 mL Falcon tube for sediment characterization; and one 20 mL amber glass vial for mercury analysis. All glass jars and vials were individually wrapped with Parafilm and frozen at -20^{0}C in the onboard freezer room. After the trip, the frozen samples were transported in coolers to the Environmental Organic Chemistry Laboratory at University of Illinois at Chicago where they were stored at -20^{0}C in a walk-in freezer room until being processed for chemical analyses.

3.2   **Chemicals and Material Preparation**

Chemical standards were purchased from AccuStandard (New Haven, Connecticut), Wellington Laboratories (Guelph, Ontario, Canada), Cambridge Isotope Laboratories (Andover, Massachusetts), Toronto Research Chemicals (Toronto, Ontario, Canada), and the Florida Centre for Heterocyclic Compounds of University of Florida (Gainesville, Florida).

All solvents (methanol, dichloromethane, acetone, and hexane) were high perform liquid chromatography (HPLC) or Optima grade and purchased from Fisher Scientific (Pittsburgh, Pennsylvania). Silica gel (100–200 mesh), alumina (50–200 µm), copper (50 mesh,

granular, reagent grade) and concentrated hydrochloric acid were also from Fisher Scientific.

Concentrated sulfuric acid was purchased from J.T. Baker (Philipsburg, New Jersey). The

characteristics of two sorbents are summarized in Table XII.

Table XII

CHARACTERISTICS OF SILICA GEL AND ALUMINA

	Silica gel	Alumina
Manufacturer	Fisher Scientific	Acros organics
Fisher Scientific catalog no.	S744-1	3666800010
CAS No.	63231-67-4	1344-28-1
Formula	SiO_2	Al_2O_3
Grade	Davisil Grade 644	Brockmann I
Particle diameter, μm	75–150	50–200
Pore size, Å	150	60
BET surface area, m^2/g	(not available)	135–165
pH (aqueous)	2.3–7.4	6.5–7.5

* All data provided by the manufacturer

Silica gel, sodium sulfate, and alumina were activated in furnace at 500^0C for at least

eight hours, and kept in the oven at 160^0C. Granular copper was activated by washing with

hydrochloric acid, water, and acetone respectively, three times for each solvent. Sorbents were

cooled in a desiccator before using for sample preparation.

Stock solutions of the analytes and surrogate solutions were prepared by dissolving

appropriate amount of analyte in hexane. The working surrogate solution concentration for

each chemical is 4 ng/mL.

Table XIII

CONCENTRATIONS OF STOCK AND WORKING SOLUTIONS OF SURROGATES

Chemical	Abbreviation	Stock concentration (μg/mL)	Initial concentration (ng/mL)	Final concentration (ng/mL)
4'-chloro-2,2'-3,3',4,5,5',6,6'nonabromodiphenyl ethers	Cl-BDE-208	50	100	4
2,2'-5,5'-tetrabromobiphenyl ethers	PCB-52L	40	100	4
4'-fluro-2,2'-3,3',4,5,5',6,6'-nonabromodiphenyl ether	F-BDE-69	50	100	4
decabromobiphenyl,[13]C12	PCB-209L	1.6	1600	4
4'-fluro-2,2',3,3',4,5,5',6,6'nonabromodiphenyl ether	F-BDE-208	50	100	4

Glassware was cleaned with Contrad® 70 soap and rinsed with tap water followed by three rinses with deionized water. Once the glassware dried, they were placed in a furnace at 500^0C overnight. Glassware was solvent washed with methanol, acetone, and dichloromethane (DCM), respectively per three times.

3.3   **Laboratory Procedure**

The laboratory method for this experiment was developed previously and is described elsewhere (Guo et al., 2014). Figure 10 illustrates the sequence of procedures used. Figure 11 shows the photos of the major steps, each of which is described in the subsections below.
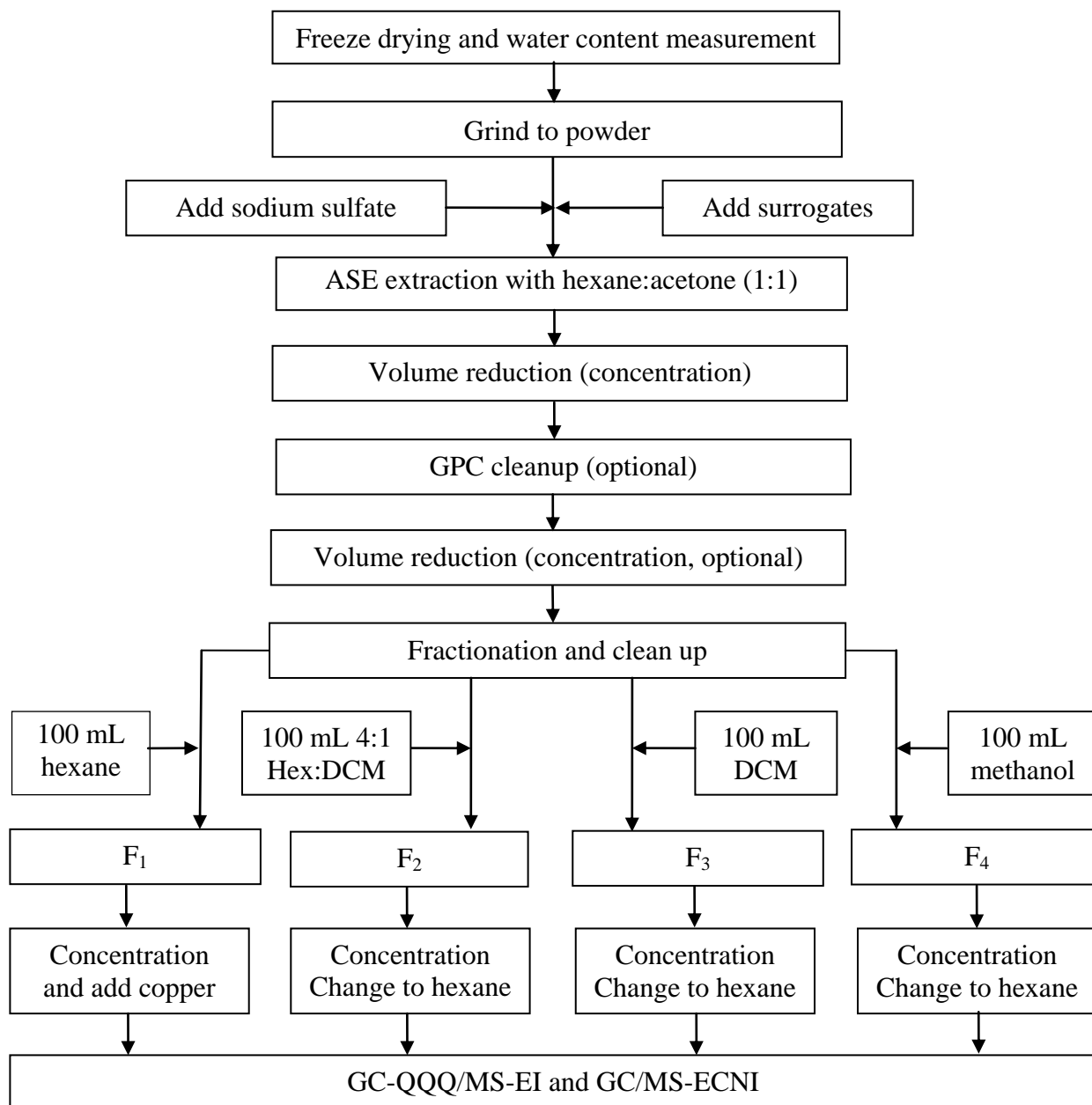
Figure 10. Analytical procedure of the chemical analysis.

(Figure source: Guo et al., 2014)

(a)   (b)   (c)

(d)   (e)
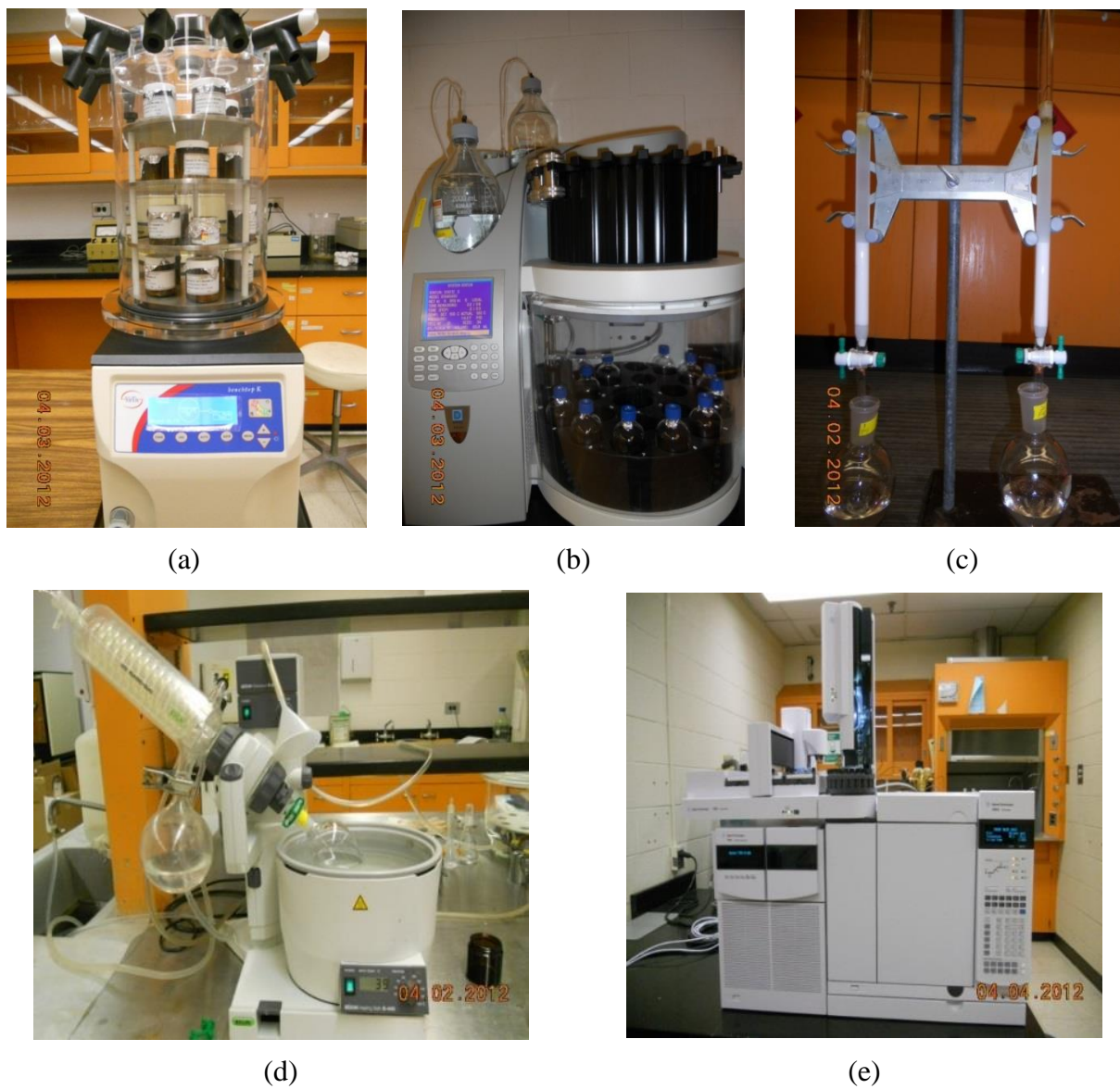
Figure 11. Pretreatment process and GC/QQQMS analysis: (a) Freeze dryer with samples, (b) Accelerated solvent extraction (ASE), (c) Cleanup columns, (d) Rotovap, (e) GC/QQQMS.

3.3.1 **Freeze Dry**

From the jar containing frozen sediment sample, the Parafilm wrapping was removed and discarded. If the jar was cracked it was wrapped tightly with aluminum foil. The foil was weighed with the jar.

After removing the lid, each jar was weighed with the sediment samples and, if used, the aluminum foil wrapping. The opening of the jars was covered tightly with the aluminum foil into which several small holes were punched. After weighing, the jars were placed on the benchtop freeze dryer (VirTis 2KBTES-55, SP Scientific, Gardiner, New York). After the samples were dried, the jars was removed from the freeze dryer and weighed again. The aluminum cover was removed. Dried sample was pulverized using a glass rod or test tube and transferred to glass vials, which were stored in a freezer until sample extraction. The emptied jars were cleaned and weighed.

The water content of each sample was determined by using following formula:

Water content (%) = $(W_{cws} - W_{cs}) / (W_{cws} - W_c) \times 100$

where W_{cws} is the weight of wet sample plus the jar, W_{cs} is the weight of dried sample plus the jar, and W_c is the weight of cleaned jar. All weights are in grams.

3.3.2 **Sample Extraction**

Freeze-dried samples were measured for the weight and transferred to the solvent-washed dried glass mortar. Each sample was ground using a glass pestle to become a fine powder. Once again, the weight was measured and recorded. About 5 g activated sodium sulfate was transferred to the bottom of a stainless steel extraction cell and followed by the

ground sample. Another 5 g sodium sulfate was used to remove the remaining sample from the mortar. To the top of the sample, another 10 g of sodium sulfate was added.

Before extraction started, 2 mL of the surrogate solution was added to the sample using a 2 mL volumetric flask. Samples were kept overnight and extracted with exchange using a Dionex ASE 350 ASE system. The operation conditions of the ASE350 were those specified for the procedure used in EPA Method 3545A. Briefly, the sediment samples were extracted for 3 cycles using hexane and acetone mixture (v/v, 1/1). The heating temperature was 100^0C, heating time 5 minutes, and static time was 10 min. Extracts were concentrated from approximately 80 mL to 2 mL using a rotary evaporator (Buchi Rotovap R-200) and solvent was exchanged to hexane.

3.3.3   **Cleanup and Fractionation**

Each glass cleanup column (11 mm i.d, 400 mm length) was solvent-washed with methanol, acetone, and DCM before use. One-fourth of the cellulose septum was plugged at the bottom and the column was filled with DCM. Next, the column was filled with 1 g of anhydrous sodium sulfate, 8 g of alumina, 4 g of silica gel, and 5 g of anhydrous sodium sulfate from the bottom to the top. The DCM was drained from the column until 1 mm remained on top of the sodium sulfate layer. After the column packing was completed, the DCM in the column was replaced by 50 mL hexane.

Concentrated extracts were loaded to a cleanup column by pipetting, the pear-shaped flask containing the extract was rinsed three times with hexane, and the rinse was added to the column to ensure the completeness of the analyte transfer. The column was eluted at a rate of about 5 mL/min, consecutively with 100 mL of hexane (F-1), followed by a 100 mL 1:1

mixture of DCM: Hexane (F-2), 100 mL of DCM (F-3), and 100 mL of methanol (F-4)

respectively. The F-1 was further cleaned up by adding granular copper for sulfur removal.

Each fraction was concentrated to approximately 1–2 mL using the rotary evaporator.

Once the flask was removed from the rotary evaporator, the inside of the collection flask was

rinsed with approximately 0.5 mL of acetone. The sample was transferred into the 2 mL

volumetric flasks and the collection flask was rinsed three times with hexane 0.5 mL each time,

and the final volume was brought up to 2 mL. The concentrated solution was then transferred to

an amber glass storage vial, sealed and stored in a refrigerator until instrumental analysis.

3.3.4 <u>**Instrumental Analysis**</u>

From the amber vials of the stored samples, 100 µL were withdrawn and placed into an

insert using a syringe. Next, 5 µL of the internal standard solution containing CB205L, CB-47

L, and 10 µL BB 209 were added to the sample before injection.

For PCBs, the samples were analyzed using Agilent 7890A GC coupled with an Agilent

7001B QQQMS. The GC/QQQMS was equipped with a multimode injection port and an

Agilent 7693 auto sampler. A Phenomenex Zebron ZB-5MS capillary column (30 m × 0.25

mm i.d. × 0.25µm film thickness) was used for the separation. The operational conditions of the

GC/QQQMS are summarized in Table XIV.

To analyze PBDEs, a 7890A GC coupled with an Agilent 7001B QQQMS was used for

all congeners except for BDE 209, which was analyzed using Agilent 6890/5973 GC/MS.

Other flame retardant analytes were also analyzed using Agilent 6890/5973 GC/MS. It was

equipped with a Gerstel programmable temperature vaporization injection port, which was

operated in solvent vent mode. The operational conditions of the GC/MS are summarized in

Table XV.

Table XIV

OPERATIONAL CONDITION OF AGILENT 6890/5973 GC/MS FOR nXFR ANALYSIS

Parameter	Value
Inlet temperature	Initial 40°C for2 min, 600°C/min to 300°C
Inlet vent flow	100 mL/min
Inlet purge flow	100 mL/min at 2.75 min
Number of injections	3 injections 20 μL for total 60 μL
GC column	Restek Rtx-1614 capillary column (15 m × 0.25 mm ID × 0.10 μm film thickness)
Carrier gas	Helium, constant flow at 1.2 mL/min
Oven temperature	Initial 50°C held for 3 min, 300°C at 10°C/min and kept for 10 min
Interface temperature	300°C
Total run time	54 min
Interface temperature	150°C
Ion source	Electron Capture Negative Ionization (ECNI), at 200°C
Ionization voltage	70 V
MS-1 and MS-2 analyzers	150°C
Collision gas	Helium (He) - 2.25 m/min Nitrogen (N_2) - 1.5 mL/min

Table XV

OPERATIONAL CONDITION OF AGILENT 7890/7000 GC/QQQMS FOR PCB
ANALYSIS

Parameter	Value
Inlet temperature	Initial 60^0C for1 min, 600^0C/min to 300^0C
Inlet vent flow	100 mL/min
Inlet purge flow	50 mL/min
Number of injections	3 injections 20 µL for total 60 µL
GC column	Phenomenex Zebron ZB-5MS (30m $\times$ 0.25 mm i.d. $\times$ 0.25µm film thickness)
Carrier gas	Helium, constant flow at 1.2 mL/min
Oven temperature	Initial 45^0C held for 2 min, 10^0C/min to 150^0C , 5^0C/min to 300^0C
Interface temperature	300^0C
Total run time	54 min
Interface temperature	150^0C
Ion source	Electron impact (EI), set at 230^0C
Ionization voltage	70v
MS-1 and MS-2 analyzers	150^0C
Collision gas	Helium (He) - 2.25 m/min Nitrogen (N_2) - 1.5 mL/min

Agilent computer software MassHunter (version B 04.00) was used for controlling
GC/QQQMS operation, data acquisition, and qualification of the concentrations. Quantification
was performed using internal standards with linear response factor. The concentrations were
calculated using either the isotope dilution or the internal standard methods. For each analyte, 5
or 6 calibration standards, with concentrations spanning from 0.01 to 10 ng/mL were used to
establish the relative response factors, with linear or quadratic regressions with 1/x weighing
factor. All calibration curves had R^2>.99. All analytes, one precursor ion, and two product ions
(quantifier Q and qualifier q) were selected (Appendix A).

4. QUALITY CONTROL AND QUALITY ASSURANCE

Quality assurance and quality control (QA/QC) are essential to the success of the project. They help generate good quality data and allow correct interpretation of the data.

In this work, the following QA/QC measures were taken.

1. Chain of custody was documented

2. Method detection limits and instrument detection limits were documented

3. Surrogate recovery was calculated to examine the method accuracy

4. Sample duplicates determined the method precision

5. Procedural blanks and instrumental blanks were performed to assess the potential contamination.

4.1 **Chain of Custody**

At the time of sample collection, the location identification number and longitude and latitude of the locations were recorded. A chain of custody form tracked the activities of sample processing and analysis. Information collected about freeze-drying samples and storage included: sample weight before and after freeze-drying, date of freeze-drying, time of freeze-drying, and freeze drying conditions. Information collected about sample preparation included: sample weight before and after grinding, volume of surrogate spiked, amount of sodium sulfate added to the sample, date and time of extraction, run quality, and analyst name. Information collected about sample cleanup included: date of sample cleanup, sample color, copper addition, date of final concentration, and quality of clean up procedure recorded. Information collected about the instrumental analysis included: the volume of internal standard added, and date of instrumental analysis.

4.2   <u>**Detection Limits**</u>

The method detection limit (MDL) was determined according to the procedures established by the EPA in Method SW846 (EPA, 1996). An MDL is described as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix type containing the analyte. The method of detection is derived by using the following equation;

$$MDL \ = \ t(n-1, \alpha = 0.99)(s)$$

where,

n = Number of samples

s = standard deviation

t (n-1, α = .99) = one-sided t-statistic

The instrumental detection limit is the concentration able to produce a response that is three times greater than the noise signal. The limit of detection (LOD) was derived using following equation:

$$LOD = \frac{IDL \ (ng/mL) \times 2 \ mL}{Sample \ size \ (g)}$$

The MDL or LOD for each analyte are reported along with the sample results. Summary and statistical analysis of the sample results for PCBs used the MDL, but the LOD was used for the other analytes.

4.3   **<u>Surrogate Recoveries</u>**

In order to monitor any loss of analytes during the analytical procedure, known amounts of surrogates were added to the samples before the extraction. A good surrogate has similar physical and chemical properties to the analyte of interest. It does not interfere with the target compounds and can be distinguished separately in the GC chromatogram. The surrogates used in this project were ^{13}C-labeled 2, 2', 5, 5'-tetrachlorobiphenyl (CB52L) and (CB209L) for PCB analytes, and (F-BDE208), (Cl-BDE208), and (F-BDE69) for halogenated flame retardants.

References refer to the procedure in which the same amounts of surrogates were added to a 1 mL volumetric flask. The purpose of references is to examine the bias caused by the microinjection process involving the microsyringe and some other unknown conditions (such as evaporation during storage). By comparing the detected concentrations of the surrogates in samples to those of the reference, recoveries were calculated.

The average recovery for CB52L was 87% (standard deviations 21.61). Average recovery for CB209L is 102% (standard deviations 20.73). The overall recovery is with the limit of expectation (60%−120%). The average recovery for F-BDE208, Cl-BDE208, F-BDE69 (GC/QQQMS), and F-BDE69 (GC/ECNI-MS) was 96% (standard deviation 20), 101% (standard deviation 26), 94% (standard deviation 20), and 87% respectively. The overall recovery is within the limit of expectation (60%−120%). The distributions can be seen in Figure 12.
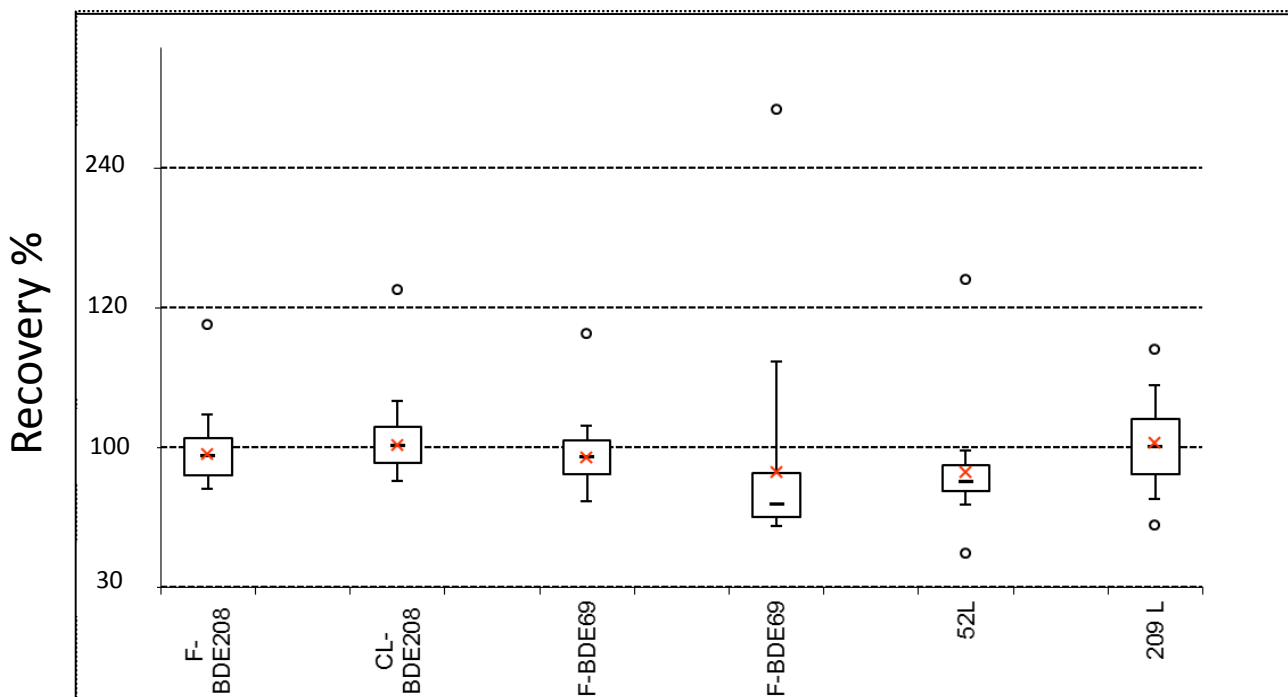
Figure 12. Surrogate recovery of F-BDE 208, Cl- BDE208, F-BDE 69, CB 52L, and CB 209L (GC/QQQMS results), F-BDE 69 (ECNI).

The compounds are ionized by two different mechanisms in MS: electron impact ionization (EI) and electron capture negative ionization (ECNI).

An EI is a hard ionization technique in which the molecule is vaporized and then bombarded by a beam of energized electrons, generating fragment ions. Electron capture negative ionization, on the other hand, is a soft chemical ionization technique in which the low energy ions (thermal electrons) produced by high energy electron bombardment of reagent gas collide with gaseous molecules of the sample, resulting in negatively charged ions.

4.4   **Duplicates**

To assess the precision of the laboratory procedure, duplicate analysis was performed

for three sets of samples. Duplicates were done for sample H061, H109, and H124. Relative

presence difference (RPD) was calculated using the following equation;

$$RPD = 200\,[(x1 - x2)/(x1 + x2)].$$

Where: $x1$ and $x2$ defer to duplicate 1 and 2.

The average RPD for $\sum_{39}$ congeners of PCBs of H061, H109, and H124 are 43.11%,

52.27%, and 9.82% respectively. These results are in H061 and H109 higher than the expected

value of 30%. This is plausible if in one sample the pollutant is non-detected and in the other

sample if it is present in very low concentrations. In this instance the RPD value=200. After

removing RPD yields to 200, the resulted RPDs for H061 and H109 are 17.50% and 26.95%

respectively. The RPDs for analyzed XFRs for HO61, H109, and H124 are 27%, 28%, and

24% respectively.

4.5   **Blanks**

The blank test is an analysis in which all steps of the analytical procedure are

implemented without a real sample. Testing of blanks reveals background levels of

contamination of solvents, sorbents, and equipment. Two types of blanks; procedural and

instrument blanks were assessed in this project.

The goal of procedural blanks is to monitor the degree of background contamination

during the laboratory sample preparation. Sodium sulfate was used as the blank matrix. The

mass of sodium sulfate used was equal to the average weight of a sediment sample plus the

weight of sodium sulfate added in the procedure (~25 g). The same extraction, concentration, cleanup, and further concentration procedures were carried out, and the blanks were analyzed with the regular samples. One procedural blank was run for every 15 samples.

The goal of instrument blanks is to separately evaluate the degree of background contamination associated with the instrumental analysis (e.g., with the microinjection syringes and separation columns). The instrument blanks involved injection of pure hexane into the instrument. An instrument blank was run in every run.

The blank results for $\sum_{39}$ PCBs and analyzed XFRs are shown in Appendices B and C.

5. RESULTS AND DISCUSSION

5.1 __Polychlorinated Biphenyls__

5.1.1 __Overview__

The objective of this section is to present and describe the concentrations of 39 PCB congeners in 59 surface sediment samples collected from Lake Huron in 2012. Of the 59 samples, 32 were collected from the main lake, 14 from Georgian Bay, and 13 from the North Channel. The 39 PCB congeners included the congeners with IUPAC numbers 4, 6, 8, 9, 11, 16, 18, 19, 22, 25, 28, 44, 52, 56, 66, 67, 71, 74, 82, 87, 99, 101, 110, 138, 146, 147, 153, 173, 174, 177, 179, 180, 187, 194, 195, 199, 203, 206, and 209.

5.1.2 __Summary of Chemical Concentrations__

The PCBs were detected in all samples analyzed (n=59). The detailed information of each sample can be found in Appendix D. The summary statistics for individual PCB congeners and the $\sum$39 PCBs presented in Table XVI. Some congeners like PCB 4, PCB 9, PCB 16, PCB 67, PCB 147, PCB 179, and PCB 174 were not detected in more than 20% of samples.

Table XVI

SUMMARY OF STATISTICS OF PCB CONGENERS OF LAKE HURON (Unit ng/g dw)

Congener	Average	Min	0.1	Q1	Median	Q3	0.9	Max
PCB 4	0.006	0.000	0.000	0.001	0.001	0.003	0.009	0.142
PCB 6	0.018	0.000	0.000	0.001	0.001	0.004	0.009	0.526
PCB 8	0.038	0.000	0.002	0.003	0.005	0.017	0.042	0.978
PCB 9	0.005	0.000	0.000	0.001	0.001	0.003	0.005	0.100
PCB 11	0.007	0.000	0.001	0.001	0.003	0.006	0.012	0.105
PCB 16	0.013	0.000	0.000	0.001	0.001	0.005	0.015	0.355
PCB 18	0.053	0.000	0.001	0.002	0.005	0.025	0.063	1.327
PCB 19	0.002	0.000	0.000	0.000	0.001	0.001	0.001	0.045
PCB 22	0.051	0.001	0.002	0.003	0.005	0.023	0.049	1.392
PCB 25	0.051	0.000	0.000	0.000	0.001	0.007	0.029	1.795
PCB 28	0.377	0.000	0.006	0.013	0.038	0.163	0.347	10.030
PCB 44	0.103	0.000	0.002	0.004	0.015	0.054	0.111	2.718
PCB 52	0.144	0.003	0.007	0.010	0.023	0.095	0.177	2.995
PCB 56	0.228	0.001	0.005	0.008	0.021	0.076	0.216	6.132
PCB 66	0.423	0.003	0.009	0.017	0.039	0.206	0.388	11.900
PCB 67	0.007	0.001	0.001	0.001	0.001	0.005	0.006	0.235
PCB 71	0.038	0.001	0.001	0.002	0.003	0.009	0.029	1.066
PCB 74	0.092	0.001	0.003	0.005	0.009	0.023	0.087	2.777
PCB 82	0.037	0.000	0.000	0.001	0.004	0.019	0.032	0.940
PCB 87	0.092	0.000	0.002	0.005	0.017	0.056	0.103	2.224
PCB 99	0.158	0.000	0.002	0.005	0.019	0.083	0.218	4.595
PCB 101	0.139	0.002	0.010	0.017	0.042	0.116	0.227	1.969
PCB 110	0.351	0.001	0.010	0.022	0.060	0.186	0.420	9.505
PCB 138	0.239	0.000	0.008	0.015	0.065	0.178	0.383	4.989
PCB 146	0.234	0.001	0.007	0.017	0.062	0.196	0.470	4.894
PCB 147	0.059	0.000	0.000	0.000	0.000	0.002	0.007	3.333
PCB 153	0.205	0.001	0.007	0.018	0.061	0.176	0.377	4.392
PCB 173	0.001	0.000	0.000	0.000	0.000	0.001	0.002	0.022
PCB 174	0.052	0.000	0.002	0.003	0.014	0.040	0.092	1.045
PCB 177	0.037	0.000	0.001	0.002	0.009	0.028	0.061	0.720
PCB 179	0.015	0.000	0.000	0.000	0.004	0.014	0.033	0.258
PCB 180	0.123	0.000	0.003	0.006	0.039	0.112	0.226	2.580
PCB 187	0.075	0.000	0.002	0.004	0.023	0.079	0.161	1.409
PCB 194	0.043	0.001	0.004	0.005	0.016	0.046	0.082	0.724
PCB 195	0.015	0.000	0.000	0.001	0.005	0.014	0.029	0.240
PCB 199	0.049	0.000	0.001	0.003	0.015	0.062	0.114	0.727
PCB 203	0.046	0.000	0.001	0.003	0.014	0.056	0.096	0.700
PCB 206	0.041	0.000	0.001	0.003	0.012	0.062	0.107	0.389
PCB 209	0.067	0.001	0.001	0.004	0.022	0.094	0.158	0.662
∑39 PCB	3.734	0.050	0.143	0.293	0.897	2.255	4.659	90.934

In our study, the average concentration of Σ39PCBs is 3.73 ng/g dry weights, and ranged from 0.05 ng/g to 90.9 ng/g dry weight. These results are consistent with previous studies. Frank et al. (1979) reported total PCB values ranging from 3 ng/g to 90 ng/g in Lake Huron sediments sampled in 1968 and 1973, which was similar to the ranges observed in Lake Ontario in the same year (maximum 57 ng/g), and in Lake Michigan in 1975 (mean 9.7 ng/g, maximum 75 ng/g). Surface sediments sampled in 2001–2002 in Lake Superior had total PCB concentrations in the range of 1.99 ng/g to 27.4 ng/g (Song et al., 2004), which were slightly lower than values measured in lake Erie (23 ng/g–28.3 ng/g) and Lake Ontario (58.3 ng/g to 63.6 ng/g). One other study conducted was found that mean total PCB concentrations ranged from 7 ng/L to 103 ng/L in Lake Michigan tributaries (Martie et al., 1990). Moreover, Pugsley et al. (1985) sampled 102 sites in the St. Clair River and the Canadian shore line and reported a mean value of 3.9 ng/g. Overall, these results suggest that Lakes Michigan, Ontario, and Erie are more polluted than the Lake Huron, while Lake Superior is comparatively less contaminated. Comparison of total PCB is not always appropriate, however, because different PCB congeners may be used by each research team. In addition, the PCB concentrations may be influenced by the sampling location.

The variation in the concentration of each PCB congener is shown in Figure 13.
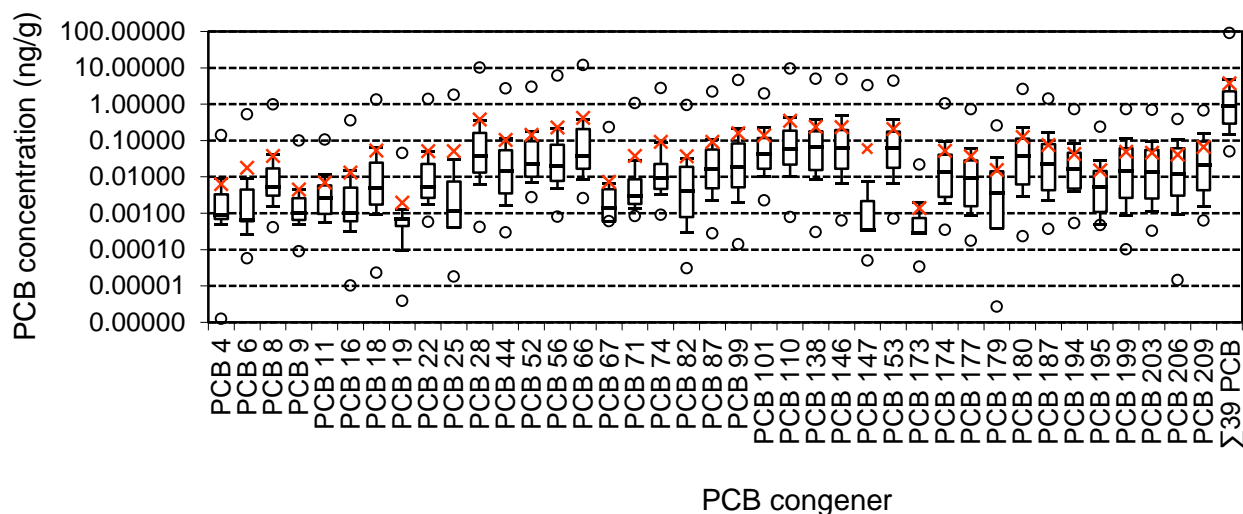
Figure 13. PCB congener distribution in the pooled samples. The vertical bar in the box represents the median; the cross represents average; the box covers the range from the first to the third quartile; the bars outside the box represent the 10th and 90th percentile values; the circles outside the box represent the maximum and the minimum values.

5.1.3   **Polychlorinated Biphenyl Congener Distribution**

The most abundant congener is PCB 138. Other prominent congeners are PCB 146,

PCB 153, PCB 110, and PCB 101. PCB 66 also abundant than the other congeners. PCB 173 is

present at the lowest concentrations, but was detected in almost all the samples. In general,

lower chlorinated compounds were found in relatively low concentrations suggesting that

higher chlorinated PCBs are more likely to be adsorbed to the sediment than lower chlorinated

PCBs. In addition, less chlorinated congeners may volatilize or be lost from sediment by photo

degradation.
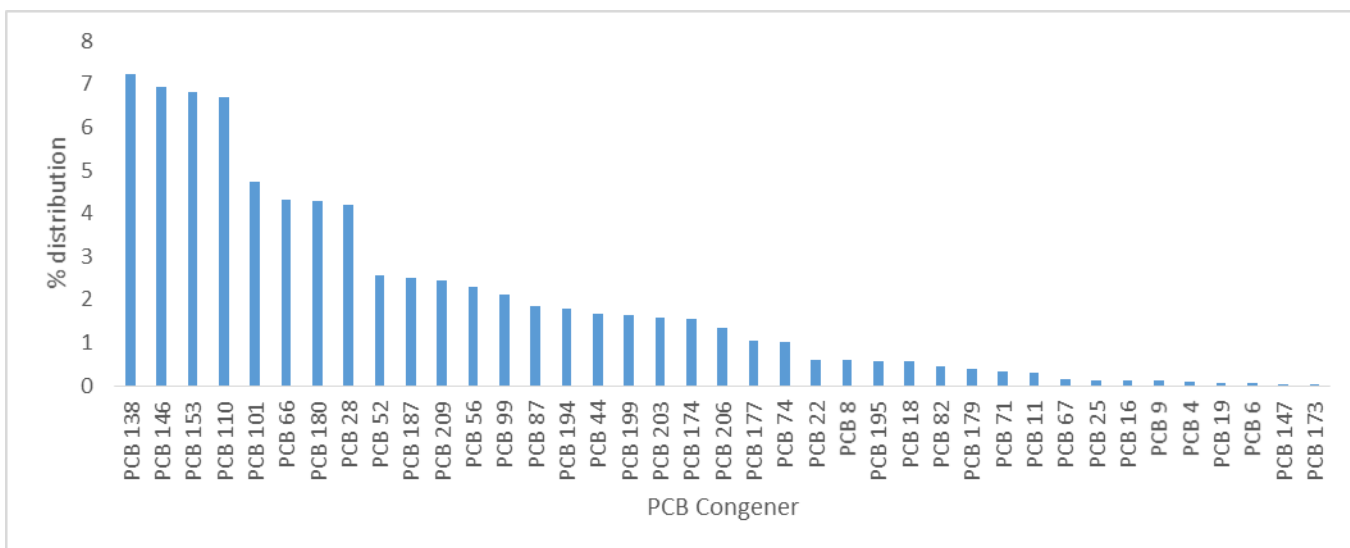
Figure 14. Percentage distribution of PCB congeners relative to $\sum$39 PCB, based on median.

The relative distribution of PCB congeners in this study (Figure 14) is similar with other studies. For example, Covaci et al. (2004) found the congener distribution of PCB138 > PCB153 > PCB 180 > PCB 101 in sediment from Western Schdelt (Belgium). In coastal marine sediment in Kuwait, the most prominent congeners were found to be: PCB138, PCB 101, PCB 110, PCB 180, PCB 153, PCB 132, PCB 149, and PCB 118 (Gevavo et al., 2006).

In this study, a considerable percentage of PCB mass is due to the penta and hexa homologs (Figure 14), which can be attributed to the release of Arocolar 1260 and/or Arocolar 1254 to Lake Huron. Congener analysis of PCBs in the Detroit River also found a large presence of higher chlorinated PCBs, which are major constitutes of the Arocolar 1260 (Oliver and Bourbonneier, 1985).

5.1.4 __Correlation of Selected Polychlorinated Biphenyl Congeners__

The relationships between selected PCB congeners (PCB 52, PCB 66, PCB 28, PCB 101, PCB 99, PCB 110, PCB 146, PCB 153, PCB 138, and PCB 180) were studied using Spearman rank correlation coefficient (Table XII). These congeners were selected since they were found in high concentration in the present study as well as literature. All PCB congeners are positively correlated.

Table XII

SPEARMAN CORRELATION FOR SELECTED PCBs

	PCB 28	PCB 52	PCB 66	PCB 101	PCB 99	PCB110	PCB 146	PCB 153	PCB 138	PCB180	$\sum$39 PCB
						Spearman Correlation Coefficients, N=59 **Probability > |r| under H0: Rho=0**					
PCB 28	1										
PCB 52	0.939	1									
PCB 66	0.931	0.958	1								
PCB 101	0.905	0.962	0.957	1							
PCB 99	0.897	0.967	0.94	0.956	1						
PCB 110	0.887	0.925	0.942	0.955	0.951	1					
PCB 146	0.826	0.888	0.891	0.948	0.939	0.954	1				
PCB 153	0.81952	0.88434	0.886	0.942	0.939	0.948	0.997	1			
PCB 138	0.834	0.904	0.916	0.963	0.947	0.949	0.983	0.977	1		
PCB 180	0.780	0.868	0.868	0.928	0.923	0.928	0.989	0.990	0.973	1	
$\sum$39 PCB	0.891	0.936	0.928	0.948	0.959	0.972	0.957	0.955	0.939	0.936	1

*Note: All are statistically significant at $<.0001$

5.1.5 **Site Comparison**

Figure 15 shows the $\sum$39 PCB concentrations by location. Location H001 is the most polluted site, with concentration 90.93 ng/g. This sample reflects 41% of the PCB mass measured in the 59 samples, and is approximately three times higher than the second-most polluted site, location H110. After location H001, the three sites with the next highest $\sum$39 PCB concentrations are H110, H027, and H032, and these samples comprise 25% of the PCB mass measured in the 59 samples.

The two locations with high levels of $\sum$39 PCB concentrations—sites H001 and H110—were at the south end of Saginaw Bay. The other two sites within the Bay, H002 and H109, also had PCB levels higher than most sites in the Lake Huron watershed.
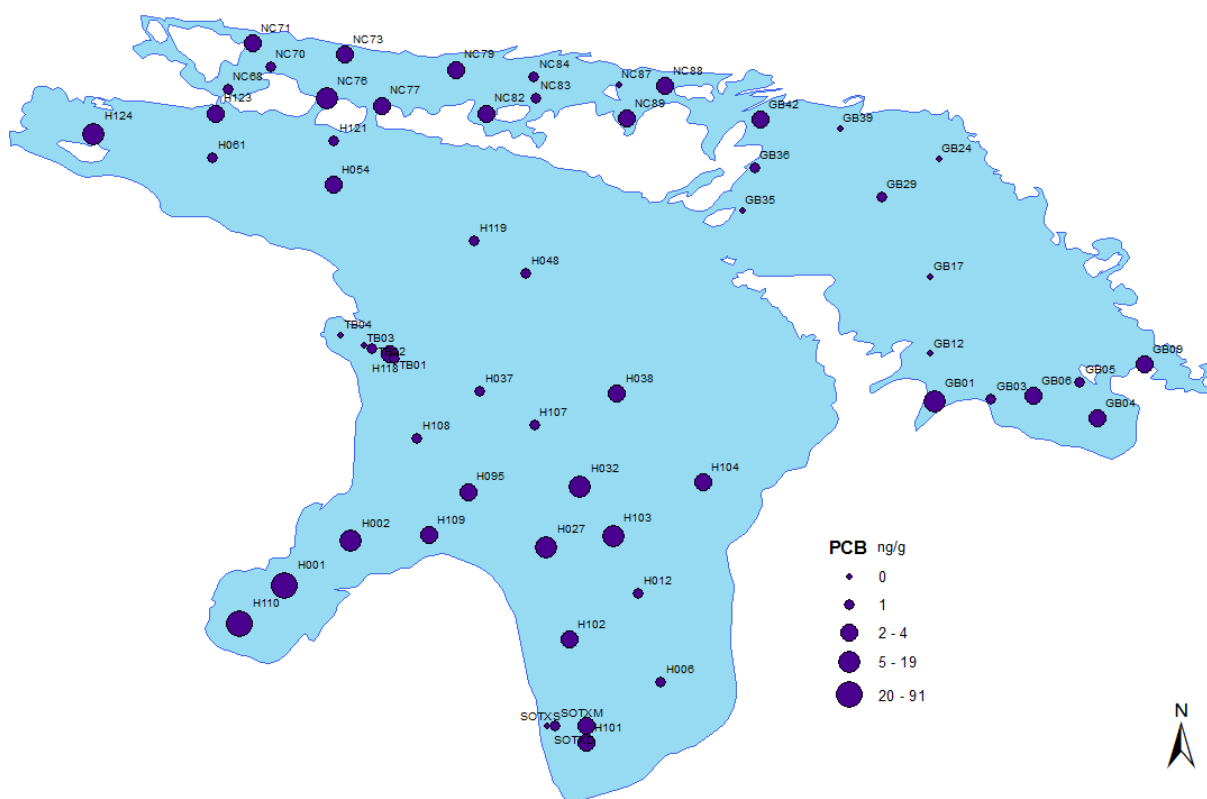
Figure 15. Total PCB ($\sum$39) concentration of Lake Huron surface sediments in year 2012.

The $\sum$39 PCB concentrations were compared among three regions in the study area—

the main lake, Georgian Bay and the North Channel—to determine whether there is a

geographical pattern in pollution. Table XVIII summarizes the $\sum$39 PCB levels in the three

regions. Most of the pollutant burden is associated with the main part of Lake Huron (average

$\sum$39 PCB 5.80 ng/g), followed by the North Channel (mean $\sum$39 PCB 1.137 ng/g) and

Georgian Bay (mean $\sum$39 PCB 0.126 ng/g). But the differences in pollutant $\sum$39 PCB

concentrations are not statistically significant (Kruskal-Wallis p>.26). The Kruskal Wallis test

was also applied to test for differences in the selected PCB congeners (PCB 28, PCB 52, PCB

110, PCB 138, PCB 146, PCB 56, PCB 153, PCB 99, and PCB 101) concentrations among the

three regions. As with $\sum 39$ PCBs, the differences among the three regions were significant

(P>.05) (Table XIX).

Table XVIII

TOTAL PCB CONCENTRATION IN THREE MAIN LOCATIONS

(Unit ng/g)

Location	Number of samples	Concentration of the $\sum 39$ PCB (ng/g)		
		Min	Average	Max
Main Lake	32	0.12	5.80	90.93
Georgian Bay	14	0.05	1.17	3.99
North Channel	13	0.15	1.40	4.57

Table XIX

KRUSKAL-WALLIS TEST COMPARING SELECTED PCB CONGENER
CONCENTRATION BY REGION OF LAKE HURON

Congener	Average PCB Concentration (ng/g)			Kruskal-Walls Result	
	GB	NC	Lake	Chi - square	P value
PCB 28	0.060	0.043	0.650	4.581	0.101
PCB 52	0.037	0.033	0.235	4.609	0.099
PCB 66	0.0736	0.060	0.722	5.509	0.063
PCB 99	0.061	0.061	0.204	3.988	0.136
PCB 101	0.041	0.051	0.251	2.886	0.236
PCB 110	0.090	0.104	0.565	2.789	0.248
PCB 138	0.094	0.127	0.347	2.653	0.265
PCB 146	0.108	0.140	0.327	2.541	0.28
PCB 153	0.098	0.137	0.279	2.73	0.255
PCB 180	0.053	0.085	0.168	3.511	0.172

Note: Statistically significant differences in mean values indicated by p<.05

Frank et al. (1973) conducted a detailed study of PCBs in Lake Huron and found that among all locations, total PCB concentrations ranged from 3 to 90 ng/g, and mean values for Georgian Bay and the North Channel were 13 ng/g and 8 ng/g, respectively. In our study, $\sum39$ PCB concentrations among all locations ranged from 0.09 to 90 ng/g, similar to that observed by Frank et al. (1973), but in contrast to the observation of Frank et al. (1973), the mean $\sum39$ PCB concentration in this study was higher in the North Channel than in Georgia Bay. In addition they have identified one more input at Alpena, which has little impact on PCB burden in Lake Huron.

5.1.6 <u>**Influence of Organic Carbon Content**</u>

In order to test the hypothesis that PCB levels vary with the organic carbon content of the sediment, the dry-weight-based PCB concentrations were normalized by the organic carbon content (OC) of the sediments.

The $\sum39$ PCB concentrations per mass of OC are shown by location in Figure 16. The pattern is different from that in Figure 15. For example, location H001 had the highest $\sum39$ PCB concentration per mass of sediment, but the location also has high OC (Appendix E), such that after normalizing to OC, the site does not stand out. This suggests OC plays an important role in adsorbing PCB in sediment (Figure 16).
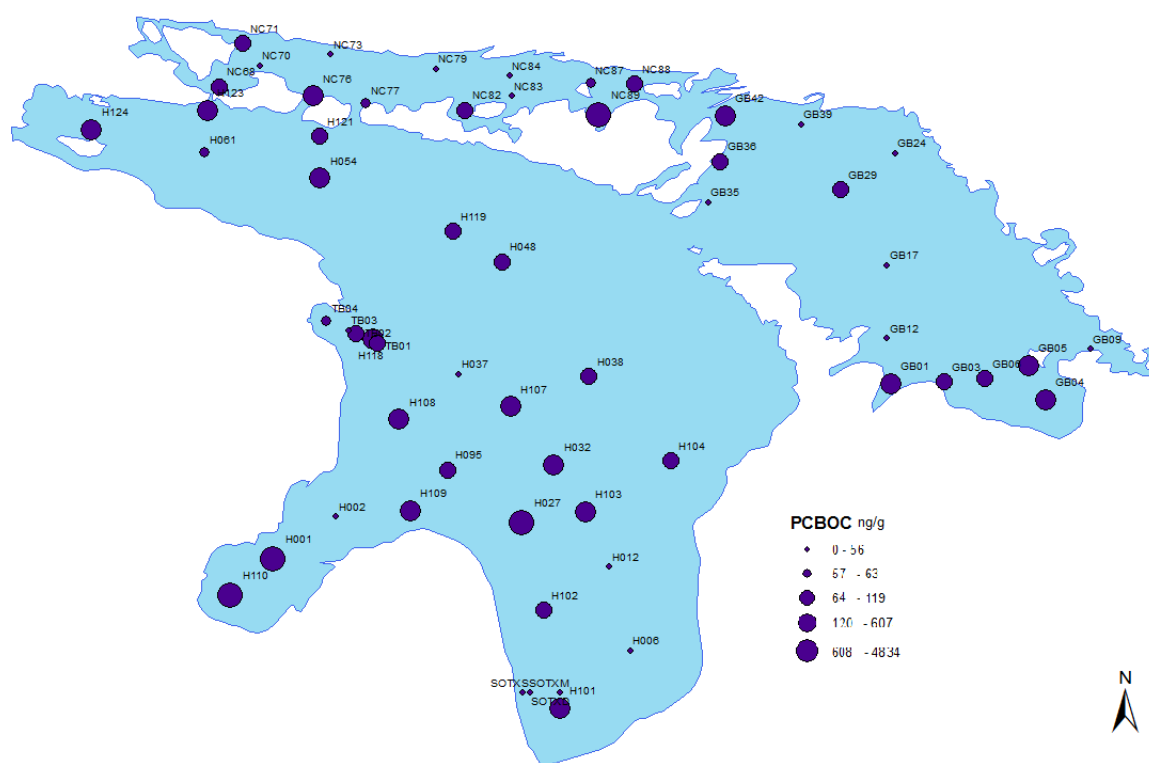
Figure 16. ∑39 PCB concentrations by sampling location based on OC.

This pattern was further explored by plotting the ∑39 PCB concentration against sediment OC content (Figure 17): A strong relationship was not observed (R^2=.35). This suggests that the influence of OC compound may be location-specific, or overwhelmed by source and transport processes.
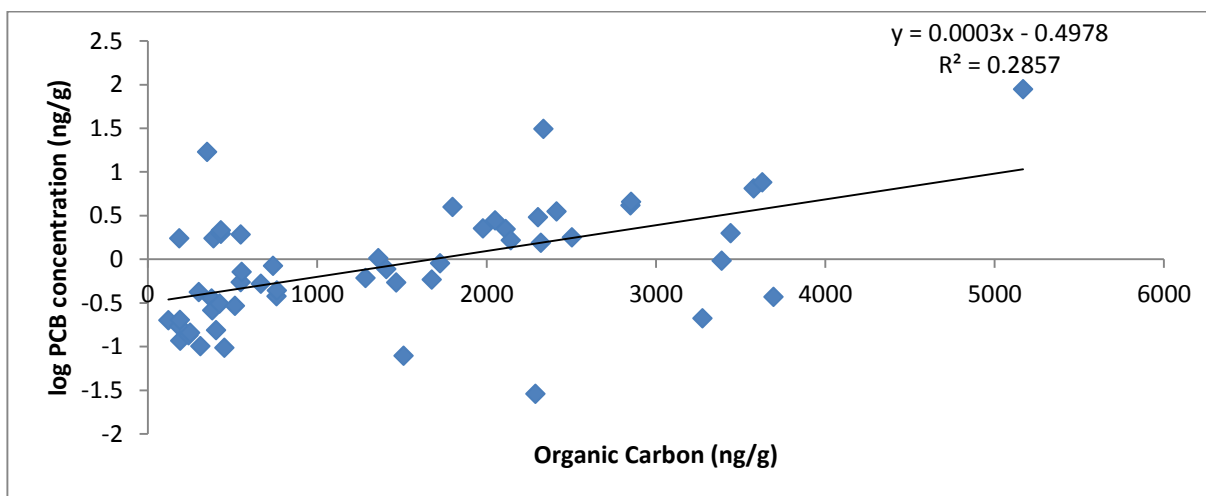
Figure 17. Trend of ∑39 PCB concentration versus OC.

Kruskal-Wallis tests were performed using OC-normalized PCB concentrations to see if statistical differences exist among the three regions. There is a statistical difference in the mean value of the PCB congeners 28, PCB 52, PCB 66, PCB 101, and PCB 110 (Table XX). This is consistent with the hypothesis that OC plays a key role in holding PCBs in the sediment samples, and different congener affinity to sediment. Differences among the regimes may also be influenced by water circulation or different sedimentation rates.

Table XX

KRUSKAL-WALLIS TEST OF COMPARING OC NORMALIZED CONCENTRATIONS
OF MAIN STUDY AREA

Congener	Average PCB Concentration (ng/g)			Kruskal-Walls Result	
	GB	NC	Lake	Chi-square	P value
PCB 28	5.4	4.8	42.6	8.02	0.02
PCB 52	2.8	3.8	20.3	8.94	0.01
PCB 66	5.2	6.5	47.2	9.93	0.01
PCB 101	4.7	7.3	22.5	8.34	0.01
PCB 99	2.7	5.1	19.0	4.25	0.13
PCB 110	6.7	10.8	36.8	6.93	0.03
PCB 138	6.7	14.1	29.3	5.22	0.07
PCB 146	7.6	14.2	27.8	3.06	0.22
PCB 153	7.0	13.9	23.5	1.95	0.38
PCB 180	3.5	9.3	14.5	2.64	0.27

5.1.7 **Principal Component Analysis**

Principal component analysis (PCA) was carried out using the R Project for Statistical Computing to explore patterns in the PCB congeners. The specific package used to implement the PCA was princomp. The 39 PCB congeners were considered as the variables, and were centered and standardized prior to analysis. The PCA was implemented for all 59 sampling locations, and then for each of the three regions (Main Lake, Georgian Bay and the North Channel). It was hypothesized that the principle components (PCs) may differ among the three regions, and indicate region-specific features of PCB sources or transport.

5.1.7.1 **Principal Component Analysis for Lake Huron**

The first two PCs accounted for 95% of the total variance in the data. Inspection of the weights in PC1 shows that they are all of similar (small) magnitude and likely are adjusting for differences in magnitude and variance of each congener.

Biplots comparing the first three PCs suggest that the congeners are not unique and clump together. Comparison of PC 2 and PC 3, PC 2 and PC 4, suggest that PCB 209 separated from the other congeners (Figure 18).

(a)   (b)
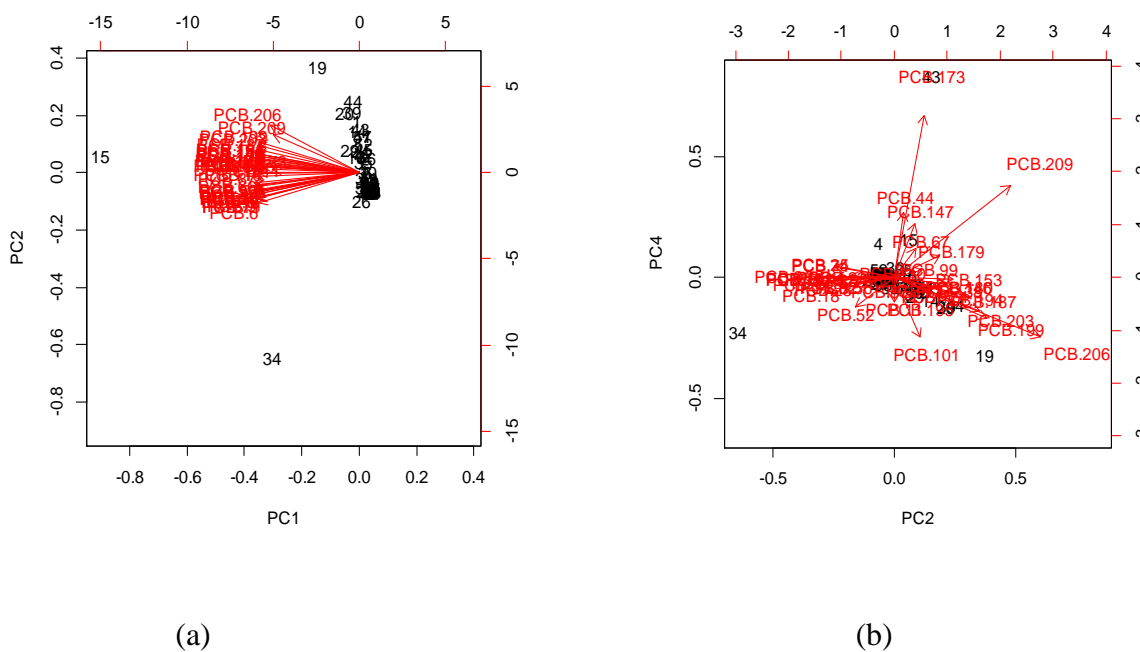
Figure 18. Biplot comparison of PC 1 and 2 (a) and PC 2 and 4 (b) of the whole lake.

5.1.7.2 **Principal Component Analysis for Georgian Bay**

Separate congener clustering is observed in Georgian Bay. The PC 1 explains 74% of variance in the data, while PC 2, PC 3, and PC 4 account for ~12.5%, ~8%, and 2% of the variance in the data set.

The PCB congeners are showing discrete distribution in PC1 to PC2. The same distribution is shown in the PC 1–PC 3. Three main categories are shown in PC 2 to PC 3, which basically the PCB 19 was separated from the others in comparing PC2 with PC 3. However, PCB 209 was not separated here (Figure 19).

(a)   (b)
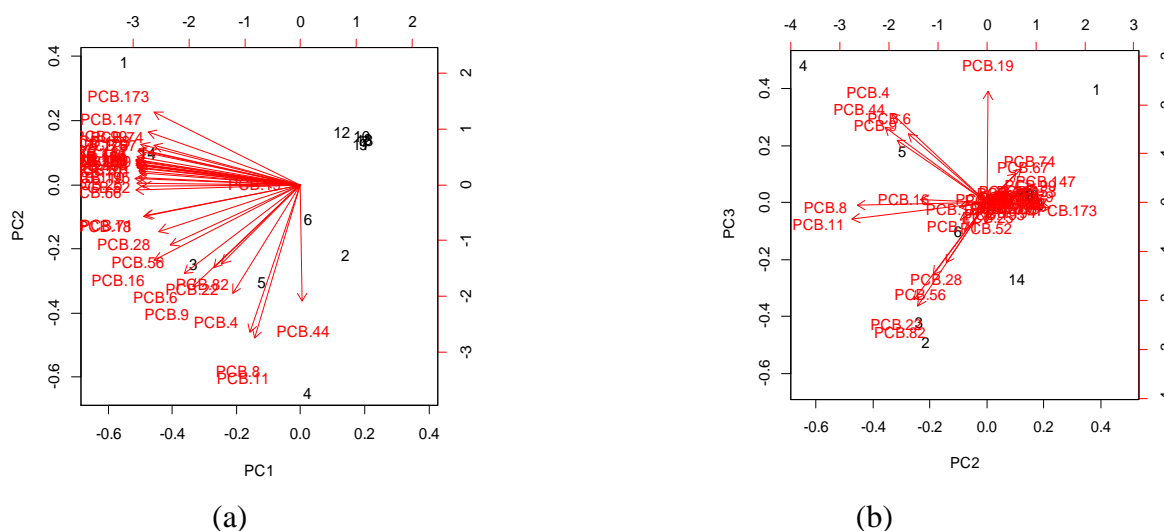
Figure 19. Biplot comparison of PC 1 and 2 (a) and PC 2 and 3 (b) of Georgian Bay.

5.1.7.3 **Principal Component Analysis for North Channel**

Sixty-seven percent of the variation of the data set is described by PC1, and 20%, 6%, and 3% of variation is described by PC 2, PC 3 and PC 4, respectively.

The pair-wise comparison, shows the discreet distribution of the congeners in PC1–PC2. Congeners PCB 19, PCB 209, PCB 25, and PCB 74 separated from the others in PC2–PC4; PCB 66 (which has highest concentration) is separated from PC1 and PC3 from the other congeners.
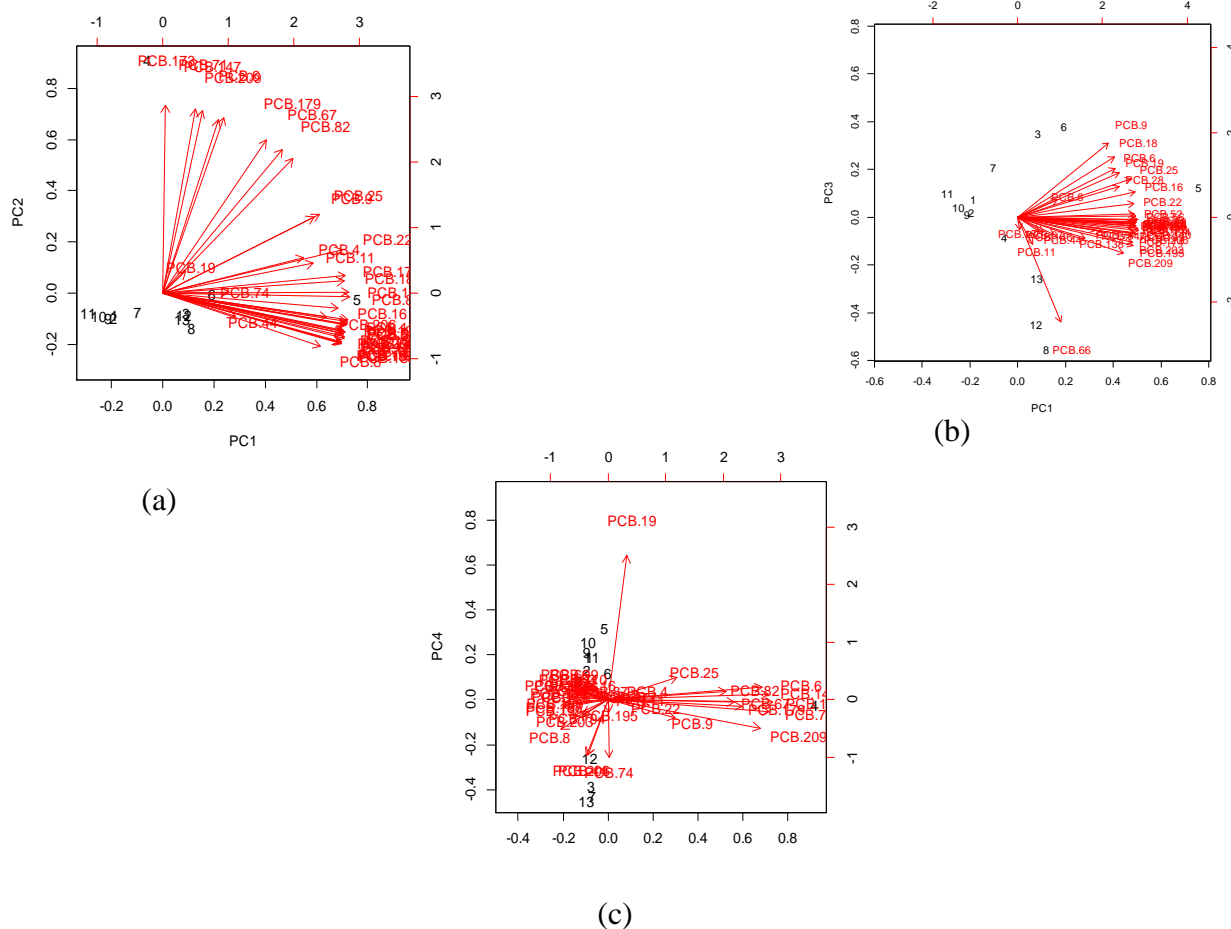
Figure 20. Biplot comparison of PC1 and PC2 (a), PC2 and PC3 (b) and PC2–PC 4 (c) of the North Channel.

5.1.7.4 **Principal Component Analysis for Main Lake**

Ninety-nine percent of the variance of the data set is explained by PC1 (95%), PC2, (3%), and PC3 (1%). Separation of congeners observed in PC2–PC3.
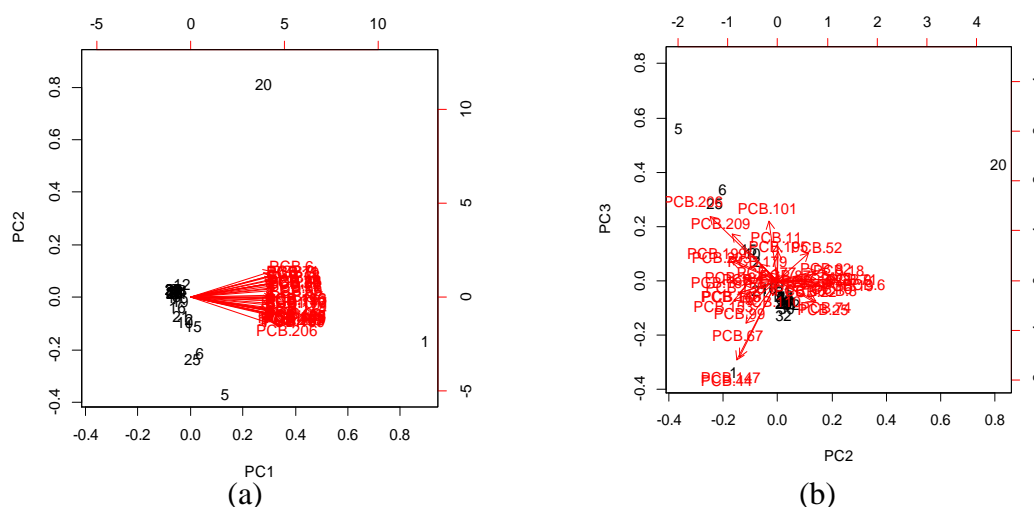
Figure 21. Biplot comparison of PC 1 and PC 2 (a), PC 2 and PC 3 (b) of the main lake.

However, overall comparison suggests, PCA that the main Lake and the whole lake have a similar congener distribution that is different from Georgian Bay and the North Channel. The similarity between the main Lake and whole Lake may be due to the large number of samples from this region relative to the other regions. These differences in congener distribution in the North Channel and Georgian Bay are due to the pollutant source of the

particular region. Most importantly, clear congener separation was not observed by this analysis.

5.2 **Chlorinated Flame Retardants**

5.2.1 **Overview**

The objective of this section is to present and describe the concentrations of chlorinated flame retardants in surface sediment samples collected from Lake Huron in 2012. Measured chemicals in this category include: DEC 602, DEC 603, DEC 604, DP, and Dechlorane plus mono adducts. Data analyses are restricted to the following chemicals for which more than 50% of samples contained quantifiable concentrations: DEC 602, DEC 603, syn-DP, and anti-DP.

5.2.2 **Summary of Chemical Concentrations**

The distribution of dechloranes quantified above the limits of detection in more than 50% of surface sediment samples are summarized in Table XXI. The median concentrations in 59 surface samples are: 57 pg/g DEC 602, 12 pg/g DEC 603, 43 pg/g syn-DP, and 201 pg/g anti-DP. The distributions of dechlorane chemicals are show in Figure 22.

TABLE XXI

DISTRIBUTION OF DECHLORANES IN SURFACE SEDIMENT SAMPLES OF LAKE HURON

unit (pg/g).	min	Q1	median	Q3	Max	Average	LOD	% of N.D
DEC 602	<LOD	16	57	164	2957	206	4.5	10.1
DEC 603	<LOD	3	12	33	1695	57	1.5	10.1
SYN-DP	<LOD	19	43	161	959	123	2.3	3.3
ANTI-DP	<LOD	84	201	900	3779	579	3.0	0.0

Note: Nondetect (N.D) =Number of samples with concentration=0/total number of samples; Q1=first quartile and Q3=third quartile.
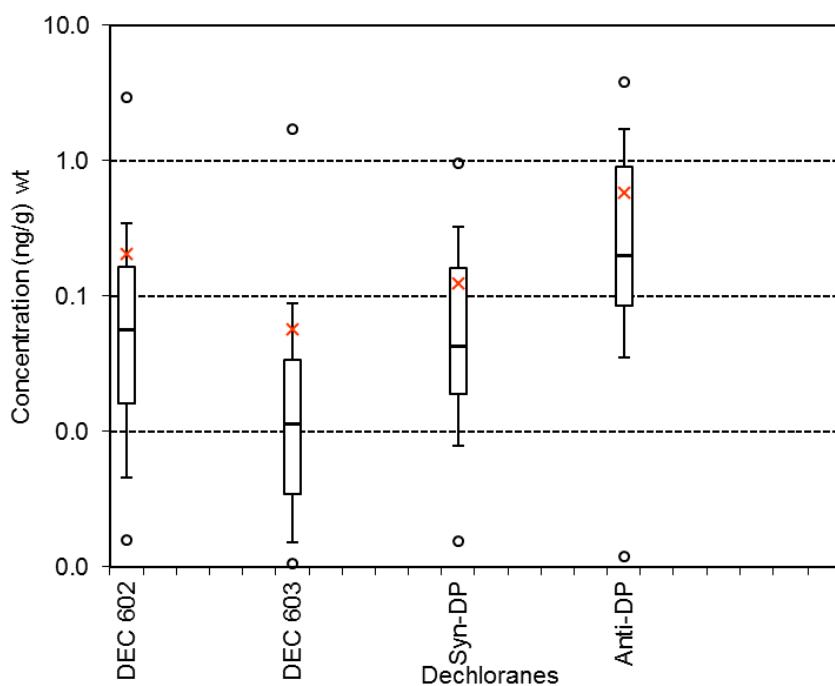
Figure 22. Dechlorane chemical distribution among 59 surface sediment samples. The line in the box represents the median; the cross represents average; the box covers the range from the first to the third quartile; the bars outside the box represent the 10th and 90th percentile values; the circles outside the box represent the maximum and the minimum values.

Hoh et al. (2006) reported that DEC 602 and DEC 603 were found in all the samples of

the Great Lakes, while DEC 604 was found in a few locations in Lake Huron and Lake

Superior. These results agreed with our results though they are not present in all the samples. The above-two chemicals have higher detection rates than DEC 604. The median value of DEC 603 is 12 pg/g and this level is comparable with other studies. According to Shen et al. (2009), concentrations of DEC 602, DEC 603, and DEC 604 vary greatly across the lakes ranging from 0.97–11000 pg/g, 0.61–600 pg/g, and 0.84–8000 pg/g in Great Lakes sediments, respectively. One other study by Shen et al. (2010) sampled surface sediments from Lakes Superior, Michigan, Huron, and Ontario and reported DEC 602, DEC 603, and DEC 604 levels to range from 0.001 to 11 ng/g, 0.001 to 0.6 ng/g, and 0.001 to 8 ng/g, respectively. Levels of DEC 603 and DEC 602 were detected in all the samples while DEC 604 was primarily detected in Lakes Erie and Ontario. In a 2011 study on North American tributaries, Shen et al. reported that DEC 602 levels ranged from non-detect to 13 ng/g, DEC 603 ranged from non-detect to 1.1 ng/g, and DEC 604 ranged from non-detect to 4.8 ng/g. Further, he reported annual trends for these chemicals in Niagara suspended sediments that ranged from 0.45 to 1.3, 0.15 to 0.28, and 0.3 to 1.3 ng/g d.w for the chemicals DEC 602, DEC 603, and DEC 604 respectively over the years 1980–2007. He also observed a decreasing trend for DEC 602 and DEC 603 (Shen et al., 2009; Hites et al., 2011).

Two isomers of DP, syn-DP and anti-DP, were separately quantified. These isomers were detected with high frequency in the surface sediment samples and had median concentrations higher than other dechlorane sediment studies (Table XXII). The median value of anti-DP is 201.163 pg/g (range 1.548–959.466 pg/g), and is approximately five-fold greater than the median value of syn-DP, which is 43.369 pg/g (range 1.189–3779.536) pg/g. In contrast, the anti-DP to syn-DP ratio in the technical mixture is 3:1.

The primary DP source for the Great Lakes is the OxyChem facility in Niagara Falls, New York (Gauthier et al., 2009; Sverko et al., 2007; Zhu and Hites, 2006; Qiu et al., 2007). This point source is consistent with the high concentrations of DP in Lake Ontario and the west-to-east DP concentration gradient in Lake Erie. However, there is a possible source of DP in Newcastle, Delaware—BP Amoco's polymer plant, which produced DP. Atmospheric transport and deposition would be another possible source of DP to the Great Lakes.

Table XXII

CONCENTRATION OF TOTAL DP (SYN AND ANTI-ISOMERS) IN SURFACE
SEDIMENTS IN THE GREAT LAKES

Unit (ng/g dw)

Location	Sampling year	Number of samples	Concentration range	Average	Reference
Lake Erie	1997/1998	40	0.061–8.62	-	Sverko et al., 2006
Lake Ontario	1998	40	2.23–586	-	Sverko et al., 2006
Lake Ontario		-	-	150	Qiu et al., 2007
Niagara river		-	-	85	
Chinese River	2006	18	N.D–0.16	0.04	Ren et al., 2010
Lake Superior	2001	6	-	0.33	Shen et al., 2010
Lake Michigan	2002	2	-	0.55	Shen et al., 2010
Lake Huron	2002	8	-	0.87	Shen et al., 2010
Lake Erie		2	-	1.2	Shen et al., 2010
Lake Ontario	2006–2007	6	-	26	Shen et al., 2010
Present study	2011	59			

5.2.3 **Fractional Abundance of Dechlorane Plus Isomers**

The DP isomer profile was calculated by dividing the concentration of syn-DP by the

concentration of total DP (syn-DP plus anti-DP). This isomer fraction is denoted fsyn-DP. This

calculation was performed on a per sample basis. In the present study, mean fsyn-DP is

0.21(standard deviation 0.1). The technical mixture of DP has fsyn-DP=.28 (standard deviation

0.01) (Reiner et al., 2009). The fsyn-DP results are similar to published studies. Studies

conducted in Great Lakes reported fsyn-DP values in the range of 0.2 to 0.36 (Hoh et al., 2006;

Marvin et al., 2007; Shen et al., 2009; Hites et al., 2007).

Biodegradation and bioavailability of the two isomers are significantly different (Hoh et al., 2006). Though syn-DP and anti-DP have similar K_{OW}, they have different water solubilities (Sverko et al., 2007). The biomagnification factor of syn-DP is lower than that of anti-DP, ranging from 0.1–0.6 ng/g and 0.8–11 ng/g for predatory fish in Lake Ontario, respectively (Hites et al., 2011). Anti-DP has been found to dominate in the sediment samples (Hites et al., 2011)

5.2.4 **Dechlorane Distribution**

Among the 59 surface sediment samples in Lake Huron, the order of the median dechlorane concentrations is: anti-DP > syn-DP > DEC 602 > DEC 603. Shen et al. (2010) observed the same distribution patterns of DP in the upper and lower Great Lakes. In Lake Huron, Shen et al. (2009) found the following distribution: total DP > DEC 602 > DEC 603; but in Lake Superior and Lake Michigan the distribution was: total DP > DEC 603 > DEC 602.

5.2.5 **Site Comparison**

The concentrations of frequently detected dechloranes were compared among three regions within Lake Huron: the main body of the lake, Georgian Bay, and the North Channel (Table XXIII). Median concentrations are higher in the North Channel than in the other areas for all chemicals (Table XXIII), and median concentrations of syn-DP and anti-DP are higher in the North Channel than the other two areas. However, this difference is not statistically significant (P>.10). No other studies were identified that enabled comparisons among these areas of Lake Huron.

Table XXIII

COMPARISON OF DECHLORANE CHEMICALS IN MAIN REGIONS OF THE LAKE

Site	Chemical	Average (ng/g)	Median(ng/g)
Lake	DEC 602	0.187	0.041
	DEC 603	0.073	0.008
	Syn-DP	0.075	0.033
	Anti-DP	0.396	0.173
Georgian Bay	DEC 602	0.160	0.050
	DEC 603	0.019	0.007
	Syn-DP	0.142	0.071
	Anti-DP	0.648	0.268
North Channel	DEC 602	0.307	0.1320
	DEC 603	0.061	0.033
	Syn-DP	0.223	0.085
	Anti-DP	0.957	0.339

Figures 23–26 show the concentrations of DEC 602, DEC 603, total-DP, and separate anti- and syn-DP levels at each of the 59 surface sediment sampling sites. There is high variability among the sampling locations, even within the three regions. As described previously, the concentration of anti-DP is higher than the other three dechloranes.
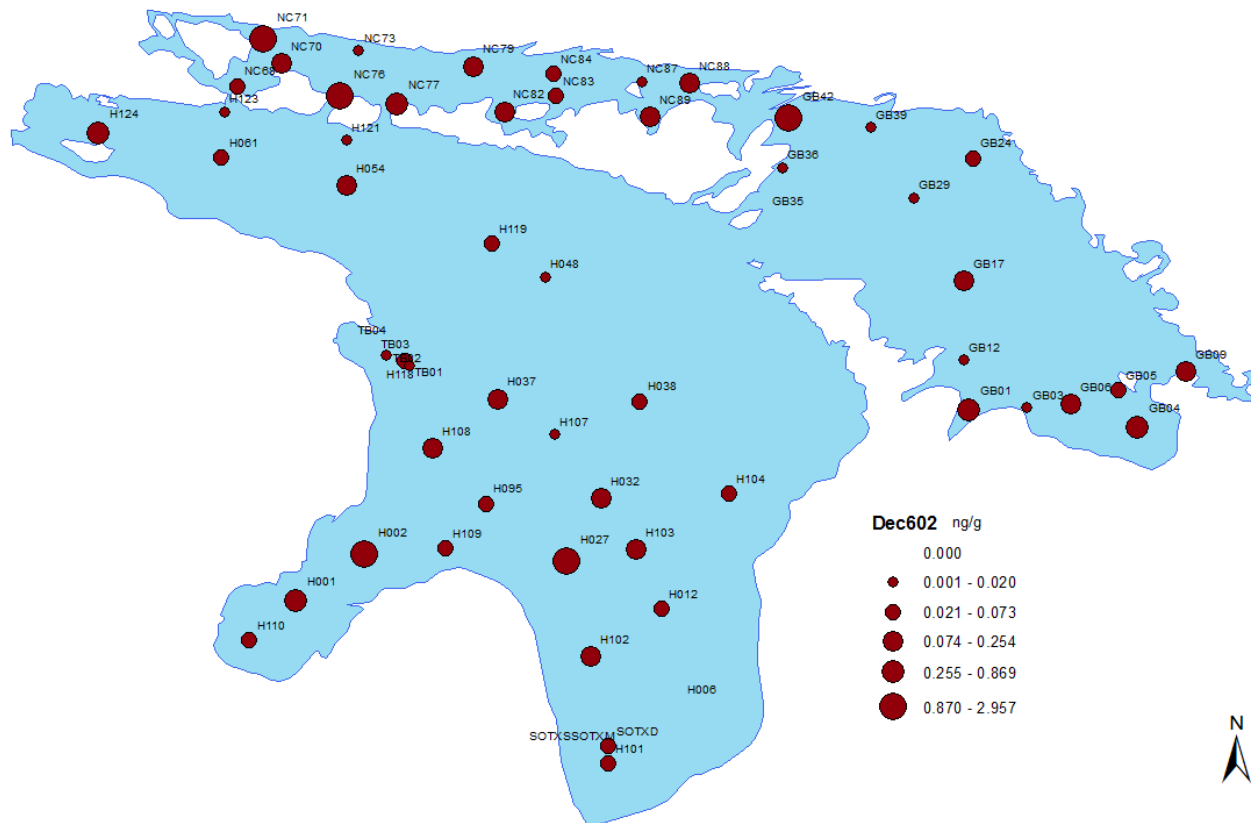
Figure 23. Dechlorane 602 distribution of Lake Huron sediment samples.
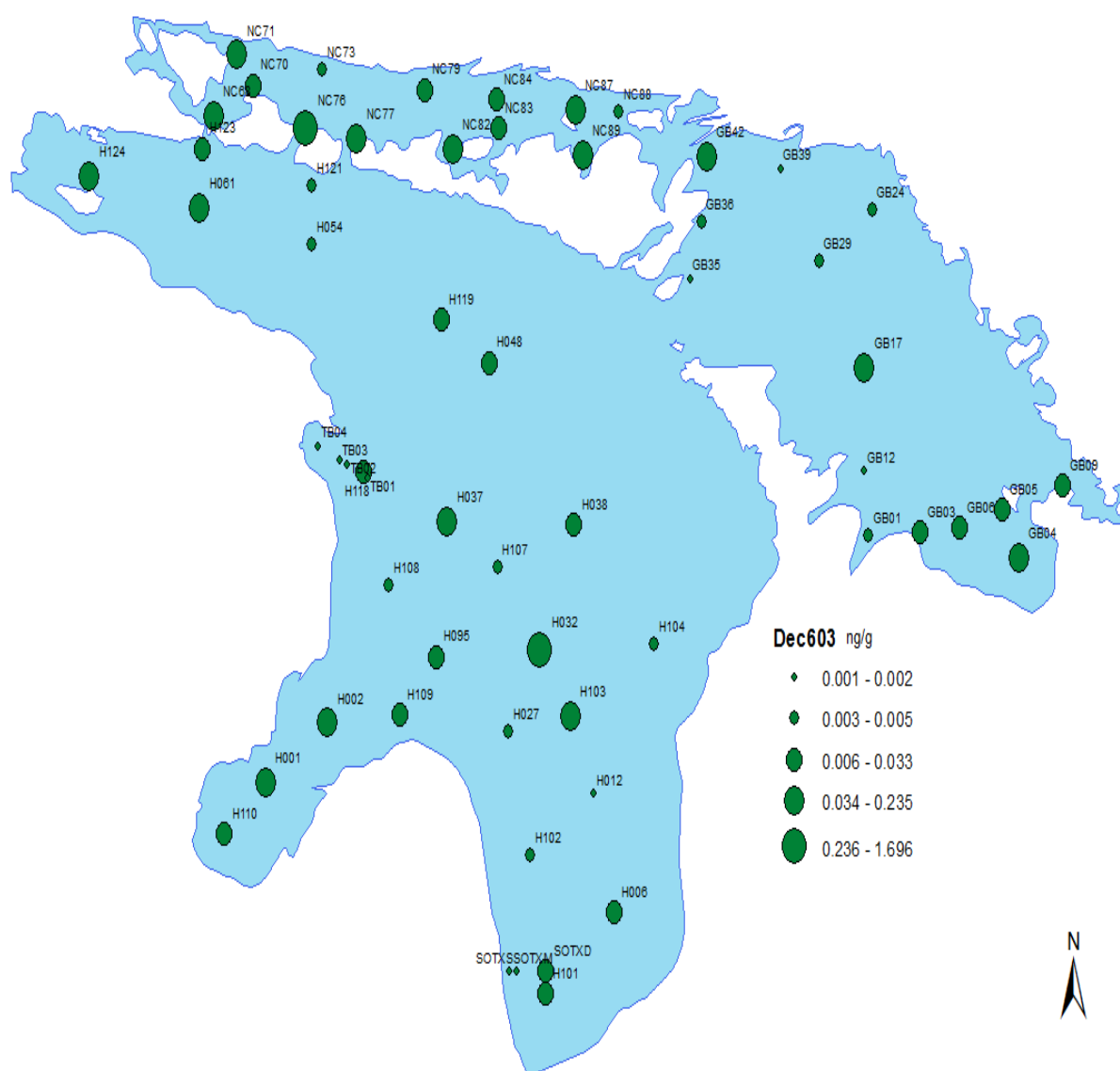
Figure 24. DEC 603 distribution of Lake Huron sediment samples.
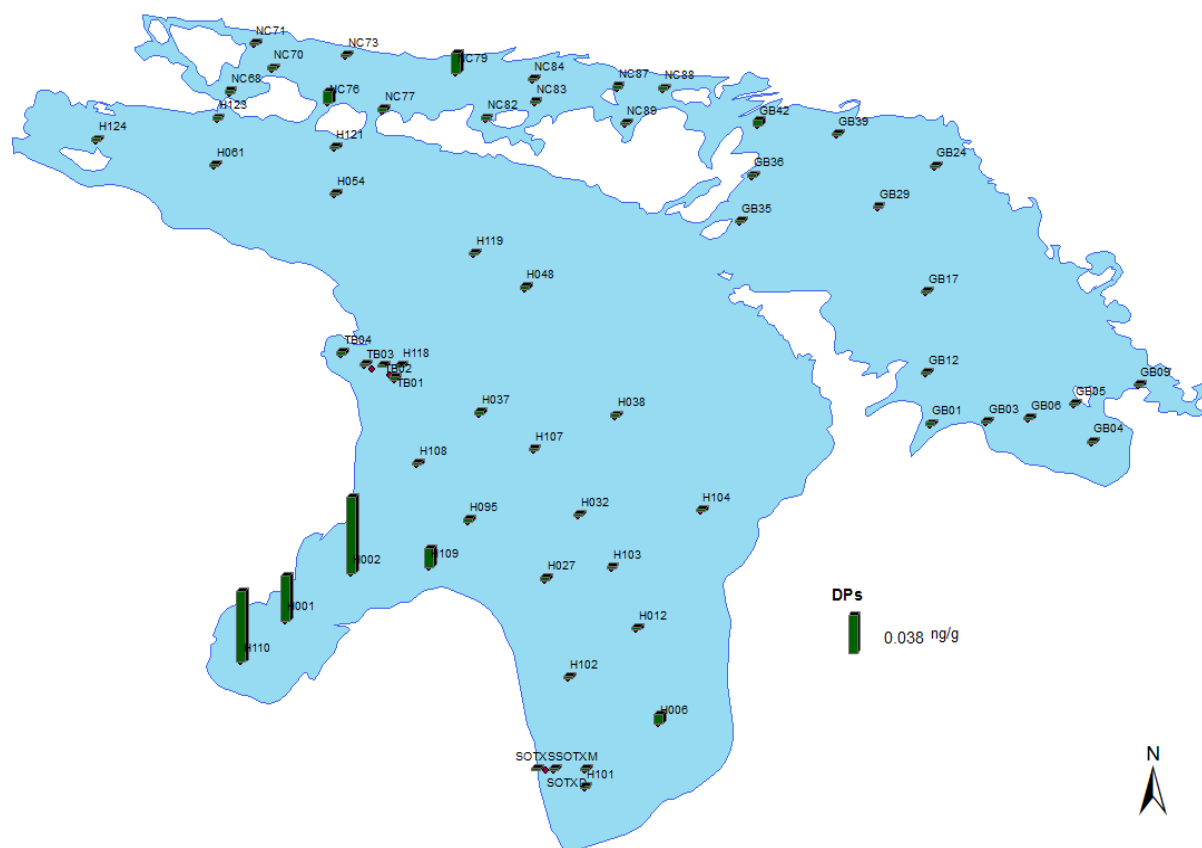
Figure 25. Total DP distribution of surface sediments of Lake Huron.
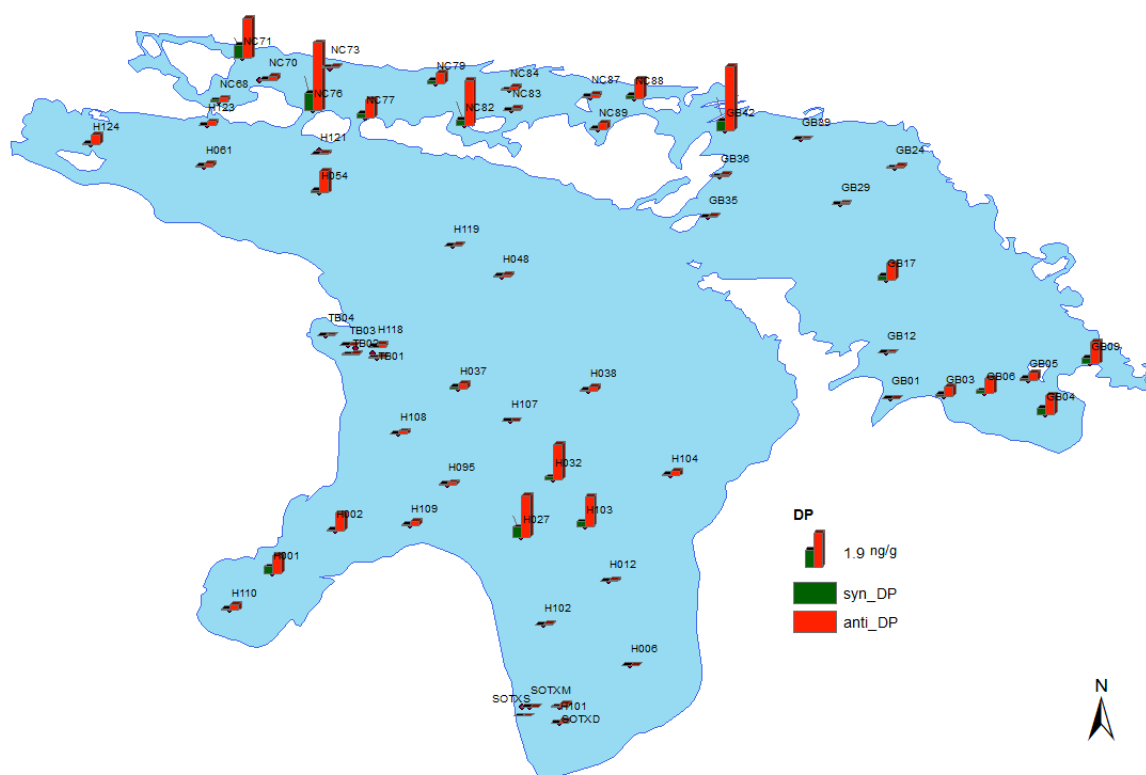
Figure 26. Anti- and syn-DP isomer distribution of surface sediment of Lake Huron.

5.2.6 **Dechlorane Plus Concentration Changes with the Distance from OxyChem Facility, Niagara Falls, New York**

I hypothesized, based on the west-to-east concentration gradient of DP in Lake Erie attributed to the point source of the OxyChem facility in Niagara Falls, New York (Qiu et al., 2007), that a concentration gradient may exist in Lake Huron. The relationships between syn-DP, anti-DP, and total DP and distance from the OxyChem facility are shown in Figures 27–29, respectively. For all chemicals, the slope of the regression lines is negative, indicating that the concentration decreases toward the west. This is consistent with the observation in Lake Erie,

and the point source of the OxyChem facility. However, the R^2 values in the linear regression are small, indicating that there are other factors influencing DP concentrations in Lake Huron surface sediments.
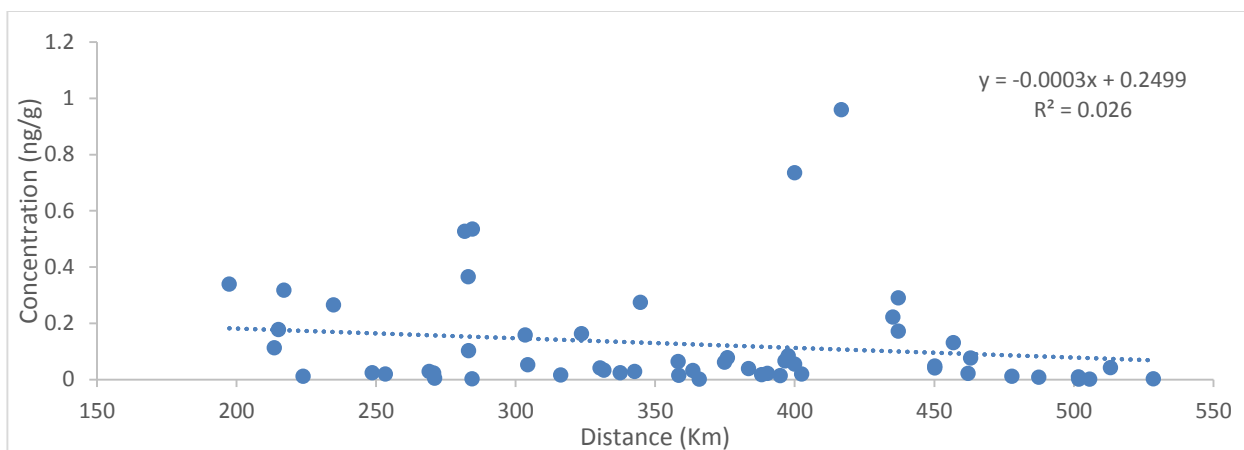
Figure 27. Concentration gradient of syn-DP with the distance to the OxyChem facility.
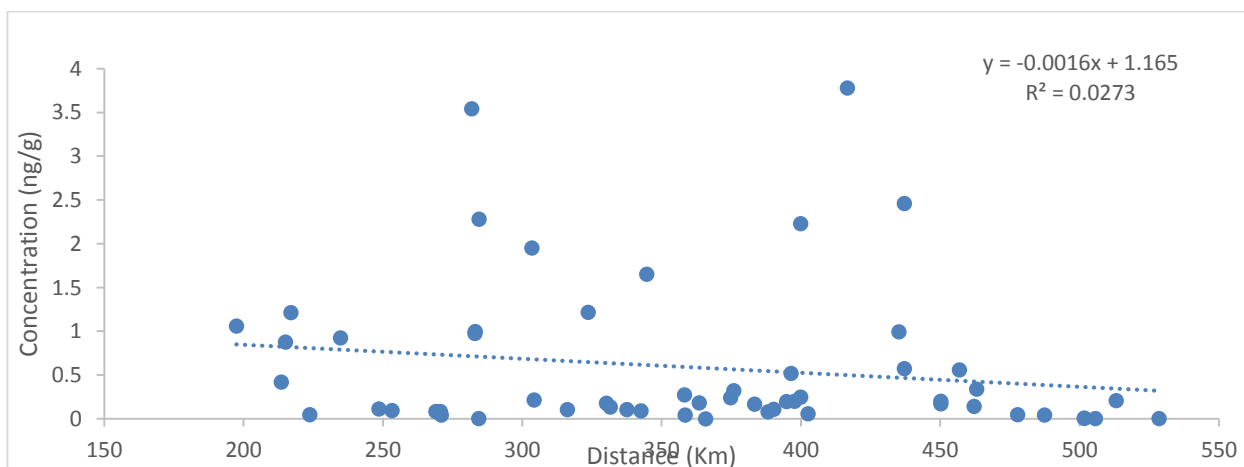
Figure 28. Concentration gradient of anti-DP with the distance to the OxyChem facility.
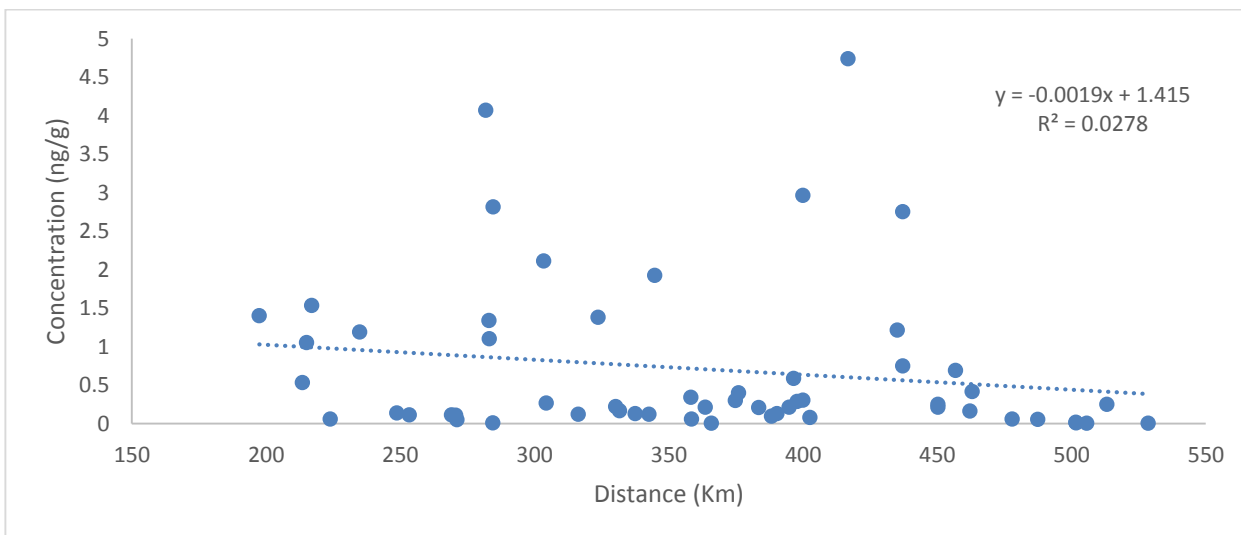
Figure 29. Concentration gradient of total-DP with the distance to the OxyChem facility.

5.3 **Brominated Flame Retardants**

5.3.1 **Polybrominated Diphenyl Ethers**

5.3.1.1 **Overview**

The objective of this section is to present and describe the concentration levels of PBDE in surface sediments of Lake Huron sampled in 2012. Congeners considered in this study include BDE 28, BDE 49, BDE 47, BDE 99, BDE 100, BDE 154, BDE 153, BDE 183, and BDE 209.

5.3.1.2 **Summary of Chemical Concentration**

The distribution of BDE-congener concentrations among the 59 surface sediment samples from Lake Huron are summarized in Table XXIV. The sum of nine congeners—BDE 28, BDE 49, BDE 47, BDE 99, BDE 100, BDE 154, BDE 153, BDE 83, and BDE 209, is denoted $\sum$9PBDE. The median concentration of the $\sum$9 BDE congeners is 2.72 ng/g dry weights (range 0.049–53.99 ng/g). Figure 30 shows that the $\sum$9 BDE concentrations

are driven by the BDE209 concentration. The median concentration of PBDE 209 is two to three orders of magnitude greater than the other congeners.

Table XXIV

STATISTICAL SUMMARY FOR THE SAMPLES OF SURFACE SEDIMENTS

OF LAKE HURON (ng/g)

	Min	Q1	Average	Median	Q3	Max	% of N.D
BDE 28	0.0003	0.0019	0.0054	0.0028	0.0048	0.0803	1.7
BDE 49	0.0001	0.0017	0.0100	0.0028	0.0048	0.2585	3.4
BDE 47	0.0019	0.0197	0.0547	0.0312	0.0558	0.4980	0
BDE 99	0.0001	0.0062	0.0156	0.0102	0.0156	0.1573	8.5
BDE 100	0.0008	0.0024	0.0115	0.0061	0.0099	0.1580	3.4
BDE 154	0.0007	0.0014	0.0104	0.0042	0.0083	0.1496	25
BDE 153	0.0011	0.0016	0.0115	0.0045	0.0085	0.1646	25
BDE 183	0.0045	0.0045	0.0168	0.0045	0.0162	0.1980	55
BDE 209	0.0086	1.2850	5.0133	2.6560	5.0109	52.3711	0
$\sum_9$BDE	0.0490	1.3427	5.1493	2.7224	5.1412	53.9986	

Note: Non-detect (N.D)=Number of samples with concentration=0/total number of samples; Q1=first quartile and Q3=third quartile.
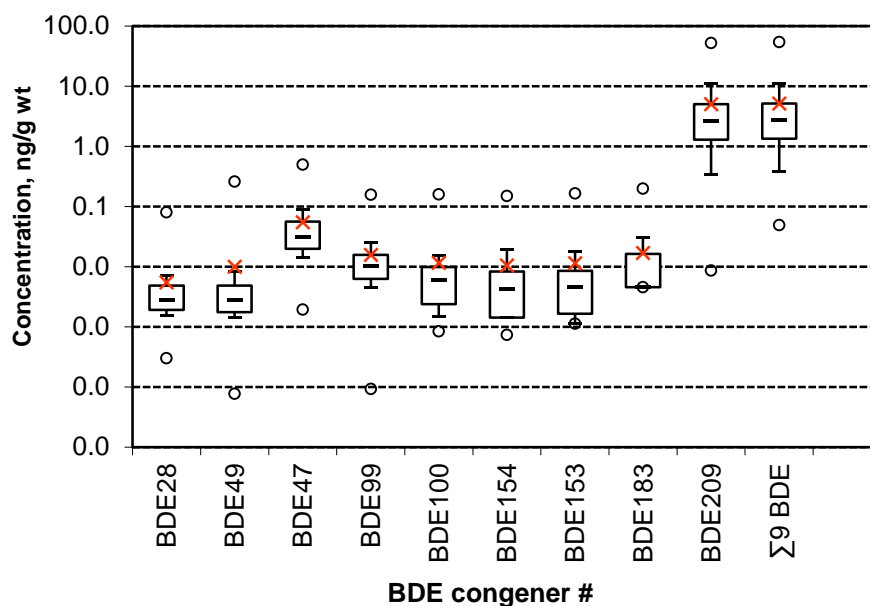
Figure 30. BDE congener distribution in the pooled samples. The line in the box represents the median; the cross represents average; the box covers the range from the first to the third quartile; the bars outside the box represent the 10th and 90th percentile values; the circles outside the box represent the maximum and the minimum values.

These results are comparable with other studies. Table XXV summarizes the PBDE concentrations in surface sediments around the world.

Table XXV

PBDE LEVELS AROUND THE WORLD

Location	Sampling Year	Number of Samples	Number of Congeners	Mean (ng/g d.w.)	Range (ng/g d.w.)	Reference
Saginaw Bay	2004	5	9	2.32	0.05–6.51	Kannan et al., 2007
Saginaw River	2004	20	9	5.37	0.17–49.44	Kannan et al., 2007
Niagara River	2006	11	9	-	0.72–148	Samara et al., 2006
San Francisco Bay	2002	48	22	-	0–212	Oros et al., 2005
Ontario	2002	2	9	4.8 and 6.3	-	Song et al., 2005b
Erie	2002	2	9	1.83 and 1.95	-	Song et al., 2005b
Michigan	2002	3	9	1.67, 3.34, 3.97	-	Song et al., 2005a
Huron	2002	3	9	1.5	-	Song et al., 2005a
Korean Coastal sediment	2004	25	20	27.8	0.45–49	Moon et al. 2007
Tokyo Bay, Japan	2002	6	-	-	0.051 – 3.6	Minh et al., 2007
Pearl river delta, China	2002-2004	10	35	9.9	0.04–94.7	Mai et al., 2005

- Not reported

5.3.1.3 **Polybrominated Diphenyl Ether Congener Distribution**

Of the congeners, BDE 209 has the highest concentration in surface sediments of Lake Huron, followed by BDE 47, BDE 99, BDE 100, respectively (Figure 31). Although PBDE 49 had the lowest concentration, it was present in all but two samples. Congeners BDE 209 and BDE 47 account for more than 96% of the total PBDE mass in the 59 samples

collected in Lake Huron. Since BDE 209 concentration levels are higher than other congeners, in order to evaluate the congener distribution pattern of other congeners, PBDE 209 was removed from Figure 31.
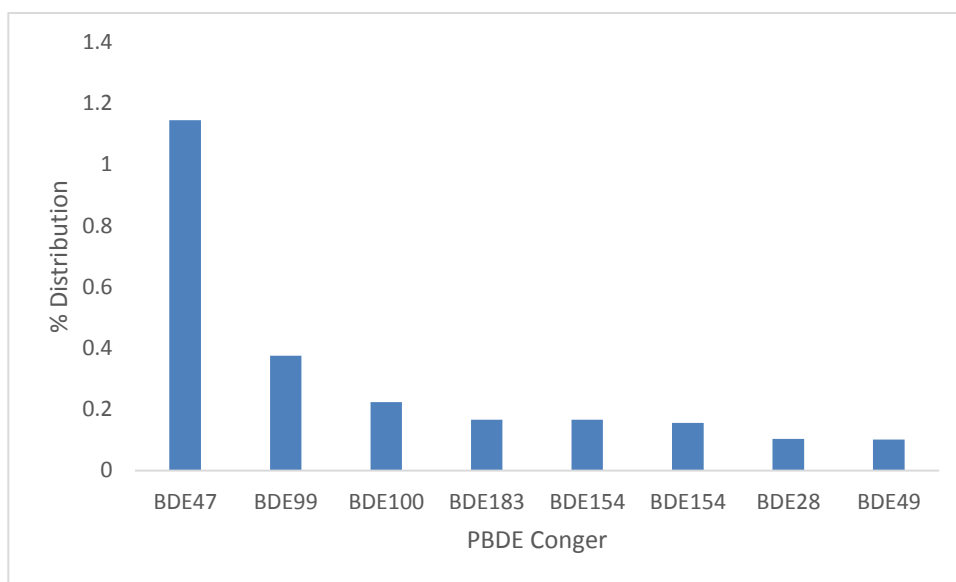
Figure 31. BDE congener distribution relative to the $\sum_8$ BDE concentration, based on median values excluding BDE 209.

The relative concentrations of BDE congeners are similar to those of the other studies. The present study shows that BDE 209 accounts for 92% of the total PBDE mass sampled in Lake Huron. Kannan et al. (2007) found that BDE 209 accounted for 68%−93% of the total PDBE concentration in sediment of the Saginaw River, and was the most abundant congener in almost all the sampling locations, including Saginaw Bay. In addition, Song et al. (2005a, 2005b, 2004) and Zhu and Hites (2005) found that BDE 209 accounted for 95%−99% of the

total BDE concentration of the samples collected from Lakes Superior, Michigan, and Erie. The same phenomenon has been found around the world. For example, Moon et al. (2007) found that BDE 209 accounted for more than 90% of BDE mass in Korean sediments. The highest BDE 209 concentrations of 11600 ng/g, 7100 ng/g, and 3190 ng/g were found in sediment samples are river sediments from Japan, Sweden, and United Kingdom respectively (Mai et al., 2007). The high concentrations of BDE 209 relative to other BDE congeners are consistent with the dominant industrial use of deca BDE, which contains BDE 209. In addition, BDE 209 has high hydrophobicity and a high affinity to sediment particles (Song et al., 2005).

The BDE congener distribution in the present study—BDE 209 > BDE 47 > BDE 99 > BDE 100—is comparable with those reported from other studies. Kannan et al. (2007) observed exactly the same pattern for the Saginaw watershed. Song et al. (2005) also reported that PBDE 47 and BDE 99 are more abundant than other congeners, and constituted 42%–52% of the $\sum9$ PBDE over the three locations—the main lake, Georgian Bay, and the North Channel—of the lake. Similarly, the present study found that the sum of BDE 47 and BDE 99 constitutes more than 62% of the $\sum9$ BDE in the sampled surface sediment of Lake Huron. Samara et al. (2006) reported that BDE 47 and BDE 99 are the most abundant congeners in Niagara River sediments. This pattern is also shown in most of the sediment samples around the world (Hale et al., 2001; Doder and Hites et al., 2002; Mai et al., 2007). Interestingly, the relative abundance of BDE 47, BDE 99, and BDE 100 in Lake Huron surface sediments is similar to that of commercial mixtures, suggesting commercial BDE mixtures, particularly the penta-BDE product, are a source to Lake Huron.
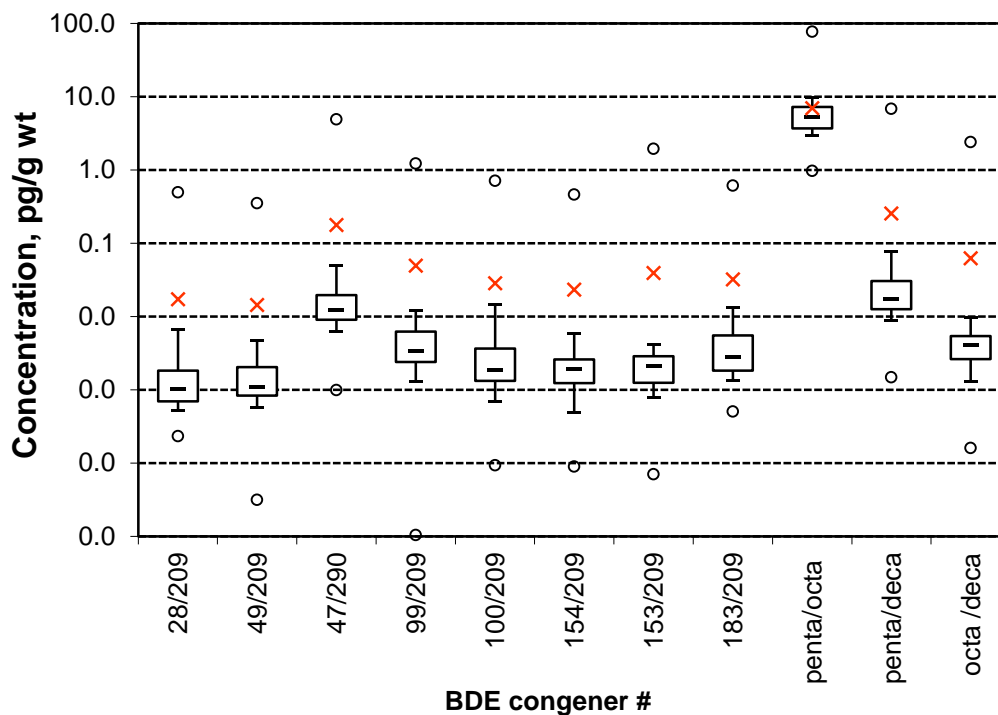
Figure 32. Individual BDE congener to BDE 209 and the ratio commercial mixtures of distribution in Lake Huron surface sediment samples. The line in the box represents the median; the cross represents average; the box covers the range from the first to the third quartile; the bars outside the box represent the 10th and 90th percentile values; the circles outside the box represent the maximum and the minimum values.

Figure 32 shows the clear picture of possible deca-BDE and penta-BDE commercial mixture contamination of Lake Huron sediments. The present study shows a 6.9:1 ratio for penta-BDE to octa-BDE, suggesting the release of higher amounts of the penta-BDE commercial mixture. It is interesting to note that Kannan et al. (2007) observed the same ratio of 6.4:1 for penta-BDE to octa-BDE congeners for Saginaw Bay. Finally, we can conclude that BDE 209 is the main source of PBDE contamination while suggesting minor contributions of penta-BDE and octa-BDE mixtures.

5.3.1.4   **Site Comparison**

Three main areas of the lake: Georgian Bay, North Channel and main Lake were compared based on their average ∑9 BDE concentrations. The average ∑9 BDE concentrations were 5.2 ng/g (range 0.3–54 ng/g), 3.6 ng/g (range 0.04–5.20 ng/g) and 6.8 ng/g (1.44–11.44 ng/g), respectively, suggesting the North Channel contains higher levels of PBDEs. The Kruskal-Wallis test results showed that three main study regions are not statistically different (p=.429).

Figure 33 shows the ∑9 BDE pollutant load at each site. Site H001, which is at the south end of Saginaw Bay, has an extremely high ∑9 BDE concentration. It is not surprising since this is close to Bay City, which has a landfill for the disposal of wastes such as demolition materials, wood, paper, garage, industrial wastes, and dredged sediments (Kannan et al., 2008). Further, there is a wastewater treatment plant close to the Saginaw River, which is a possible route by which BDE may enter Lake Huron. However, the high ∑9 BDE concentrations near Saginaw Bay are comparable with those reported in the literature (Kannan et al., 2008).

Concentrations of PBDE are higher than expected in the North Channel, suggesting possible local sources. Relatively high PBDE concentrations were also seen at the east end of Georgian Bay.
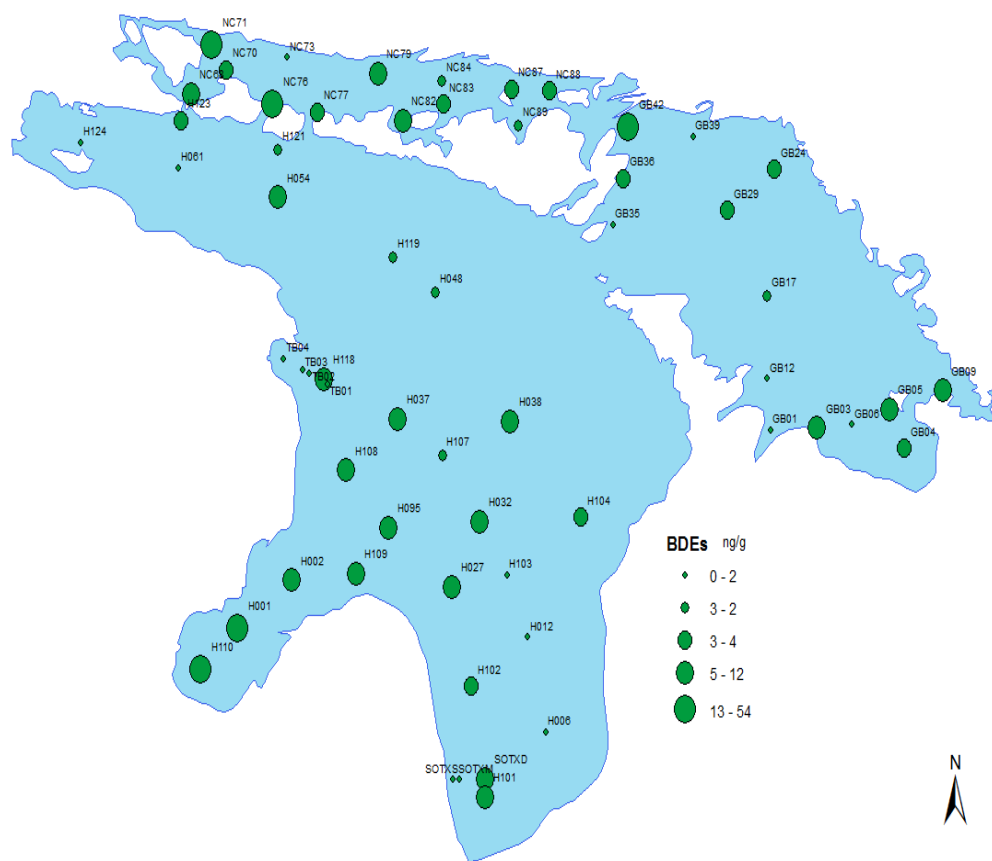
Figure 33. $\sum_9$ BDE distribution of surface sediment of Lake Huron.

5.3.2   **Other Brominated Flame Retardants**

5.3.2.1   **Overview**

The objective of this section is to present the concentrations of non-PBDE flame retardants in surface sediments collected from Lake Huron in 2012. Chemicals such as BTBPE, DBDPE, EHTBB, PBT, HBB, BB 153, ATBPE, 1,2-dibromo-4-(1,2dibromo ethyl cyclohexane) (TBECH), pentabromoethyl benzene (PBEB), pentachloronitrobenzene(PCNB) were quantified. Statistical analysis was restricted to following chemicals for which more than 50% of samples have quantifiable concentrations: BTBPE, DBDPE, EHTBB, ATBPE, PBB, PBT, HBB, and BB153. Complete results for all the chemicals are shown in Appendix F.

5.3.2.2   **Summary Statistics of Chemicals**

The distribution of some emerging flame retardants quantified in more than 50% of the surface sediments are summarized in Table XXVI. The median dry-weight-based concentrations of surface sediment samples for BTBPE, DBDPE, EHTBB, ATBPE, PBB, PBT, HBB, and BB153 are 133 pg/g, 50 pg/g, 127pg/g, 2 pg/g, 3 pg/g, 4 pg/g, 29 pg/g and 0.9 pg/g, respectively.

Table XXVI

DISTRIBUTION OF NON-PBDE EMERGING FLAME RETARDANTS OF SURFACE
SEDIMENTS IN LAKE HURON (unit pg/g)

	Min	Q1	Median	Q3	Max	Average	LOD	%N.D.
BTBPE	<LOD	55	133	318	3445	311	1.2	12
DBDPE	<LOD	50	50	180	700	136	50	46
EHTBB	<LOD	25	127	261	1369	203	4	20
ATBPE	<LOD	1	2	2	4	2	0.7	17
PBB	<LOD	2	3	4	30	3	0.4	14
PBT	<LOD	3	4	5	6	3	0.1	17
HBB	<LOD	24	29	38	5560	169	0.4	0
BB153	<LOD	<LOD	0.9	8	1500	34	0.6	48

Note: Non-detect (N.D) =Number of samples with concentration=0/total number of samples; Q1=first quartile and Q3=third quartile.

In general, these emerging flame retardants are present at lower frequencies (more frequently below the LOD) than PBDEs and dechloranes.
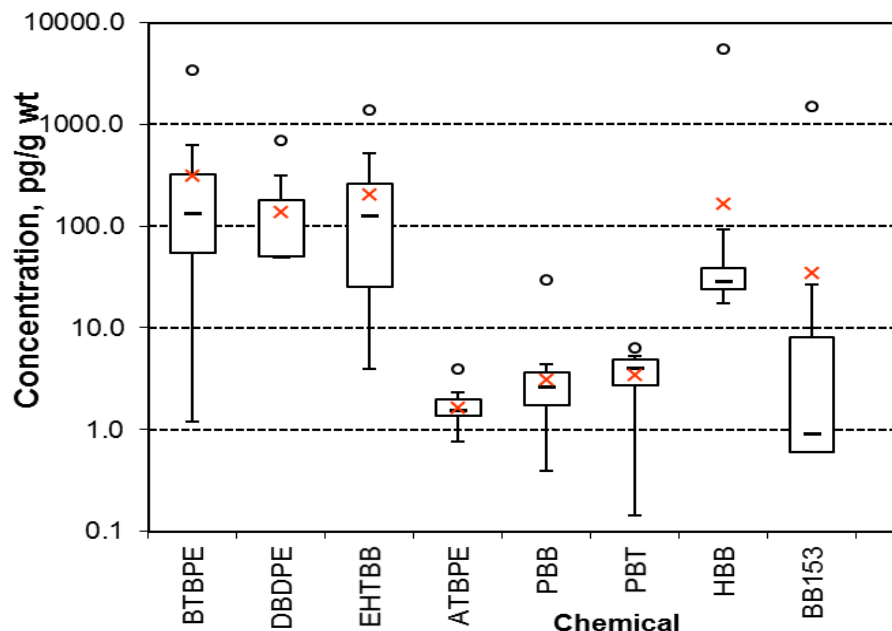
Figure 34. Non-BDE brominated flame retardants distribution in the pooled samples. The line in the box represents the median; the cross represents average; the box covers the range from the first to the third quartile; the bars outside the box represent the 10th and 90th percentile values; the circles outside the box represent the maximum and the minimum values.

5.3.2.4 **1,2-Bis(2,4,6-tribromophenoxy) Ethane**

The concentrations of BTBPE in the surface sediment of Lake Huron ranged from 1.2 to 3445 pg g^{-1} on dry weight basis (Table XXVI).

In 2007, BTBPE was first detected in the environment (Qiu et al., 2007) near a chemical production facility in Arkansas (Covaci et al., 2011). Klosterhaus et al. (2012) detected BTBPE in the sediment of San Francisco Bay that was sampled in 2007, with maximum and median concentrations of 0.06 ng/g and 0.02 ng/g (n=10), respectively. In addition, Lopez et al. (2011) reported that BTBPE in Western Scheldt estuary sediments (n=4) in the Netherlands was lower than the detection limits of 300 pg/g. It is produced in China but information on production is limited (Mai et al., 2008). Wu et al. (2012) conducted a study identifying alternative flame

retardants in sediments near an e-waste disposal area, and concentrations of BTBPE varied

from 30 pg/g to 1.22×10^5 ng/g. Rickuland et al. (2008) collected surface sediment samples of

11 lakes and found that concentrations of BTBPE ranged from 230 to 1400 pg/g. In addition,

Hu et al. 2010 reported that the BTBPE concentration in Baiyangdian Lake and its inflowing

rivers in northern China ranged from 1.1×10^3 to 6.8×10^4 pg/g in dry weight.

5.3.2.5 **<u>Decabromodiphenyl Ethane</u>**

Decabromodiphenyl ethane was first detected in Swedish sewage sludge (about

100 ng/g dw), in sediments from Western Scheldt (24 ng/g dry wt), and in air samples (0.6

ng/m^3) near a Swedish electronics dismantling facility (Kierkegaard et al., 2004). Since then

DBDPE has been detected in various environmental samples around the world. Ricklund et al.

(2008) conducted an international survey of DBDPE in sewage sludge samples collected from

42 wastewater treatment plants in 12 different countries, revealing that DBDPE was present in

sludge from all countries with a highest concentration of 216 ng/g dry wt.

Yang et al. (2012) reported DBDPE levels in surface sediments of Lakes Superior,

Michigan, Huron, Erie, and Ontario to range from 0.11 to 0.6 ng/g, 0.28 to 2.8 ng/g, 1.1 to 2.5

ng/g, 0.27 to 0.54 ng/g, and 0.54 to 0.87 ng/g, respectively. The rank order of the Great Lakes

by concentration of DBDPE is the same as that by concentration of BTBPE. However, Venier

et al. (2010) studied 15 sediment samples collected from the Great Lakes water shed for

DBDPE levels, but did not detect the chemical in any of the samples. Wei et al. (2012) studied

six sites of southern and eastern Arkansas sampled in 2009. At sites near the major DBDPE

manufacturing plants, concentrations up to 870 ng/g were reported, which is the highest ever

reported for surface sediments. Shi et al. (2009) and Zhang et al. (2009) reported concentrations

of DBDPE as high as 400 ng/g from southern China where many electronic industries and e-waste recycling facilities are located.

Zhu et al. (2013) studied surface sediments of the East China sea (n=24) and river sediment samples of the Lingiang, Qujiang, Qiantang rivers (n=6). The mean DBDPE concentration levels were of 0.47 ng/g and 6.38 ng/g, respectively. Guerra et al. (2011) reported DBDPE concentrations of 4.8–23 ng/g in sediments from the Liobregat river basin in Spain. Chen et al. (2013) studied seven rivers in China, including the Dongiang, Zhujiang, Dayannhe, Beijing, and Xijiang Rivers, the Shunde tributaries, and the Pearl River estuary for DBDPE levels, and reported chemical concentration ranges from 10.2 ng/g to 193 ng/g. These results confirmed that DBDPE is widespread in the environment.

5.3.2.6   **2-Ethylhexyl 2, 3, 4, 5- Tetrabromo Benzoate**

Higher concentration levels were observed for EHTBB, with a mean concentration of 203 pg/g (range 3.9–1368 pg/g), compared to the other flame retardants in the present study. Xie et al. (2011) did not quantify EHTBB in the air or sea water samples of the Atlantic and Southern Oceans, with a detection limit of 0.016 pg/m^3.

5.3.2.7   **Hexabromobiphenyls, Poly Bromotoluene**

There is limited information about the production and use of HBB, and its presence in the environment. Yang et al. (2012) reported that HBB has been quantified in more than 76% of the sediment samples in the Great Lakes, and found in high concentrations at a site that could be under the influence of the input from Saginaw Bay. The high concentrations in Saginaw Bay may be explained by the Velsicol chemical plant near the Pine River, which discharges into Lake Huron through the Saginaw Bay area. In this study, HBB was found in

high concentrations at sampling locations H001 and the H110, which are inside of Saginaw Bay. Watanabe and Sakai (2003) reported HBB detected in the range of < 0.9 to 4.3 µg/kg dry weight in 3 out of the 126 samples collected in Japan. Watanabe and Sakai (2003) collected sediments from a river close to Osaka and several estuaries in Japan, and detected HBB levels ranging from < 2 µg/kg to 26 µg/kg in the river sediment samples, but HBB was not detected in the estuary and the marine sediments.

Levels of PBTs were investigated in 23 samples in Berlin and Havel, Germany. The total PBT concentration was 216 µg/kg dw and the concentration ranged from <1 to 25 µg/kg dw (Schwarzbauer et al., 2001; Covaci et al., 2011).

Moller et al. (2011) sampled air and seawater from east China to the high Arctic in 2010 and PBBs, PBTs, and HBB were detected in concentrations of 0.09–2 pg/m^3, 0.1–4.5 pg/gm^3, and 0.1–5.9 pg/m^3, respectively.

In addition to the sediment, these chemicals have been found in aquatic biota illustrating their bioaccumulative properties. Luross et al. (2002) examined 6-year-old lake trout in Lakes Superior, Huron, Erie, and Ontario, and reported PBB concentrations of 1.1 ± 0.57 ng/g, 3.1 ±1.7 ng/g, 0.33±0.08 ng/g, and 0.25±0.13 ng/g respectively, suggesting Lake Huron is more contaminated by PBBs than the other lakes. Among these, BB 153 was the most contributed component of high PBB in this study. Zhu and Hites (2004) observed the same results for their study of Great Lakes fish samples collected in of 1980, 1984, 1990, 1992, 1994, 1996, 1998, and 2000 showing higher concentrations of BB 153 in Lake Huron lake trout samples collected in 2000.

However, our results deviate from this, and indicate that the levels of HBB are higher than the BB-153 levels in surface sediments. These results may not be comparable to other authors due to the different physicochemical parameters of the congeners. Gauthier et al. (2007) conducted a study using homogenate eggs of six colonies of herring gulls in the Great Lakes basins in 2004. He detected considerable levels of flame retardants (HBB 0.24–0.53 ng/g and PBT 0.004–0.02 ng/g), suggesting the contamination of aquatic birds of the Great Lakes Basin. This suggested the possibility of human exposure to flame retardants due to the contaminated sediments of the Great Lakes basin.
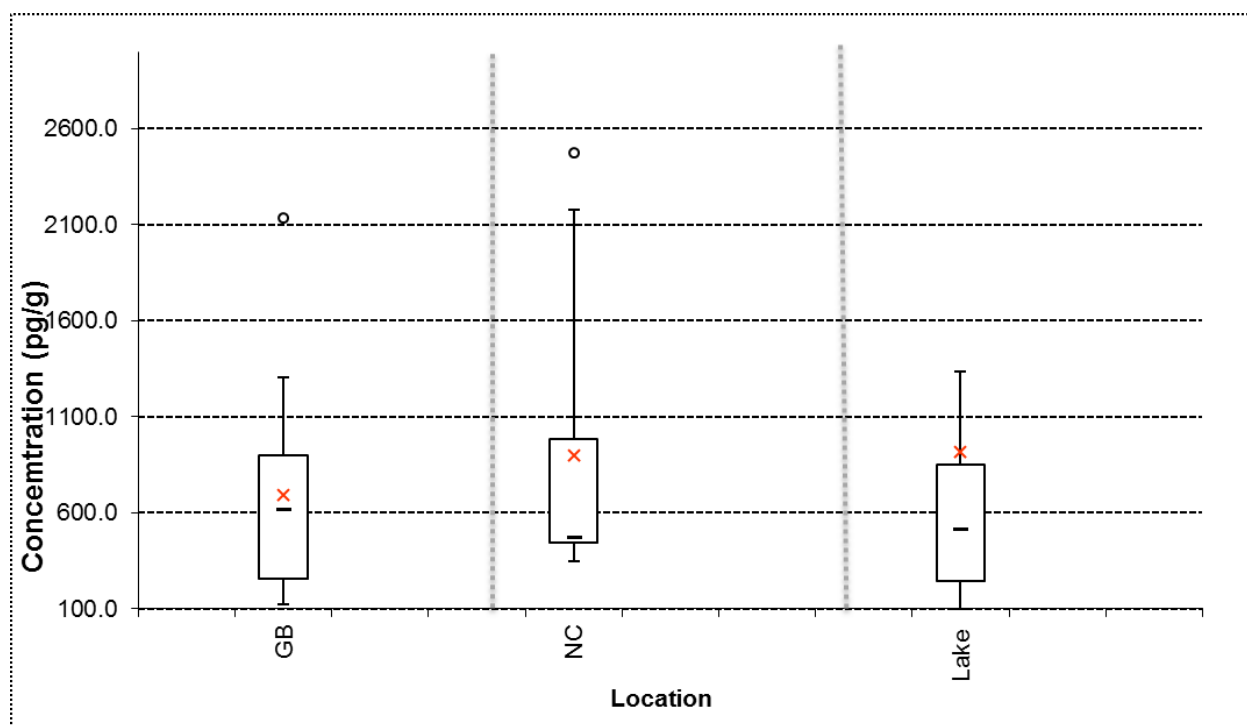
Figure 35. Total non-BDE brominated flame retardant distribution in the main regions of the Lake Huron. The line in the box represents the median; the cross represents average; the box covers the range from the first to the third quartile; the bars outside the box represent the 10th and 90th percentile values; the circles outside the box represent the maximum and the minimum values.

5.3.2.8   **Site Comparison of Total Non-Brominated Diphenyl Flame Retardants**

These results shows that average concentrations of the sum of the flame retardants are similar in the main body of Lake Huron and the North Channel area, with average concentrations of total non-BDE XFR of 920 pg/g and 901 pg/g, respectively. The high concentrations at sampling location H001 (close to Saginaw Bay) lead the average main Lake Huron concentration levels to be slightly higher. Most importantly, the concentration levels of all the site in the proximity of the North Channel is higher than other sites in the lake and Georgian Bay, except for sampling site H001. These results may suggest possible input of non-BDE brominated flame retardants to Lake Huron from the North Channel area. However, this difference in the sites of total non-PBDE brominated flame retardants is not statistically significant (P=.418).

6. CONCLUSION

Persistent organic pollutants like PCBs and chlorinated and brominated flame retardants are detectible in surface sediments of Lake Huron. Since sediment acts as a reservoir and secondary pollution source of these POPs, analysis of sediment concentration of these chemicals is important. The aim of this research was to measure the concentrations of selected PCBs and other halogenated flame retardants in surface sediments of Lake Huron and to compare the pollutant loads in three regions within Lake Huron. The major findings of this research are as follows:

1. PCBs are present and quantified in all surface sediment samples. A total of 39 PCB congeners were analyzed. The median PCB concentration in the tissue samples was 3.74 ng/g dry weight (dw), and a range of 0.076 to 90.9 ng/g dw.

2. PCB 138 is the most prevalent congener (median basis), followed by PCB 28 and PCB 101. The six indicator PCBs (28,101,138,153 and 180) together counted for about 37% of $\sum_{39}$ PCBs. PCB 19 contributed the smallest mass.

3. Sampling sites H001 and H110 have the highest PCB levels in the present study. Both sites are in the Saginaw Bay area, which is in close proximity to Bay City. This is a highly industrialized and populated area.

4. Organic carbon in the sediments plays an important role in absorbing PCB to sediments. Affinity to sediment is congener dependent.

5. Mirex, dechlorane 600s, and DP were the chlorinated flame retardants measured in the surface sediments of Lake Huron. More than 50% of the surface sediment samples contained quantifiable concentrations of DEC 602, DEC 603, and isomers of DPs (syn-DP and anti-DP), with average concentrations 206 pg/g, 57

pg/g, and 123 pg/g 579 pg/g respectively. Anti-DP is present at higher levels than syn-DP.

6. Dechloranes in sediments are higher in the North Channel than in the main lake and Georgian Bay of Lake Huron. There is an observed decreasing trend of concentration levels of DPs (syn-DP, Anti-DP, and Total DP) with the distance from the Oxychem facility in Niagara, New York.

7. The average concentration of BDE 209 is 2.72 ng/g dw and ranges from 0.049 ng/g to 53.99 ng/g dw. BDE 209 is the most abundant congener, followed by the BDE 47. Deca-BDE contamination is high; there is considerable contamination by penta-BDE and octa-BDE commercial products as well.

8. In site-wise comparison, the North Channel shows the higher BDE levels. Average concentration of BDE in the lake, Georgian Bay, and the North Channel is 5.2 ng/g (range 0.3–54 ng/g), 3.6 ng/g (range 0.04–5.20 ng/g), and 6.8 ng/g (range 1.44–11.44 ng/g) dw, respectively.

9. Chemicals such as BTBPE, DBDPE, EHTBB, PBT, HBB, BB 153, Chloradane, ATBPE, TBECH, PBEB, and pentachloronitrobenzene were analyzed. Statistical analysis was restricted to the following chemicals which have quantifiable concentrations in >50% of the samples: BTBPE, DBDPE, EHTBB, ATBPE, PBB, PBT, HBB, and BB153. Average surface concentration levels of analyzed chemicals were 311 pg/g, 136 pg/g, 203 pg/g, 2 pg/g, 3 pg/g, 3 pg/g, 169 pg/g, and 34 pg/g respectively. The North Channel has the highest non-BDE XFR levels than the other two main sites. Average total concentration levels of non-BDE XFRs arte 920 pg/ g, 901 pg/g, and 691 pg/g respectively.

Laboratory contamination is often a concern when dealing with very low concentrations, such as parts per trillion levels as in this study. Detectible levels of chemicals were found in the procedural blanks preformed. Hence, blank correction should be performed for the accurate results.

CITED LITERATURE

Agency for Toxic Substances and Disease Registry (2000). Toxicological profile for polychlorinated biphenyls (PCBs). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Alaee, M., Arias, P., Sjödin, A., & Bergman, Å. (2003). An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment International*, *29*(6), 683–689.

Alcock, R. E., Behnisch, P. A., Jones, K. C., & Hagenmaier, H. (1998). Dioxin-like PCBs in the environment-human exposure and the significance of sources. *Chemosphere*, *37*(8), 1457–1472.

Birnbaum, L. S., & Staskal, D. F. (2003). Brominated flame retardants: Cause for Concern? *Environ Health Perspectives*, *112*(1), 9–17. doi:10.1289/ehp.6559

Birnbaum, L. S., & Staskal, D. F. (2004). Brominated flame retardants: Cause for concern? *Environmental Health Perspectives*, *112*(1), 9.

Botts, L., and Krushelnicki, B. (1995). *Great Lakes Atlas* (3rd ed.). Chicago, IL: Government of Canada (Toronto, Ontario) and US Environmental Protection Agency, Great Lakes National Program Office.

Cairns, T., and Siegmund, E. G. (1981). PCBs: Regulatory history and analytical problems. *Analytical Chemistry*, *53*(11), 1183A–1193A.

Carpenter, D. O., Arcaro, K. F., Bush, B., Niemi, W. D., Pang, S., & Vakharia, D. D. (1998). Human health and chemical mixtures: An overview. *Environmental Health Perspectives*, *106*(Suppl 6), 1263.

Chen, S. J., Tian, M., Wang, J., Shi, T., Luo, Y., Luo, X. J., & Mai, B. X. (2011). Dechlorane plus (DP) in air and plants at an electronic waste (e-waste) site in south China. *Environmental Pollution*, *159*(5), 1290–1296.

Chen, S. J., Feng, A. H., He, M. J., Chen, M. Y., Luo, X. J., & Mai, B. X. (2013). Current levels and composition profiles of PBDEs and alternative flame retardants in surface sediments from the Pearl River Delta, southern China: Comparison with historical data. *Science of the Total Environment*, *444*, 205–211. doi:10.1016/j.scitotenv.2012.11.104

Cogliano, V. J. (1998). Assessing the cancer risk from environmental PCBs. *Environmental Health Perspectives*, *106*(6), 317.

Covaci, A., Gheorghe, A., Voorspoels, S., Maervoet, J., Steen Redeker, E., Blust, R., & Schepens, P. (2005). Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): Analytical aspects and depth profiles. *Environment International*, *31*(3), 367–375.

Covaci, A., Harrad, S., Abdallah, M. A., Ali, N., Law, R. J., Herzke, D., & de Wit, C. A. (2011). Novel brominated flame retardants: A review of their analysis, environmental fate, and behaviour. *Environ International*, 37(2), 532–556. doi:10.1016/j.envint.2010.11.007.

Darnerud, P. O. (2003). Toxic effects of brominated flame retardants in man and in wildlife. *Environment International*, *29*(6), 841–853.

de Solla, S. R., & Martin, P. A. (2009). PCB accumulation in osprey exposed to local sources in lake sediment. *Environmental Pollution*, *157*(1), 347–355.

De Vault, D. S., Hesselberg, R., Rodgers, P. W., & Feist, T. J. (1996). Contaminant trends in lake trout and walleye from the Laurentian Great Lakes. *Journal of Great Lakes Research*, *22*(4), 884–895.

de Wit, C. A. (2002). An overview of brominated flame retardants in the environment. *Chemosphere*, *46*(5), 583–624.

Di Carlo, F. J., Seifter, J., & DeCarlo, V. J. (1978). Assessment of the hazards of polybrominated biphenyls. *Environmental Health Perspectives*, *23*, 351.

Eisenreich, S. J., Looney, B. B., & Thornton, J. D. (1981). Airborne organic contaminants in the Great Lakes ecosystem. *Environmental Science & Technology*, *15*(1), 30–38.

Erickson, M. D. (2001). Introduction: PCB properties, uses, occurrence, and regulatory history. In L. W. Robertson, & L. G. Hansen (Eds.), *PCBS: Recent Advances in Environmental Toxicology and Health Effects* (pp. xi–xxx). Lexington, KY: University Press of Kentucky.

Feo, M. L., Barón, E., Eljarrat, E., & Barceló, D. (2012). Dechlorane plus and related compounds in aquatic and terrestrial biota: A review. *Analytical and Bioanalytical Chemistry*, *404*(9), 2625–2637.

Fouial-Djebbar, D., Ahmed, A. B. H., & Budzinski, H. (2010). Determination of organochlorine compounds in coastal marine sediments from the southern west of the Mediterranean Sea. *International Journal of Environmental Science & Technology*, *7*(2), 271–280.

Frank, R., Thomas, R. L., Holdrinet, M., Kemp, A. L. W., Braun, H. E., & Dawson, R. (1979). Organochlorine insecticides and PCB in the sediments of Lake Huron (1969) and Georgian Bay and North Channel (1973). *Science of the Total Environment*, *13*(2), 101–117.

Fry, D. M. (1995). Reproductive effects in birds exposed to pesticides and industrial chemicals. *Environmental Health Perspectives*, *103*(Suppl 7), 165.

Gasull, M., Bosch de Basea, M., Puigdoménech, E., Pumarega, J., & Porta, M. (2011). Empirical analyses of the influence of diet on human concentrations of persistent organic pollutants: A systematic review of all studies conducted in Spain. *Environment International 37*(7), 1226–1235.

Gauthier, L. T., & Letcher, R. J. (2009). Isomers of dechlorane plus flame retardant in the eggs of herring gulls (Larus argentatus) from the Laurentian Great Lakes of North America: Temporal changes and spatial distribution. *Chemosphere*, *75*(1), 115–120.

Gauthier, L. T., Hebert, C. E., Weseloh, D. C., & Letcher, R. J. (2007). Current-use flame retardants in the eggs of herring gulls (Larus argentatus) from the Laurentian Great Lakes. *Environmental Science & Technology*, *41*(13), 4561–4567.

Gauthier, L. T., Potter, D., Hebert, C. E., & Letcher, R. J. (2008). Temporal trends and spatial distribution of non-polybrominated diphenyl ether flame retardants in the eggs of colonial populations of Great Lakes herring gulls. *Environmental Science & Technology*, *43*(2), 312–317.

Gevao, B., Beg, M. U., Al-Omair, A., Helaleh, M., & Zafar, J. (2006). Spatial distribution of polychlorinated biphenyls in coastal marine sediments receiving industrial effluents in Kuwait. *Archives of Environmental Contamination and Toxicology*, *50*(2), 166–174.

Gilbertson, M. (1983). Etiology of chick edema disease in herring gulls in the lower Great Lakes. *Chemosphere*, *12*(3), 357–370.

Gilbertson, M., & Fox, G. A. (1977). Pollutant-associated embryonic mortality of Great Lakes herring gulls. *Environmental Pollution* (1970), *12*(3), 211–216.

Guerra, P., Fernie, K., Jiménez, B., Pacepavicius, G., Shen, L., Reiner, E., & Alaee, M. (2011). Dechlorane plus and related compounds in peregrine falcon (Falco peregrinus) eggs from Canada and Spain. *Environmental Science & Technology*, *45*(4), 1284–1290.

Guo, J., Li, Z., Sandy, A. L., & Li, A. (2014). Method Development for Simultaneous Analyses of Multiple Legacy and Emerging Organic Chemicals in Sediments. Journal of Chromatography A.

Guvenius, D. M., Aronsson, A., Ekman-Ordeberg, G., Bergman, A., & Noren, K. (2003). Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenylols, and pentachlorophenol. *Environmental Health Perspectives*, *111*(9), 1235–1241.

Guzelian, P. S. (1982). Comparative toxicology of chlordecone (Kepone) in humans and experimental animals. *Annual Review of Pharmacology and Toxicology*, *22*(1), 89–113.

Haase, R. F., McCaffrey, R. J., Santiago-Rivera, A. L., Morse, G. S., & Tarbell, A. (2009). Evidence of an age-related threshold effect of polychlorinated biphenyls (PCBs) on neuropsychological functioning in a Native American population. *Environmental Research*, *109*(1), 73–85.

Hansen, L. G. (1998). Stepping backward to improve assessment of PCB congener toxicities. *Environmental Health Perspectives*, *106*(Suppl 1), 171.

Hansen, L. G. (1999). *The ortho side of PCBs: Occurrence and disposition*. Boston, MA: Kluwer Academic.

Hardy, M. L. (2002). A comparison of the properties of the major commercial PBDPO/PBDE product to those of major PBB and PCB products. *Chemosphere*, *46*(5), 717–728.

Hickey, J. P., Batterman, S. A., & Chernyak, S. M. (2006). Trends of chlorinated organic contaminants in Great Lakes trout and walleye from 1970 to 1998. *Archives of Environmental Contamination and Toxicology*, *50*(1), 97–110.

Hites, R. A. (2004). Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environmental Science & Technology*, *38*(4), 945–956.

Hoh, E., Zhu, L., & Hites, R. A. (2006). Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. *Environmental Science & Technology*, *40*(4), 1184–1189.

Howell, N. L., Suarez, M. P., Rifai, H. S., & Koenig, L. (2008). Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas. *Chemosphere*, *70*(4), 593–606.

Hu, G., Xu, Z., Dai, J., Mai, B., Cao, H., Wang, J., & Xu, M. (2010). Distribution of polybrominated diphenyl ethers and decabromodiphenylethane in surface sediments from Fuhe River and Baiyangdian Lake, north China. *J Environ Sci (China)*, *22*(12), 1833–1839. doi:10.1016/s1001-0742(09)60328-4

Huang, M. C., Chao, H. R., Wang, S. L., Hung, H. C., Wang, Y. S., & Pan, W. H. (2007). Associations of diet with body burden of dibenzo–p–dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs): Observations on pregnant women from central Taiwan. *Food Additives & Contaminants*, *24*(7), 784–791.

Hyötyläinen, T., & Olkari, A. (1999). The toxicity and concentrations of PAHs in creosote-contaminated lake sediment. *Chemosphere*, *38*(5), 1135–1144.

IPCS (International Program on Chemical Safety). (1994b). *Polybrominated biphenyls*. Environmental Health Criteria no. 152. Geneva, Switzerland: WHO.

Jacobson, J. L., Jacobson, S. W., & Humphrey, H. E. B. (1990). Effects of in utero exposure to polychlorinated biphenyls and related contaminants on cognitive functioning in young children. *The Journal of Pediatrics*, *116*(1), 38–45.

Kang, J. H., Kim, J. C., Jin, G. Z., Park, H., Baek, S. Y., & Chang, Y. S. (2010). Detection of dechlorane plus in fish from urban-industrial rivers. *Chemosphere*, *79*(8), 850–854.

Kannan, K., Imagawa, T., Blankenship, A. L., & Giesy, J. P. (1998). Isomer-specific analysis and toxic evaluation of polychlorinated naphthalenes in soil, sediment, and biota collected near the site of a former chlor-alkali plant. *Environmental Science & Technology*, *32*(17), 2507–2514.

Kay, K. (1977). Polybrominated biphenyls (PBB) environmental contamination in Michigan, 1973–1976. *Environmental Research*, *13*(1), 74–93.

Kierkegaard, A., Bjorklund, J., & Friden, U. (2004). Identification of the flame retardant decabromodiphenyl ethane in the environment. *Environmental Science & Technology*, *38*, 3247–53.

Klosterhaus, S. L., Stapleton, H. M., La Guardia, M. J., & Greig, D. J. (2012). Brominated and chlorinated flame retardants in San Francisco Bay sediments and wildlife. *Environ Int*, *47*, 56–65. doi:10.1016/j.envint.2012.06.005

Lauby-Secretan, B., Loomis, D., Grosse, Y., El Ghissassi, F., Bouvard, V., Benbrahim-Tallaa, L., & Straif, K. (2013). Carcinogenicity of polychlorinated biphenyls and polybrominated biphenyls. *The Lancet Oncology*, *14*(4), 287.

Li, A., Rockne, K. J., Sturchio, N., Song, W., Ford, J. C., Buckley, D. R., & Mills, W. J. (2006). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4. Influencing factors, trends, and implications. *Environmental Science & Technology*, *40*(24), 7528–7534.

Li, A., Rockne, K. J., Sturchio, N., Song, W., Ford, J. C., & Wei, H. (2009). PCBs in sediments of the Great Lakes—distribution and trends, homolog and chlorine patterns, and in situ degradation. *Environmental Pollution*, *157*(1), 141–147.

Lopez, P., Brandsma, S. A., Leonards, P. E., & de Boer, J. (2011). Optimization and development of analytical methods for the determination of new brominated flame retardants and polybrominated diphenyl ethers in sediments and suspended particulate matter. *Analytical Bioanalitycal Chemistry*, *400*(3), 871–883.

Luross, J. M., Alaee, M., Sergeant, D. B., Cannon, C. M., Michael Whittle, D., Solomon, K. R., & Muir, D. C. (2002). Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes. *Chemosphere*, *46*(5), 665–672.

Main, K. M., Kiviranta, H., Virtanen, H. E., Sundqvist, E., Tuomisto, J. T., Tuomisto, J., Toppari, J. (2007). Flame retardants in placenta and breast milk and cryptorchidism in newborn boys. *Environ Health Perspective*, *115*(10). Retrieved from

http://dx.doi.org/10.1289%2Fehp.9924

Mayer, F. L., Mehrle, P. M., & Sanders, H. O. (1977). Residue dynamics and biological effects of polychlorinated biphenyls in aquatic organisms. *Archives of Environmental Contamination and Toxicology*, *5*(1), 501–511.

Mai, B. X., Chen, S. J., Luo, X. J., Chen, L. G., Yang, Q. S., Sheng, G. Y., . . . Zeng, E. Y. (2005). Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environmental Science and Technology*, *39*, 3521–7.

McFarland, V. A., & Clarke, J. U. (1989). Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: Considerations for a congener-specific analysis. *Environmental Health Perspectives*, *81*, 225.

Moller, A., Xie, Z., Cai, M., Zhong, G., Huang, P., Cai, M., Ebinghaus, R. (2011). Polybrominated diphenyl ethers versus alternate brominated flame retardants and dechloranes from East Asia to the Arctic. *Environ Science & Technology*, *45*(16), 6793–6799. doi:10.1021/es201850n

Moon, H., Kannan, K., Lee, S., & Choi, M. (2007). Polybrominated diphenyl ethers (PBDEs) in sediment and bivalves from Korean coastal waters. *Chemosphere*, *66*(2), 243–251.

Oliver, B. G., & Nicol, K. D. (1982). Chlorobenzenes in sediments, water, and selected fish from Lakes Superior, Huron, Erie, and Ontario. *Environmental Science & Technology*, *16*(8), 532–536.

Pugsley, C. W., Hebert, P. D., Wood, G. W., Brotea, G., & Obal, T. W. (1985). Distribution of contaminants in clams and sediments from the Huron-Erie corridor. I–PCBs and octachlorostyrene. *Journal of Great Lakes Research*, *11*(3), 275–289.

Qi, H., Liu, L., Jia, H., Li, Y. F., Ren, N. Q., You, H., Ding, Y. (2010). Dechlorane plus in surficial water and sediment in a northeastern Chinese river. *Environmental Science & Technology*, *44*(7), 2305–2308.

Qiu, X., Marvin, C. H., & Hites, R. A. (2007). Dechlorane plus and other flame retardants in a sediment core from Lake Ontario. *Environmental Science & Technology*, *41*(17), 6014–6019.

Painter, S., Marvin, C., Rosa, F., Reynoldson, T. B., Charlton, M. N., Fox, M., Estenik, J. F. (2001). Sediment contamination in Lake Erie: A 25-year retrospective analysis. *Journal of Great Lakes Research*, *27*(4), 434–448.

Ren, G., Yu, Z., Ma, S., Li, H., Peng, P., Sheng, G., & Fu, J. (2009). Determination of dechlorane plus in serum from electronics dismantling workers in south China. *Environmental Science & Technology*, *43*(24), 9453–9457.

Ricklund, N., Kierkegaard, A., & McLachlan, M. S. (2008). An international survey of decabromodiphenyl ethane (deBDethane) and decabromodiphenyl ether (decaBDE) in sewage sludge samples. *Chemosphere*, *73*(11), 1799–1804. doi:10.1016/j.chemosphere.2008.08.047

Risebrough, R., and Brodine, V. (1970). More letters in wind. *Environment*, *12*(1), 16–27.

Rogers, J. M., & Grabowski, C. T. (1984). Postnatal mirex cataractogenesis in rats: Lens cation balance, growth and histology. *Experimental Eye Research*, *39*(5), 563–573.

Robertson, L. W., and Hansen, L. G. (Eds.) (2001). *PCBs: Recent advances in environmental toxicology and health effects.* Lexington, KY: University Press of Kentucky.

Rutala, W. A., Katz, E. B., Sherertz, R. J., & Sarubbi, F. A. (1983). Environmental study of a methicillin-resistant Staphylococcus aureus epidemic in a burn unit. *Journal of Clinical Microbiology*, *18*(3), 683–688.

Safe, S. (1993). Toxicology, structure-function relationship, and human and environmental health impacts of polychlorinated biphenyls: Progress and problems. *Environmental Health Perspectives*, *100*, 259.

Samara, F., Tsai, C. W., & Aga, D. S. (2006). Determination of potential sources of PCBs and PBDEs in sediments of the Niagara River. *Environmental Pollution*, *139*(3), 489–497.

Schecter, A., Päpke, O., Tung, K. C., Staskal, D., & Birnbaum, L. (2004). Polybrominated diphenyl ethers contamination of United States food. *Environmental science & technology*, 38(20), 5306-5311.

Shen, L., Reiner, E. J., Helm, P. A., Marvin, C. H., Hill, B., Zhang, X., & Brindle, I. D. (2011). Historic trends of dechloranes 602, 603, 604, dechlorane plus, and other norbornene derivatives and their bioaccumulation potential in Lake Ontario. *Environmental Science & Technology*, *45*(8), 3333–3340.

Shen, L., Reiner, E. J., MacPherson, K. A., Kolic, T. M., Sverko, E., Helm, P. A., & Marvin, C. H. (2009). Identification and screening analysis of halogenated norbornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603, and 604. *Environmental Science & Technology*, *44*(2), 760–766.

Shi, T., Chen, S. J., Luo, X. J., Zhang, X. L., Tang, C. M., Luo, Y., Mai, B. X. (2009). Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China. *Chemosphere*, *74*(7), 910–916. doi:10.1016/j.*Chemosphere*.2008.10.047

Sjödin, A., Patterson Jr, D. G., & Bergman, Å. (2003). A review on human exposure to brominated flame retardants—particularly polybrominated diphenyl ethers. *Environment International*, *29*(6), 829–839.

Song, W., Ford, J. C., Li, A., Mills, W. J., Buckley, D. R., & Rockne, K. J. (2004). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 1. Lake Superior. *Environmental Science & Technology*, *38*(12), 3286–3293.

Song, W., Li, A., Ford, J. C., Sturchio, N. C., Rockne, K. J., Buckley, D. R., & Mills, W. J. (2005). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 2. Lakes Michigan and Huron. *Environmental Science & Technology*, *39*(10), 3474–3479.

Stapleton, H. M., Keller, J. M., Schantz, M. M., Kucklick, J. R., Leigh, S. D., & Wise, S. A. (2007). Determination of polybrominated diphenyl ethers in environmental standard reference materials. *Analytical and Bioanalytical Chemistry*, *387*(7), 2365–2379.

Strandberg, B., Dodder, N. G., Basu, I., & Hites, R. A. (2001). Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environmental Science & Technology*, *35*(6), 1078–1083.

Sverko, E., Tomy, G. T., Reiner, E. J., Li, Y. F., McCarry, B. E., Arnot, J. A., & Hites, R. A. (2011). Dechlorane plus and related compounds in the environment: A review. *Environmental Science & Technology*, *45*(12), 5088–5098.

Tillitt, D. E., Ankley, G. T., Giesy, J. P., Ludwig, J. P., Kurita-Matsuba, H., Weseloh, D. V., & Kubiak, T. J. (1992). Polychlorinated biphenyl residues and egg mortality in double-crested cormorants from the Great Lakes. *Environmental Toxicology and Chemistry*, *11*(9), 1281–1288.

US Environmental Protection Agency (1979). EPA bans PCB manufacture; phases out uses [Press release]. Retrieved from: http://www.epa.gov/history/topics/pcbs/01.html

Van den Berg, M., Birnbaum, L. S., Denison, M., De Vito, M., Farland, W., Feeley, M., & Peterson, R. E. (2006). The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences*, *93*(2), 223–241.

Venier, M., Ma, Y., & Hites, R. A. (2012). Bromobenzene flame retardants in the Great Lakes atmosphere. *Environmental Science & Technology*, *46*(16), 8653–8660.

Venier, M., Wierda, M., Bowerman, W. W., & Hites, R. A. (2010). Flame retardants and organochlorine pollutants in bald eagle plasma from the Great Lakes region. *Chemosphere*, *80*(10), 1234–1240.

Watanabe, I., & Sakai, S. I. (2003). Environmental release and behavior of brominated flame retardants. *Environment International*, *29*(6), 665–682.

Warren, N., Allan, I. J., Carter, J. E., House, W. A., & Parker, A. (2003). Pesticides and other micro-organic contaminants in freshwater sedimentary environments—a review. *Applied Geochemistry*, *18*(2), 159–194.

Wei, H., Turyk, M., Cali, S., Dorevitch, S., Erdal, S., & Li, A. (2009). Particle size fractionation and human exposure of polybrominated diphenyl ethers in indoor dust from Chicago. *Journal of Environmental Science and Health*, Part A, *44*(13), 1353–1361.

Wei, H., Aziz-Schwanbeck, A. C., Zou, Y., Corcoran, M. B., Poghosyan, A., Li, A., Sturchio, N. C. (2012). Polybromodiphenyl ethers and decabromodiphenyl ethane in aquatic sediments from southern and eastern Arkansas, United States. *Environmental Science & Technology 46*(15), 8017–8024.

Wu, J., Zhang, Y., Luo, X., She, Y., Yu, L., Chen, S., & Mai, B. (2012). A review of polybrominated diphenyl ethers and alternative brominated flame retardants in wildlife from China: Levels, trends, and bioaccumulation characteristics. *Journal of Environ Science (China)*, *24*(2), 183–194.

Xie, Z., Moller, A., Ahrens, L., Sturm, R., & Ebinghaus, R. (2011). Brominated flame retardants in seawater and atmosphere of the Atlantic and the Southern Ocean. *Environmental Science & Technology*, *45*(5), 1820–1826

Yang, R., Wei, H., Guo, J., & Li, A. (2012). Emerging brominated flame retardants in the sediment of the Great Lakes. *Environmental Science and Technology*, *46*(6), 3119–3126.

Yang, R., Wei, H., Guo, J., McLeod, C., Li, A., & Sturchio, N. C. (2011). Historically and currently used dechloranes in the sediments of the Great Lakes. *Environmental Science & Technology*, *45*(12), 5156–5163.

Zhang, X. L., Luo, X. J., Chen, S. J., Wu, J. P., & Mai, B. X. (2009). Spatial distribution and vertical profile of polybrominated diphenyl ethers, tetrabromobisphenol A, and decabromodiphenylethane in river sediment from an industrialized region of south China. *Environmental Pollution*, *157*(6), 1917–1923.

Zhao, Z., Zhong, G., Möller, A., Xie, Z., Sturm, R., Ebinghaus, R., Zhang, G. (2011). Levels and distribution of dechlorane plus in coastal sediments of the Yellow Sea, North China. *Chemosphere*, *83*(7), 984–990.

Zhu, B., Lam, J. C., Yang, S., & Lam, P. K. (2013). Conventional and emerging halogenated flame retardants (HFRs) in sediment of Yangtze River Delta (YRD) region, east China. *Chemosphere*, *93*(3), 555-560.

Zou, Y., Christensen, E. R., & Li, A. (2013). Characteristic pattern analysis of polybromodiphenyl ethers in Great Lakes sediments: A combination of eigenspace projection and positive matrix factorization analysis. *Environmetrics*, *24*(1), 41–50.

APPENDICES

APPENDIX A

TABLE XXVII

DATA QUANTIFICATION

Abbreviation	Full Name	Precursor	Quantification		Qualification	
			Ion	CE	Ion	CE
	PCBs					
PCB4	2,2'-Dichlorobiphenyl	221.8	152	31	196	25
PCB6	2,3'-Dichlorobiphenyl	221.8	152	31	196	25
PCB8	2,4'-Dichlorobiphenyl	221.8	152	31	196	25
PCB9	2,5-Dichlorobiphenyl	221.8	152	31	196	25
PCB11	3,3'-dichlorobiphenyl	221.8	152	31	196	25
PCB18	2,2',5-Trichlorobiphenyl	255.8	186	31	221	15
PCB22	2,3,4'-Trichlorobiphenyl	255.8	186	31	221	15
PCB25	2,3',4-Trichlorobiphenyl	255.8	186	31	221	15
PCB28	2,4,4'-Trichlorobiphenyl	255.8	186	31	221	15
PCB44	2,2',3,5'-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB52	2,2',5,5'-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB56	2,3,3',4-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB66	2,3',4,4'-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB67	2,3',4,5-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB71	2,3',4',6-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB74	2,4,4',5-Tetrachlorobiphenyl	291.7	222	31	257	13
PCB82	2,2',3,3',4-Pentachlorobiphenyl	325.7	256	31	291	15
PCB87	2,2',3,4,5'-Pentachlorobiphenyl	325.7	256	31	291	15
PCB99	2,2',4,4',5-Pentachlorobiphenyl	325.7	256	31	291	15
PCB101	2,2',4,5,5'-Pentachlorobiphenyl	325.7	256	31	291	15
PCB110	2,3,3',4',6-Pentachlorobiphenyl	325.7	256	31	291	15
PCB138	2,2',3,4,4',5'-Hexachlorobiphenyl	359.6	290	33	325	15
PCB146	2,2',3,4',5,5'-Hexachlorobiphenyl	359.6	290	33	325	15
PCB147	2,2',3,4',5,6-Hexachlorobiphenyl	359.6	290	33	325	15
PCB153	2,2',4,4',5,5'-Hexachlorobiphenyl	359.6	290	33	325	15
PCB173	2,2',3,3',4,5,6-Heptachlorobiphenyl	393.6	324	33	359	15
PCB174	2,2',3,3',4,5,6'-Heptachlorobiphenyl	393.6	324	33	359	15
PCB177	2,2',3,3',4,5',6'-Heptachlorobiphenyl	393.6	324	33	359	15
PCB179	2,2',3,3',5,6,6'-Heptachlorobiphenyl	393.6	324	33	359	15
PCB180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	393.6	324	33	359	15
PCB187	2,2',3,4',5,5',6-Heptachlorobiphenyl	393.6	324	33	359	15
PCB194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	429.6	360	35	395	17
PCB195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	429.6	360	35	395	17
PCB199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	429.6	360	35	395	17
PCB203	2,2',3,4,4',5,5',6-Octachlorobiphenyl	429.6	360	35	395	17
PCB209	Decachlorobiphenyl	497.6	428	33	426	3

APPENDIX A (continued)

DATA QUANTIFICATION

Abbreviation	Full Name	Precursor	Quantification		Qualification	
			Ion	CE	Ion	CE
EHTBB	2-ethylhexyl2,3,4,5-tetrabromobenzoate	437.6	421	21	393	41
BB153	2,2',4,4',5,5'-hexabromodiphenyl	627.5	547	17	549	18
BB101	2,2'4,5,5'-pentabromobiphenyl	547.6	469	15	467	15
HBB	hexabromobenzene	551.6	471	27	473	27
TBB	1,3,5-tribromobenzene	313.7	235	23	233	23
PBB	pentabromobenzene	471.6	393	25	391	25
PBT	pentabromotoluene	485.6	407	17	405	17
PBEB	pentabromoethylbenzene	499.7	485	19	421	10
TBECH-1 [a]	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	346.8	267	1	185	5
TBECH-2 [a]	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	346.8	267	1	185	5
HCDBCO	hexachlorocyclopentadienyl-dibromocyclooctane	374.7	295	5	293	4
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane	356.6	278	11	329	11
syn-DP	dechlorane plus (syn)	344.6	309	4	273	9
anti-DP	dechlorane plus (anti)	344.6	309	4	273	9
Dec 602	dechlorane 602	512.7	371	45	478	13
Dec 603	dechlorane 603	600.7	263	13	261	13
Dec 604	dechlorane 604 component A	693.6	442	7	440	7
ATBPE	2,4,6-tribromophenyl allyl ether	369.7	210	8	291	2
HBCD	α-hexabromocyclododecane	560.7	319	1	399	1
HBCD	γ- hexabromocyclododecane	560.7	319	1	399	1
HBCD	β- hexabromocyclododecane	560.7	319	1	399	1
	PBDEs					
BDE28	2,4,4'-tribromodiphenyl ether	407.6	248	21	246	21
BDE47	2,2',4,4'-tetrabromodiphenyl ether	485.6	326	23	328	23
BDE49	2,2´,4,5´-tetrabromodiphenyl ether	485.6	326	23	328	23
BDE99	2,2,4,4,5-pentabromodiphenyl ether	563.6	404	23	406	23
BDE100	2,2,4,4,6-pentabromodiphenyl ether	563.6	404	23	406	23
BDE153	2,2,4,4,5,5-hexabromodiphenyl ether	643.5	484	23	486	23
BDE154	2,2',4,4',5,6'-hexabromodiphenyl ether	643.5	484	23	486	23
BDE183	2,2,3,4,4,5,6-heptabromodiphenyl ether	723.6	564	25	562	27
BDE209 [b]	decabromodiphenyl ether	484.6	486.6			
TDCPP	tris (1,3-dichloroisopropyl) phosphate	380.7	159	13	161	13

APPENDIX A (continued)

DATA QUANTIFICATION

Abbreviation	Full Name	Precursor	Quantification		Qualification	
			Ion	CE	Ion	CE
	IS and Surrogates					
PCB47L	2,4,2',4'-tetrachlorobiphenyl, 13C12	303.8	234	31	269	13
PCB52L	2,2',5,5'-tetrachlorobiphenyl, 13C12	303.8	234	31	269	13
PCB205L	2,3,3',4,4',5,5',6-octachlorobiphenyl, 13C12	439.7	370	33	405	17
PCB209L	decachlorobiphenyl, 13C12	509.6	440	35	438	35
F-BDE69	4'-fluoro-2,3,4,6-tetrabromodiphenyl ether	503.6	344	21	346	21
F-BDE208 [b]	4'-fluoro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether	484.6	486.6	426.5		
Cl-BDE208 [b]	4'-chloro-2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether	484.6	486.6	442.6		
BB209 [b]	decabromobiphenyl	79	81			

APPENDIX B

TABLE XXVIII

BLANK CONCENTRATION LEVELS FOR PCB CONGENERS

Sample	GBNC FIELDB-1	GBNC FIELDB-2	GBNC Trip -1	GBNC Trip -2	Freeze dry blank-1	Freeze dry blank-2	Freeze dry blank-3	PB-2	PB-4
PCB-4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-9	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-8	0.000	0.001	0.001	0.001	0.001	0.000	0.000	0.001	0.000
PCB-19	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-11	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-18	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-16	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-25	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-28	0.002	0.003	0.004	0.002	0.003	0.001	0.000	0.001	0.000
PCB-22	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000	0.000
PCB-52	1.267	0.954	0.849	0.867	0.558	0.512	0.049	0.194	0.175
PCB-52	0.005	0.005	0.005	0.004	0.004	0.003	0.000	0.001	0.001
PCB-71	0.002	0.002	0.002	0.002	0.001	0.001	0.000	0.000	0.000
PCB-67	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-74	0.001	0.003	0.003	0.003	0.002	0.002	0.000	0.001	0.000
PCB-66	0.004	0.004	0.004	0.004	0.003	0.003	0.000	0.001	0.001
PCB-56	0.000	0.000	0.000	0.002	0.001	0.001	0.000	0.001	0.000
PCB-10	0.005	0.007	0.007	0.006	0.006	0.004	0.001	0.002	0.001
PCB-99	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
PCB-87	0.000	0.000	0.001	0.001	0.002	0.000	0.000	0.000	0.000
									0.000
PCB-11	0.001	0.003	0.004	0.003	0.005	0.002	0.000	0.002	

Sample	GBNC FIELDB-1	GBNC FIELDB-2	GBNC Trip -1	GBNC Trip -2	Freeze dry blank-1	Freeze dry blank-2	Freeze dry blank-3	PB-2	PB-4
PCB-82	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-14	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-14	0.000	0.001	0.002	0.001	0.004	0.001	0.000	0.000	0.000
PCB-17	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-17	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-18	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-19	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-20	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-19	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-19	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-20	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PCB-20	1.079	0.815	0.710	0.700	0.515	0.452	0.179	0.128	0.130
PCB-20	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000

APPENDIX C
TABLE XXIX

BLANK CONCENTRATION LEVELS FOR QUANTIFIED XFRS

Sample/concentration (ng/g)	PB-1	PB-2	PB-2	PB-4	Freeze dry blank	Freeze dry blank	Freeze dry blank	GBNC TRIP-1	GBNC TRIP-2	GBNC FIELD-1	GBNC FIELD-2
Dec602	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DEC603	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DEC604	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
SYN-DP	0.001	0.001	0.000	0.000	0.002	0.005	0.001	0.004	0.007	0.003	0.004
ANTI-DP	0.001	0.001	0.000	0.000	0.001	0.005	0.001	0.004	0.007	0.003	0.004
BTBPE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DBDPE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
EHTBB	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
BDE28	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.002	0.001	0.002
BDE-49	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
BDE-47	0.002	0.001	0.001	0.001	0.003	0.002	0.002	0.004	0.023	0.007	0.010
BDE99	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
BDE100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.005	0.003	0.001
BDE-154	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
BDE-153	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
BDE183	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
BDE209	0.036	0.045	0.008	0.031	0.142	0.018	0.029	0.190	0.287	0.227	0.190
ATBPE	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.002
PBB	0.001	0.001	0.001	0.001	0.002	0.000	0.000	0.000	0.003	0.003	0.003
PBT	0.001	0.001	0.000	0.000	0.002	0.002	0.000	0.000	0.000	0.003	0.004
HBB	0.006	0.008	0.002	0.002	0.020	0.006	0.002	0.000	0.016	0.037	0.033
BB153	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

APPENDIX D

TABLE XXX

TOTAL PCB (Σ 39 PCB) IN EACH SITE

Location	$\sum$39 PCB	Location	$\sum$39 PCB	Location	$\sum$39 PCB
GB01	3.989	H037	0.609	NC70	0.605
GB03	0.360	H038	0.897	NC71	1.704
GB04	2.782	H048	0.295	NC73	0.908
GB05	2.003	H054	3.026	NC76	4.579
GB06	1.539	H061	0.448	NC77	1.998
GB09	1.040	H095	2.522	NC79	0.921
GB12	0.079	H101	2.007	NC82	2.264
GB17	0.050	H102	0.800	NC83	0.549
GB24	0.121	H103	6.641	NC84	0.381
GB29	0.147	H104	1.106	NC87	0.157
GB35	0.159	H107	0.204	NC88	1.811
GB36	0.532	H108	0.421	NC89	1.744
GB 39	0.086	H109	2.246	TB01	0.313
GB42	3.585	H110	31.060	TB02	0.172
H001	90.934	H118	1.964	TB03	0.125
H002	4.981	H119	0.290	TB04	0.119
H006	0.225	H121	0.273	SOTX	0.166
H012	0.380	H123	1.817	TXD	2.337
H027	16.935	H124	4.233	TXM	0.507
H032	7.600	NC68	0.556		

APPENDIX E

TABLE XXXI

PERCENTAGE OF ORGANIC CARBON IN SAMPLED LOCATIONS IN LAKE HURON
2012

Location	% of organic carbon	Location	% of organic carbon	Location	% of organic carbon
GB01	1.79	H038	0.73	NC70	1.67
GB03	0.37	H048	0.51	NC71	2.14
GB04	2.04	H054	2.30	NC76	2.85
GB05	0.55	H061	0.76	NC77	3.44
GB06	2.31	H095	2.11	NC79	1.72
GB09	3.38	H101	0.54	NC82	1.97
GB12	1.50	H102	1.40	NC83	1.46
GB17	2.28	H103	3.57	NC84	0.75
GB24	0.30	H104	1.36	NC87	0.23
GB29	0.24	H107	0.121	NC88	2.50
GB35	0.40	H108	0.29	NC89	0.18
GB36	0.66	H109	0.43	TB01	0.42
GB42	2.415	H110	2.33	TB02	0.18
H001	5.16	H118	0.42	TB04	0.18
H006	3.27	H119	0.38	SOTX	0.45
H012	3.69	H121	0.18		
H027	0.34	H123	0.38		
H032	3.62	H124	2.85		
H037	1.28	NC68	0.54		

APPENDIX F

TABLE XXXII

SUMMARY STATISTICS FOR THE NON-QUANTIFIED XFRS

Chemical	Min	Max	Average	% ND
DPMA	0	0.023	0.001	76.8
MIREX	0	0.035	0.003	78
CP	0	0.041	0.002	84.7
CL10	0	0	0	100
DEC601	0	0	0	100
Cl11	0	0	0	100
HCDBCO	0	0.09	0.002	81.4
PCNB	0	0.012	0.001	79.7
TBECH-1	0	0.018	0.001	89.8
TBECH-2	0	0.016	0.001	89.8
PBEB	0	0.006	0	94.9
PBB101	0	0.147	0.004	50.8

APPENDIX G
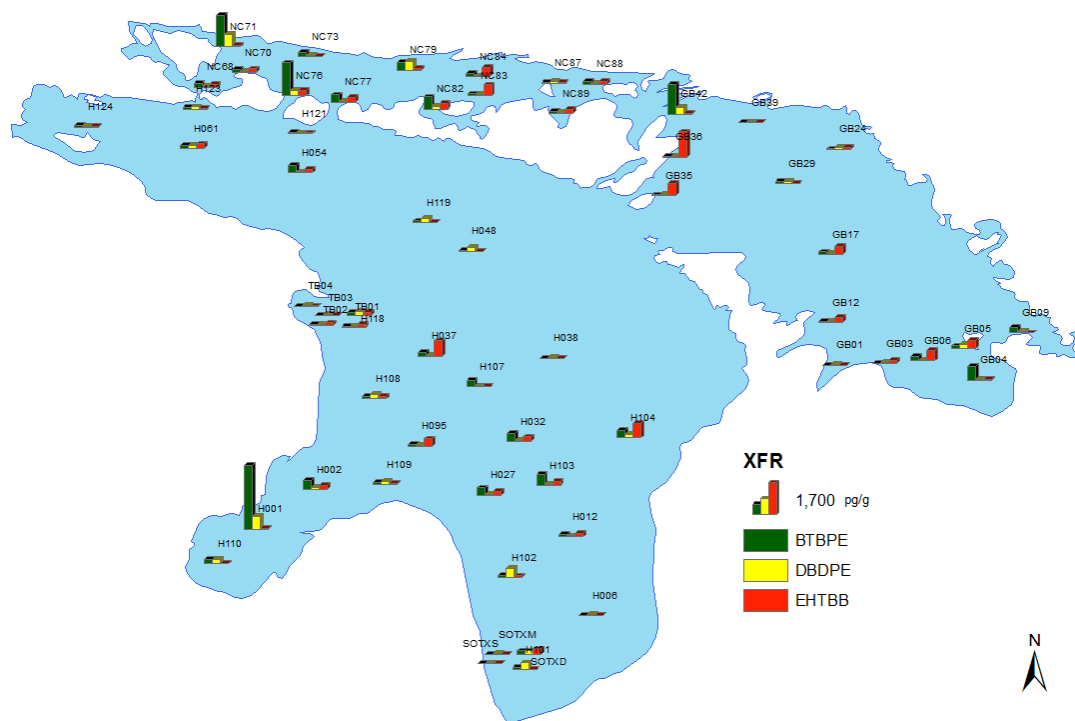
Figure 36. BTBPE, DBDPE, and EHTBB distribution of surface sediment samples from Lake Huron.
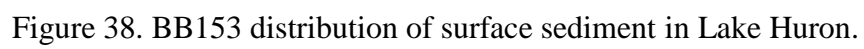
APPENDIX H
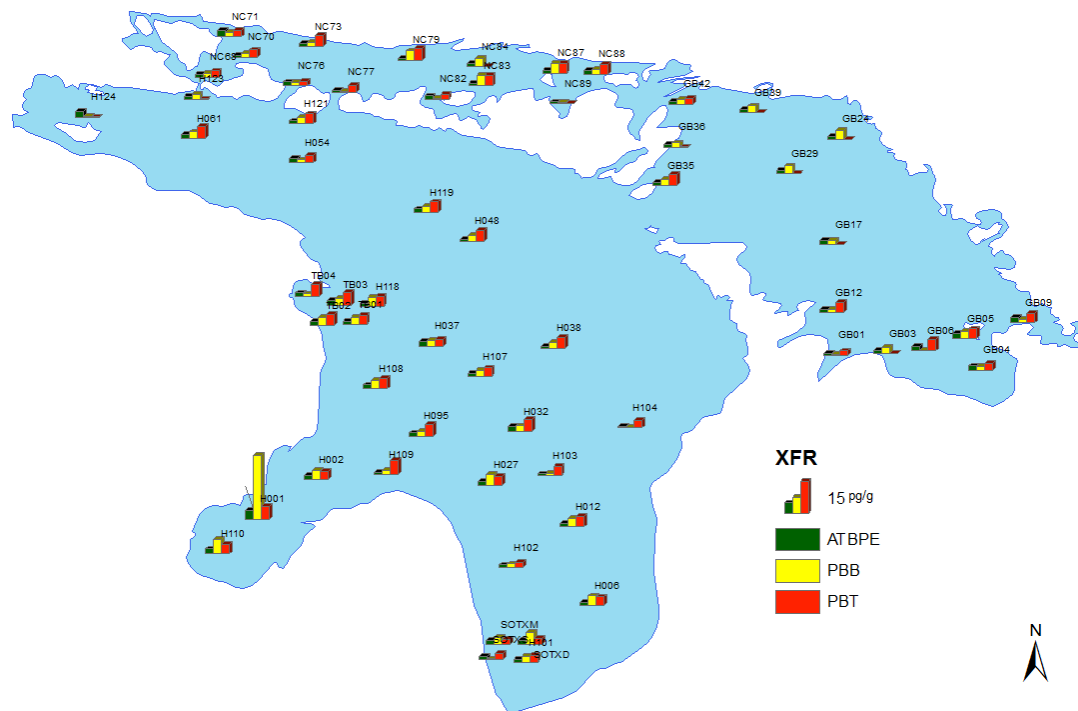
Figure 37. ATBPE, PBB, and PBT distribution of surface sediments in Lake Huron samples.

APPENDIX I
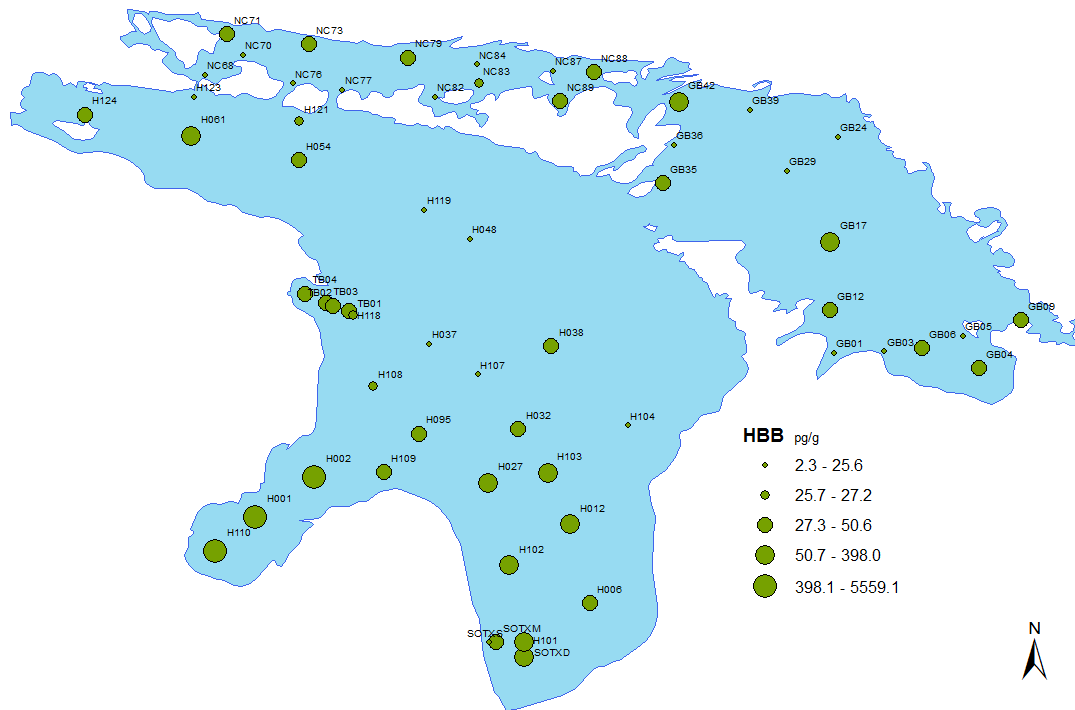

Figure 38. BB153 distribution of surface sediment in Lake Huron.

APPENDIX J

Figure 39. HBB distribution of surface sediment in Lake Huron.

APPENDIX K

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APPENDIX L

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VITA

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Study the vibrio infection of Hippocampus kuda under captive conditions

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 Member, Young Scientist Forum (YSF), National Science and Technology
Commission, Sri Lanka

Presentations:

 Ranasinghe, R.A.P.G., Epa, U.P.K., Chandratne, N., Mallawarachchi, J.
(2010). *A study on increasing larval survival of Hippocampus kuda (seahorse)
under culture conditions.* Presented at the 16th annual session Sri Lanka
Association for Fisheries and Aquatic Resources. 16:21.

 Ranasinghe, R. A.P.G., Epa, U.P.K., (2010). *Breeding of the endangered sea
horse, Hippocampus kuda, and constraints for larval development under
captivity.* Presented at the 30th annual session of the Institute of Biology. 30:14.