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CORES FROM TWO INLAND LAKES IN MICHIGAN

presented by

Patrick William Bradley

has been accepted towards fulfillment
of the requirements for the

Master of
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degree in

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DETERMINATION OF SELECT POLYBROMINATED DIPHENYL ETHERS AND
METHOXYLATED POLYBROMINATED DIPHENYL ETHERS IN SEDIMENT
CORES FROM TWO INLAND LAKES IN MICHIGAN

By

Patrick William Bradley

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ABSTRACT

DETERMINATION OF SELECT POLYBROMINATED DIPHENYL ETHERS AND METHOXYLATED POLYBROMINATED DIPHENYL ETHERS IN SEDIMENT CORES FROM TWO INLAND LAKES IN MICHIGAN

By

Patrick William Bradley

This study was conducted to determine if select polybrominated diphenyl ether (PBDE) and methoxylated polybrominated diphenyl ether (MeO-PBDE) congeners existed in two inland lakes in Michigan, and if so, to evaluate the patterns of relative concentrations of congeners in the mixture. During 2006, sediment cores were collected from the deepest portions of White and Muskegon Lakes. The cores were divided into sections and subjected to analysis for carbon and organic matter content, PBDE and MeO-PBDE concentrations, and strata aging by lead-210 dating. PBDEs were detected in all strata in both lakes, while only Muskegon Lake sediments contained appreciable amounts of MeO-PBDEs. Total PBDE concentrations in both lakes were comparable, but patterns of relative concentrations of congeners were somewhat different. This was likely due to different input sources and remediation histories. The overall trend in both lakes is one of declining PBDE input. Organic matter and carbon content was correlated with PBDE concentration. It is not known why methoxylated PBDE concentrations are dissimilar between lakes, but it may be due to differences in the aquatic community present in each lake.

DEDICATION

For my wife, Christina, who offered unconditional support and encouragement during the course of this thesis, and for my children, Natalie, Gabrielle, Carter, and Isabelle, who were patient and understanding with me as I completed my work. I am forever grateful.

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CHAPTER I

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a group of compounds that contain 209 possible different compounds and isomers (congeners) that vary in the percentage as well as the location of bromination, with the number of bromine atoms bonded to the base structure ranging from one to ten (Figure 1). PBDEs were produced mainly in the form of three commercial mixture types; Pentabromodiphenyl Ether (PeBDE, DE-71, Bromkal 70), Octabromodiphenyl Ether (OBDE, Saytex 111), and Decabromodiphenyl Ether (DBDE). Each mixture contains a unique combination of congeners (CEPA, 2004). Pentabromodiphenyl ether, in particular, has been viewed as the commercial mixture of greatest concern. This mixture is composed of approximately 30% tetrabromodiphenyl ethers, 60% pentabromodiphenyl ethers, and 10% hexabromodiphenyl ethers. Specific congeners within a homolog group have been referred to either by the CAS number or according to the scheme proposed by Ballschmiter and Zell for PCBs, which was later revised by Schulte and Malisch to conform to IUPAC rules. Congeners of greatest abundance in the PeBDE mixture Bromkal 70 are PBDE47, PBDE99, PBDE100, PBDE85, PBDE153, PBDE154, and PBDE138 (Sjödin, 1998).

This class of compound has been used extensively as a flame retardant additive in plastics (particularly in polyurethane foam) and since the PBDE structure is resistant to microbial and chemical breakdown. PBDE can also be found in treated municipal sewage sludge (biosolids) (Ciparis and Hale, 2005). Bioavailability, as well as environmental fate and transport, can be directly related to the physical and chemical

properties of each specific level of bromination, as well as the compound's lipophilicity and tendency to sorb to organic carbon associated with sediment (Ter Laak et al., 2009). Other studies, however, have demonstrated poor correlation between total organic carbon and PBDE concentrations. These poor correlations have been attributed to the combined effect of transport, mixing, and depositional mechanisms with uncontaminated sediments, or possibly due to the continuous input of fresh PBDEs (Chen et al., 2009).

Concerns about the possible deleterious effects of PBDEs on human health and the environment have led to restrictions on the use and production of these compounds in the United States and especially in Europe. California, Hawaii, New York, Maine, and other States have passed bills to reduce or eliminate PBDE usage, while states such as Michigan are currently considering similar legislation (MDEQ, 2008). In Europe, many countries have banned outright the production and import of brominated flame retardants (BFRs). The Stockholm Convention recognizes PeBDE as meeting the criteria of Annex D, indicating that this mixture may have the potential to cause harm to humans and the environment. Similarly, the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR Convention) has placed PBDEs on its List of Chemicals for Priority Action.

PBDEs have been shown to be ubiquitous in the environment. These compounds have been detected in sediments from Switzerland, China, and the United Kingdom (Kohler et al., 2008; Chen et al., 2009; Vane et al., 2009), in Canadian air, surface water, and precipitation samples (Ueno et al., 2008), and in biota from remote or isolated locations (Kelly et al., 2008; Haglund et al., 1997). Some congeners have been shown to

bioaccumulate in mussels ($> \log \text{BCF}$ of 6) (de Witt, 2002) and in fish and rays (Christensen et al., 2002).

Previous sediment core studies have determined that tri- to hexa-BDE congeners deposited in the 1970s are still present at significant concentrations (Covaci et al., 2005; Nylund, et al. 1992; Li et al., 2006). Some evidence suggests that the persistent, lesser brominated congeners, primarily nona-hexaBDEs, may be a byproduct of deca-BDE photolytic debromination in the environment (Söderström et al., 2004). Some of the most commonly found PBDE congeners in environmental samples (BDE47, BDE99, BDE100) have been shown to be only minor breakdown components of photolyzed BDE209.

PBDEs are suspected bioaccumulative toxic compounds. Some studies suggest that by initiating the AhR-mediated pathway, PBDEs can hinder neurodevelopment, cause liver damage and disrupt thyroid hormone levels (Zhou et al., 2002; Eriksson et al., 2001). Another study has shown that the distribution of PBDEs within the tissues of a study organism is different depending upon congener. BDE47, BDE99, BDE100, and BDE153 have been shown to be preferentially deposited in the adipose tissues of mice, but levels of BDE153 were 10-fold greater than BDE47 in brain. In addition, BDE153 and BDE100 were preferentially absorbed over BDE47 and BDE99 (Staskal et al., 2006).

Environmental transport of PBDEs can occur through several mechanisms. Regional and global distribution via the atmosphere has been demonstrated for both PBDEs and their hydroxylated and methoxylated derivatives (Kelly et al., 2008; Wang et al., 2009). PBDE distribution in the Great Lakes region is widespread. Concentrations range from relatively small in more remote sections of Michigan's Upper Peninsula to relatively high concentrations in the metro Chicago area (Strandberg et al., 2001).

Prevalent congeners distributed by atmospheric deposition include PBDE47, PBDE99, PBDE100, PBDE 153, and PBDE 154.

Another mechanism of transport is dissolution in the aqueous phase. Both PBDEs and hydroxylated PBDEs (OH-PBDEs) have been detected and quantified in rain, snow, and surface water, although no regional depositional trend could be discerned in snow samples (Ueno et al., 2008). Particulate organic carbon, present in the matrix and the relative insolubility of the more highly brominated PBDEs in water (Log K_{ow} 8.55 to 10.33) likely affects PBDE transport in watershed runoff (Palm et al., 2002). Environmentally relevant humic acid concentrations have also been shown to directly facilitate the transport of PBDEs (Ter Laak et al., 2009).

Some PBDE congeners have been shown to be abundant in lake and river sediments (Zhu et al., 2005; Eljarrat et al., 2004). Sources can be either local or regional in nature based upon the congener profiles present. For example, Wang et al. (2009) have demonstrated that BDE47 is the predominant congener in remote Tibetan soils, followed by BDE28 and BDE99. No BDE209 was detected, suggesting that atmospheric deposition selectively transports lesser brominated, lighter congeners.

Recent studies have found a correlation between methoxylated and hydroxylated PBDEs. A laboratory feeding study demonstrated that methoxylated forms of the parent PBDE congener can be detected as metabolites in the feces of dosed mice (Staskal et al., 2006). Methoxylated PBDEs (MeO-PBDEs) have been found in both freshwater (Kierkegaard et al., 2004) and marine fish (Haglund et al., 1997). Other studies have postulated that, at least in the marine environment, MeO-PBDEs are a natural product of sponges and filamentous green algae (Cameron et al., 2000; Kuniyoshi et al., 1985).

Thus, in freshwater systems, it may be possible to use metabolite concentrations in sediment as an indicator of PBDE exposure in aquatic organisms.

Hydroxylated and methoxylated PBDE isomers may be more toxic to organisms than exposure to the parent compound. Hydroxylated adducts have been shown to promote a variety of adverse effects (Hallgren et al., 2002; Canton et al., 2006; Harju et al., 2007). Some studies suggest that MeO-BDEs and OH-BDEs are generated as part of the same metabolic pathway, such as hydroxylation of the parent PBDE in the liver followed by methoxylation by microorganisms in the intestine (Haglund et al., 1997). Other more recent studies, however, have shed doubt on this theory. This research suggests that the primary source of OH-PBDEs in the marine environment result from the demethylation of naturally produced MeO-PBDEs (Yi et al., 2009). These compounds are lipophilic as well. The octanol-water partitioning coefficient of MeO-BDE47 and MeO-BDE68 approach $\log K_{ow} \approx 6.85$, indicating the likelihood that these metabolites are bioaccumulative (Teuten et al., 2005).

PBDEs and the methoxylated adducts of these compounds have been the subject of recent studies exploring the possible deleterious effects these persistent pollutants may have on both aquatic and terrestrial organisms, and these compounds have been shown to accumulate in the Great Lakes (Zhu and Hites, 2005). Samples for this study were collected in conjunction with the Michigan Inland Lakes Sediment Trend Monitoring Program which is made possible through a grant from the Michigan Department of Environmental Quality. The purpose of this program is to inventory toxic pollutants in the state's inland lakes in order to assess the current status of the region's surface waters, and to identify possible issues for future scrutiny. While an in-depth inventory has been

established for several other species of halogenated organic contaminants in Michigan inland lakes through this program, data gaps for the brominated flame retardants exist.

The purpose of this study is to elucidate whether or not:

- Concentrations of total PBDEs and MeO-PBDEs vary among sections within a specific sediment core.
- PBDE congener and MeO-PBDE congener profiles vary among sections within a specific sediment core.
- Concentrations of total PBDEs and MeO-PBDEs vary among sediment cores of different lakes.
- PBDE congener profiles and MeO-PBDE congener profiles vary among sediment cores of different lakes.
- The total organic carbon content of specific sediment cores is correlated to PBDE and MeO-PBDE concentrations.

CHAPTER II

MATERIALS AND METHODS

Sample Collection

Samples were collected using the Monitoring Vessel Nibi, which was specially designed for taking core samples without disturbing the lake bottom in the process (MC-400 Lake/Shelf Multi-corer). Coring was done in quadruplicate in a single sampling episode. One core each was designated for use in metals determination (Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Ba, Pb, and U), organic contaminant determination (polybrominated diphenyl ethers and methoxylated metabolites, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides), porewater collection, and aging. Cores collected in this study were collected from the deepest portion of the lake basin. The White Lake sampling site is located at 43° 22.949' N & 86° 22.902' W and at a depth of 21.6 meters. The Muskegon Lake sampling site is located at 43° 14.060' N & 86° 16.996' W and at a depth of 14.9 meters. Both cores were taken during the 2006 sampling year.

Once collected, cores were transported to a temporary on-shore processing station for sectioning. All cores were sectioned at 0.5 cm intervals for the top eight centimeters and at 1.0 cm intervals thereafter. Sections were then individually stored in glass jars and cooled in preparation for shipping to MSU. Once at the laboratory, organics samples were stored at -20°C until analysis.

Sample Analysis

Sediment Core Aging and Sedimentation Rate Determination

Cores chosen for aging were sent to the Freshwater Institute (Winnipeg, Manitoba, CA) for ^{210}Pb aging by use of methods described previously (MDEQ, 2002). Briefly, sedimentation rates for each core sample were determined using the four different models; constant flux constant sedimentation (CF:CS), segmented CF:CS (SCF:CF), rapid steady state mixing (RSSM), and constant rate of supply (CRS). The validity of each model was verified using stable isotope abundance in the sample (^{210}Pb and ^{137}Cs).

^{210}Pb is formed by decay of ^{222}Rn from atmospheric and water column sources. The presence of this isotope in lake sediments is usually observed as increasing in concentration as sediment age decreases. In addition, leaded gasoline use peaked in the early to mid 1970's, allowing for the use of excess elemental lead as another confirmatory tool in the sedimentation rate model selection.

^{137}Cs was produced during thermonuclear weapons testing throughout the 1950's and 1960's, peaking in 1963. Detection of this peak in sediment cores provides another means of confirming proper sedimentation rate estimation. To aid in comparison with other analyte profiles, the dates associated with both White Lake and Muskegon Lake sediment strata are taken directly from the Inland Lakes Sediment Trends Monitoring 2005-2007 Final Report. Sample strata aging data are presented in Appendix A.

Organic Matter and Carbon Determination

Carbon and organic matter content of strata were determined by the Soil and Plant Nutrient Laboratory, Michigan State University. The laboratory first determined carbon content using the chromic acid oxidation (external heat applied) method (Missouri

Agricultural Experiment Station, 1998). Organic matter content was determined via calculation assuming that 58% of the organic matter is composed of carbon. Organic matter and carbon percentages are presented (Table 1).

Sample Extraction and Extract Clean-up

Sample extraction and cleanup procedures followed the protocol outlined in EPA Method 1614 (USEPA, 2003). In order to achieve sufficient mass for analysis, sediment strata were combined prior to extraction. For example, equal masses of the first two one-centimeter aliquots from the Muskegon Lake sediment core generated during field processing, samples MU 1 and MU 2, were decanted if necessary and combined to create a pooled sample, MU 1+2. This procedure was continued for all sample strata generated from the sediment core, reducing the total number of core subsamples by a factor of 2X.

After compositing, twenty grams of sample was weighed, mixed with granular sodium sulfate, and put into a soxhlet extraction apparatus containing 3:1 dichloromethane in acetone. Each sample received 1.0 ml of ^{13}C labeled internal standard (MBDE-MXFS) while the laboratory control spike, matrix spike, and matrix spike duplicate also received 1.0 ml of native polybrominated diphenyl ether stock solution (BDE-MXF), (Wellington Laboratories, Guelph, Ontario, Canada). Samples were permitted to reflux overnight (18 ± 2 h). No methoxylated PBDE standards were available at the time of extraction.

After extraction, extracts were allowed to cool and then transferred to Turbovap concentration tubes (Caliper Life Sciences, Hopkinton, MA), and concentrated to approximately 1.0 ml in preparation for sample splitting. Since multiple analyses were

required for each extract, extracts received a 1:1 split, with half of the volume reserved for PAH and PBDE analysis, and the other reserved for PCB and pesticide analysis. After PAH analysis, extracts were prepared for HRGC/HRMS PBDE analysis by again performing a 1:1 split, reserving one 250 µl aliquot for possible future total bromine analysis.

PBDE extracts received silica gel column clean up to improve detection limits. Each extract received 10 µl of ^{13}C labeled clean up standard (MBDE139),(Wellington Laboratories, Guelph, Canada) and was then loaded onto the top of a liquid chromatography column which was pre-eluted with 50 ml of hexane. Each column contained, from bottom to top, a glass wool plug, 1 g granular sodium sulfate, 1 g silica gel, 4 g basic silica gel, 1 g neutral silica gel, 8 g acidic silica gel, 2 g neutral silica gel, and 4 g granular sodium sulfate. Specific procedures for acidic and basic silica gel preparation can be found in the EPA method (USEPA, 2003). Extracts were first eluted from the column with 200 ml hexane. This first fraction contained all the PBDEs as determined during initial method evaluation, and was set aside for later concentration. The second fraction containing the methoxylated PBDEs was eluted with 1:1 dichloromethane in hexane. Both fractions were then concentrated to approximately 1 ml using the Turbovap and transferred to 1 ml amber chromatography vials. Formation of precipitates was observed during concentration, so copper granules were added to the extracts to remove sulfur. The extract/copper slurry was stored overnight.

Determination of a final concentration was achieved by adding the extract to 10 µl of nonane in a wide mouth low volume vial insert, and evaporating the mixture to 10 µl

using nitrogen evaporation. The extracts were capped and packaged for shipment to the University of Saskatchewan for analytical determination.

HRGC/HRMS Analysis

In an effort to prevent contamination of the high resolution mass spectral system, attempts were made to screen sample extracts for high levels of PBDEs using HRGC/LRMS techniques (EPA Method 1614 modified), but poor instrument sensitivity and relatively low analyte concentration prevented sample screening by these methodologies. Extracts were shipped to the University of Saskatchewan without screening results.

High resolution analytical determination was achieved after sample receipt at the analytical facility. Samples were sorted into fraction one extracts for PBDE analysis and fraction two extracts for methoxylated PBDE analysis, and all extracts received 10 µl of ¹³C labeled injection standard prior to analysis (MBDE-138), (Wellington Laboratories, Guelph, Canada). Identification and quantification of all target compounds was performed using a Hewlett-Packard 5890 series II high-resolution gas chromatograph interfaced to a Micromass Autospec high-resolution mass spectrometer (HRGC-HRMS) (Micromass, Beverly, MD). Chromatographic separation was achieved on a DB-5MS fused silica capillary column for all target compounds (30 m length, 0.25 mm ID, 0.1 µm film thickness, Agilent, Carlsbad, CA), with helium used as carrier gas. The mass spectrometer was operated in a selected ion-monitoring (SIM) mode. The resolution for all reference gas peaks in all time windows was more than 7,000. The injector temperature was held at 285 °C and the ion source was kept at 285 °C. The electron

ionization energy was 37 eV and the ion current was 750 μ A. The GC temperature programs used for both the PBDEs and the Methoxylated PBDE are available in Appendix B. PBDE calibration standards were purchased from Wellington Laboratories as a complete set (BFR-CVS), and calibration levels one through four were used to construct the PBDE calibration curve. Methoxylated PBDE calibration standards (levels one through five) were not commercially available at this time and were obtained from the Environmental Toxicology Laboratory at the University of Saskatchewan (Appendix C).

Data generated during the course of analysis (OPUS data, Micromass, Beverly, MD) was converted using Databridge for the MassLynx V4.1 platform (Micromass/Waters Corporation, Milford, MA). PBDE sample concentrations were determined by using a four point calibration curve and referencing labeled analog in each homolog group. Methoxylated PBDE quantitation was achieved using a five point calibration curve and by referencing the injection standard, as no labeled methoxylated compounds were available at the time of analysis.

Quality Assurance

Standard laboratory quality assurance protocols were observed during the extraction of sediment samples. An unspiked laboratory blank was prepared during each extraction episode, and a matrix spike / matrix spike duplicate spike set and laboratory control spike set was prepared for the PBDE analysis set for each lake. Recoveries for the Muskegon Lake MS/MSD/LCS set are 77-100%, 72-98%, and 89-119% respectively, while White Lake sample recoveries ranged from 82-101%, 82-313%, and 78-149%

respectively. The higher recoveries in the White Lake QC data set are observed in two congeners, BDE47 and BDE99, and may be attributed to chromatographic interference observed during sample integration. QC sample data is available in Table 2.

Labeled compound recovery was highly variable from lake to lake and from sample to sample within a lake and ranged from not recovered (White Lake only, congener ^{13}C BDE100) to 111% in experimental samples (Appendix D). Detection limits were sample specific, and equal to 3x the signal to noise (S/N) value for each native congener. Clean up standard recovery ranged from 14% to 46% in experimental samples and roughly paralleled labeled compound recovery, indicating that some percentage of the target compounds may be lost during the clean-up procedure, however S/N values for detected compounds were always greater than 3:1, and for PBDEs, any losses during sample preparation are accounted for using the isotope dilution quantification method. Possible losses of methoxylated PBDEs can not be quantified since labeled compounds were not available during sample extraction.

Instrument performance was monitored using a series of initial calibration verification injections. Each sequence contained at least one verification injection, and recoveries of native and labeled compounds ranged from 68-126% in all but one verification injection (-CS3 of the PATRICK-5B sequence). This injection appears to have been poor due to low solvent/standard levels within the GC vial (Appendix E).

CHAPTER III

RESULTS

Aging and Sedimentation Rates

Age was determined for a total of 52 sediment samples from White Lake and 51 sediment samples from Muskegon Lake. White Lake sediments were assigned deposition years from 2006 to older than 1901 (<1901) based upon averaged data and using the SCF:CS sedimentation model. ^{210}Pb confirmation was not applicable in this case as it has been postulated that sediment resuspension confounded the typical excess lead curve, as it is usually observed as a linear decrease in abundance from the upper sediment layers to the lower layers. No such pattern was observed here. A ^{137}Cs peak was not detected, as would be expected with sediments of this age, and so could not be used as a means of confirmation. The disappearance of excess ^{210}Pb tends to support this choice, as excess lead begins to appear at approximately 1900 using this model.

Muskegon Lake sediments were pooled in the same manner as White Lake sediments, and the CF:CS sedimentation rate model is the best fit for this data, since neither a ^{210}Pb peak nor a ^{137}Cs peak are observed in Muskegon Lake sediments.

Sediment strata year assignments range from 2006 to 1966.

In order to accurately reflect the ages represented in the pooled PBDE samples, dating results for samples in the first eight centimeters were averaged determined as the average of four 0.5cm sections. The remaining sections, sectioned in 1cm intervals, were determined as the average of two. Data for both lakes is presented in Appendix A.

Organic Matter and Carbon Percentage Determination

Carbon and organic matter content was determined at 1 cm intervals for sediments from both lakes. In order to accurately represent pooled experimental samples, results from consecutive 1 cm layers were averaged.

Carbon content in sediments ranged from 13.6% in samples WH 3+4 and WH 7+8 to 1.73% in sample WH 39+40 and from 11.1% in sample MU 5+6 to 8.77% in sample MU 39+40. Organic matter was derived from the carbon content results for each sample assuming that the organic matter is equivalent to 58% carbon (MSU Soil and Plant Nutrient Laboratory, personal communication). Organic matter content ranges from 23.5% in samples WH 3+4 and WH 7+8 to 3.05% in sample WH 39+40 and from 19.1% in sample MU 5+6 to 15.2% in sample MU 39+40. Carbon and organic matter data is presented in Table 1.

Percent Moisture

Percent moisture content of each composite sample was determined in order to present concentrations based on dry weight. Moisture content ranged from 88.5% in sample WH 25+26 to 59.7% in sample WH 41+42 and from 81.5% in sample MU 3+4 to 77.7% in sample MU 29+30. Percent moisture data is presented in Appendix F.

Polybrominated Diphenyl Ethers

A total of twenty two sediment samples from White Lake and twenty one sediment samples from Muskegon Lake were analyzed for twenty three polybrominated diphenyl ethers. All congeners were detected at least once in White Lake sediments, and

total PBDE concentrations ranged from 206 pg/g dry weight (dw) (sample WH 39+40) to 2426 pg/g dw (sample WH 7+8). In contrast, BDE30, BDE77, and BDE126 were not detected in any samples from Muskegon Lake. Total PBDE concentrations in Muskegon Lake ranged from 983 pg/g dw (sample MU 33+34) to 3883 pg/g dw (sample MU 33+34). Data for PBDE concentrations (pg/g dw) are presented in Appendices G and H.

Methoxylated Polybrominated Diphenyl Ethers

A total of twenty two sediment samples from White Lake and twenty one sediment samples from Muskegon Lake were analyzed for twelve species of methoxylated polybrominated diphenyl ethers. The only MeO-BDEs detected in White Lake sediments were 6MBDE47 and 6MBDE85 where concentrations ranged from not detected (< DL) to 9.90 pg/g dw. In Muskegon Lake congeners 3PMBDE68, 6MBDE47, 5MBDE99, 4MBDE101, and 6MBDE85 were detected. Total MeO-BDE concentrations ranged from ND in earlier sediment layers to 115 pg/g dw in sample MU3+4. Data for MeO-BDE concentrations (pg/g dw) in Muskegon and White Lakes are presented in Appendices I and J.

Analytical Considerations

The analytical techniques used closely paralleled the USEPA promulgated method for PBDE extraction and analysis (Method 1614 – Draft, 2003). There were a few instances, however, in which method guidelines could not be strictly adhered to in this study. For example, ¹³C labeled analogs could not be acquired for the methoxylated analytes prior to extraction of the sediment samples. This resulted in quantitation of

these compounds being based on an internal standard (^{13}C BDE 138 injection standard) rather than quantitation via isotope dilution. Consequently, a four-fold dilution factor was applied to sample results to account for sample splitting prior to instrumental injection. In addition, at the time that the high resolution mass spectrometer was available for use the instrument was experiencing issues with sensitivity in the high mass ranges greater than m/z 575. This prevented the analysis of the more highly brominated congeners such as deca-BDE. Primary to secondary ion ratios were also difficult to obtain in a consistent manner, as the software program used had difficulty identifying the correct ions. Manual inspection of ion ratios was used to confirm proper target compound identity, but some identification uncertainty exists for congeners present in the downfield sections of the chromatogram, as baseline noise increased during later retention times.

Several extraction related complications also arose during sample processing. During initial concentration, the method blank associated with samples MU 1+2 thru MU 21+22 was lost due to glassware breakage. Another method blank was immediately prepared and carried through the remainder of the preparative procedure in parallel with the associated experimental samples. After analysis, however, the re-extracted method blank was observed to have elevated levels of target analytes, while most samples associated with the blank had no evidence of this suspected cross-contamination (see Table 6), however laboratory contamination can not be conclusively ruled out for the associated samples. All other method blanks prepared during the course of this study showed little or no evidence of cross contamination. No MeO-PBDEs were detected in and method blank. Several extracts were inadvertently concentrated to dryness during

clean-up, but no adverse effects were observed in sample internal standard recoveries, and sample data quality is assumed to be unaffected.

CHAPTER IV

DISCUSSION

One goal of this study was to determine if PBDEs and/or methoxylated PBDEs exist within the sediment core of a lake, and if present, to compare the congener profiles within the sediment strata. Cores were taken from White Lake and Muskegon Lake, both of which are inland lakes located in the western section of the lower peninsula of Michigan, and both are proximal to Lake Michigan and to each other. A second goal of this study was to evaluate the relationship of these brominated compounds to other persistent anthropogenic compounds present in the sediments of these lakes. Concentrations of PAHs, PCBs, and select chlorinated insecticides have previously been measured in samples from these lakes as part of a sediment trends monitoring program.

Muskegon Lake is a mesotrophic lake situated within Muskegon County. It has a surface area of 16.8 km^2 and a maximum depth of approximately 15 meters. It is within a watershed that measures approximately 53 km^2 and ultimately drains into Lake Michigan, which is approximately 1000 meters away. This lake is situated in an urban area and receives heavy recreational use as well as input from upstream wastewater treatment facilities and various industrial sites along its shore. These include the Sappi Fine Paper plant and the Sealed Air manufacturing plant. The sedimentation rate for this lake has been calculated to be $1607 \text{ g/m}^2/\text{yr}$ (Parsons et al., 2008). White Lake is also a mesotrophic lake that is located within Muskegon County and has a surface area of 10.4 km^2 and a maximum depth of approximately 22 meters. Its watershed area is estimated at 1390 km^2 , some of which is rural in nature. White Lake is classified as a drowned river-mouth (freshwater estuary) and drains into Lake Michigan via a short

outflow to the west of the lake. It is also utilized recreationally, but has less recreational usage than Muskegon Lake. The sedimentation rate in this lake has been calculated to be $977 \text{ g/m}^2/\text{yr}$ (Parsons et al., 2008).

White Lake has a legacy of pollution from human activities. Beginning in the late 1800's, Whitehall Leather tannery operations on the shores of White Lake (Tannery Bay) led to widespread contamination of the lake sediments with chromium, which continued until the early 1970's. In addition, discharges from Hooker /Occidental Chemical Corporation, DuPont Chemical, and Koch Chemical likely added additional halogenated organics, including PCBs, to the lake's persistent organic pollutant burden (USEPA, 2004). In consideration of these issues the United States Army Corps of Engineers and the Michigan Department of Environmental Quality developed a feasibility study and remediation plan. Remediation via dredging of White Lake sediments was completed in October of 2003 with particular focus on the Tannery Bay and the Dowies Point area lakebed. Sediment cores used in the present study were collected in 2006.

Aging and Sedimentation Rates

Sediment core aging data obtained from the Freshwater Institute in Winnipeg indicated that the sedimentation rate in Muskegon Lake was greater than the rate in White Lake. Consequently, sediment core strata taken from White Lake represent a greater temporal range, with the deepest strata ages estimated to be pre-1901. Muskegon Lake core strata ages range from present to 1966 (Appendix A). This presents a challenge when comparing the PBDE and MeO-BDE data from one lake to another. To clarify data interpretation, some comparisons were made using only strata that matched in age

(Figure 2). Since the strata age estimation is achieved as a line-fitting exercise, sediment disturbances may not be reflected in the aging results, as was the case in White Lake.

Organic Matter and Carbon Percentage Determination

Percent carbon and organic matter (OM) data for both White and Muskegon Lake follow a similar trend. In Muskegon Lake, total PBDE concentrations (Σ PBDE₂₃) tend to track carbon percentages while the same is generally true for White Lake (Figure 3). As can be seen in Figure 4, Muskegon Lake carbon percentages peak at 2002 when total PBDE concentration maxima are also observed. Reductions in carbon percentages are observed in Muskegon Lake in 1974 and 1968, with corresponding lesser total PBDE concentrations in the corresponding strata. White Lake carbon concentration maxima occur in years 2004, 1999, and 1973; minima occur in 2002, 1983, and <1901 layers; and consistent concentrations occur between 1983 and 1976. Total PBDE concentrations generally follow this same trend. Correlations between organic matter concentration and contaminant concentration have been observed in other studies. Strong relationships between carbon content and total PBDE concentrations in Great Lakes sediments were reported by Li et al. (2006), and it was postulated that the affinity of PBDEs for OM in air and water may be greater than that of PCBs and PAHs due to higher K_{ow} values. This pattern was not observed for the methoxylated BDEs (Figure 5). While PBDEs associated with sediment are generally attributed to depositional processes outside of the lentic system, it may be that methoxylated BDEs are synthesized within the aquatic compartment as metabolites of parent PBDEs, or generated as natural products of certain

filamentous green algal communities, and therefore are not immediately associated with atmospheric organic particulates or allocthanous carbon sources within the watershed.

Another means of evaluating the relationship between carbon and total PBDEs is to normalize PBDE concentration to carbon values (Figure 6). Past studies have shown that organic carbon partition coefficients (K_{oc}) in sediments exhibit a high degree of invariance over a broad range of sediment samples (Kile et al., 1995). In this study the carbon normalized PBDE data present a similar trend in both lakes when compared to the non-normalized data, especially in White Lake, indicating a relatively linear relationship between the concentration of total PBDEs and carbon content. Compared to the Kile study, however, the carbon-normalized concentration data exhibit somewhat increased variability. This may be caused by several factors. First, since only a fraction of the total commercially-produced PBDE congeners were quantitatively determined in this study, it may be possible that unquantified congeners are contributing to variations in sediment K_{oc} values. Second, tenacious sorption of neutral organic compounds has been shown to affect K_{oc} values in older soils (Steinberg et al., 1987). These soils exhibit hysteretic sorption/desorption isotherms possibly due to retarded diffusion via microscale partitioning. In addition, a previous study by Scribner et al. (1992) observed that the nonpolar herbicide simazine, after 20 years of continuous application to an agricultural field, was present in an increasing portion of the in soil in a slowly reversible sorbed state. The slowed desorption kinetics of aged anthropogenic organic compounds may affect the ability of these compounds to reach equilibrium in both sediment stratum pore water and within the sediment column itself, as well as result in reduced bioavailability for microbial decomposition.

Polybrominated Diphenyl Ethers

Total Polybrominated Diphenyl Ethers

Total PBDE values for both lakes were calculated by summing all twenty three congeners available in the analytical suite. Non-detected congeners were reported as zero (Table 3). Total PBDE concentrations in Muskegon Lake begin to increase in 1974, and peaked in 1991 at 3883 pg/g. Since then, concentrations gradually decreased to 2050 pg/g in the 2006 layer (Figure 7). This trend is inconsistent with other anthropogenic compounds measured in concurrent core samples for this lake. Examination of the Sediment Monitoring project data reveals that total PAH concentrations peaked in 1977 while total PCB as well as total p,p'-DDE concentrations peaked in 1966. These trends are most likely a result of differences in annual peak production for the various compound classes. Total PBDE concentrations in White Lake exhibit a somewhat different profile. Concentrations peaked in 1999 at 2426 pg/g with a second smaller peak being observed in 1973 at 1369 pg/g. Both carbon and OM concentrations also exhibit an uncharacteristic upswing at this point in time (Figure 7). This may be an artifact of remediation activities (sediment resuspension) in the basin near where the sediment core was sampled. Total PAH concentrations peak in 1990, p,p'-DDE in 1966 (consistent with Muskegon Lake levels), and total PCBs in 1920. The total PCB maximum appears to be incongruent with sediment strata age, and no reason for this is readily apparent.

Interestingly, total PBDE concentrations in Muskegon Lake decrease steadily from 1968 to 1974, and 1968 concentrations roughly equal 1985 levels. White Lake levels also increase steadily in the last three strata, but due to the limitations of the dating

methodology, accurate dates could not be assigned to these samples (older than 1901). It is not likely that actual total PBDE concentrations are elevated in these older strata, and may reflect some uncertainty in the analytical procedure. Congeners BDE171, BDE47, and BDE183 represent the bulk of the total PBDE mass here. Examination of raw sample data reveals that some chromatographic noise was present during quantitation of these congeners, and may have contributed to elevated values in these samples.

Total PBDE concentrations in both White and Muskegon Lakes are similar to those found in the literature for similar matrices. A recent study measured total PBDE concentrations (Σ_9) from 0.019 to 0.91 ng/g dw in sediments from the Beijiang River, situated in an industrial region of China, and these levels compare similarly to levels present in this study (Σ_{23} White Lake = 0.002 to 2.43 ng/g dw; Σ_{23} Muskegon Lake = 0.983 to 3.88 ng/g dw) (Chen et al., 2009). Another found much higher total PBDE levels (Σ_{15} not including BDE209) in UK sediment samples from Clyde Estuary ranging from 1.00 to 307 ng/g dw. Input to the estuary likely includes landfill runoff, sewage plant discharge, and both heavy and light industrial discharges (Vane et al., 2009).

Comparison of Congener Profiles – All Congeners - Upper Layer

The percent contribution of each congener of the uppermost sediment layer from each lake, dated to 2006, was compared to determine if differences existed between the lakes (Figure 8). Present congener contributions to both lakes were similar, which suggests that regional (atmospheric), as opposed to local (watershed) sources now dominate input to the lakes. Congener BDE47 is the most prevalent congener in both samples, followed by BDE183 in Muskegon Lake and BDE99 in White Lake. Both

BDE47 and BDE99 are congeners commonly found in abundance in sediment samples (Kohler et al., 2008; Vane et al., 2009; Zhu and Hites, 2005; Li et al., 2006).

Comparison of Congener Profiles – Select Congeners

In order to more clearly compare the dominant congeners that exist in both lake core samples, seven of the most frequently occurring congeners were selected (Table 4). Selection of these congeners was achieved by identifying the five congeners that contributed most to total PBDE concentration in each stratum for each lake. The frequency of occurrence of each congener was determined for all samples in both lakes, and the seven most frequent were selected for further evaluation. These include, in order of greatest frequency, BDE47, BDE99, BDE183, BDE171, BDE49, BDE100, and BDE180 (Figures 9 and 10). In addition, to enable a direct temporal comparison between lakes, only sediment strata that were of equal ages were compared between the two sites. This resulted in the selection of ten samples, dating from 2006 to 1966.

The most frequently occurring congeners in Muskegon and White Lake sediments are similar to those found in other studies. Other than BDE209, which could not be measured in this study due to instrument limitations, BDE47 was found to be the most abundant congener both in Great Lakes sediments and sediments in this study (Li et al., 2006). A recent study found BDE47 to be the most abundant congener in the Clyde Estuary, UK, followed by BDE99, BDE183, and BDE153 (Vane et al., 2009). This also corresponds to the major components of the commercial mixture BK-70, of which BDE47, BDE100, and BDE99 are the three major components.

In Muskegon Lake, congeners BDE47, BDE99, BDE49, and BDE100 all follow a similar trend, as does BDE49, BDE180, and BDE183 in White Lake (Figure 2).

Concentrations of each gradually increase from the mid to late 1970's to a peak concentration in the mid-1990's, and then a gradual decrease in concentration up to the present. In White Lake BDE47, BDE99, and BDE100 reveal a steady increase in concentration beginning in 1983, and maximum concentrations are achieved in the uppermost sediments. In addition, BDE47 and BDE99 appear at greater concentrations in the 1966 stratum than in the 1983, 1985, and 1993 layers.

In Muskegon Lake (BDE47, BDE99, and BDE100) and in White Lake (BDE49, BDE180, and BDE183) the trend of gradually decreasing concentrations from the mid 1990's to present is consistent with previous studies, and may be attributed to decreasing production and use of PeBDE mixtures and the increased use of OctaBDE and DecaBDE mixtures due to legislative pressure (from approximately 3.6 million metric tons, combined, worldwide in 1992 to 67,000 metric tons in 2003). Another factor contributing to the decline in PBDE concentrations may be changes in urban wastewater treatment processes. Combined sewer overflow (CSO) projects have been required by the Michigan Department of Environment Quality since the late 1980's. CSO projects separate storm drain flow from sewer flow to prevent untreated sewage from accidental discharge into rivers during high-flow storm events. It is possible that this reduction of untreated sewage input from the watershed has contributed to the reduced levels of PBDEs in the sediment record. Knoth et al. (2007) found significant concentrations of BDE99, BDE47, BDE100, BDE153, BDE154, and BDE183 in wastewater treatment

sludge, indicating that sorption onto wastewater sludge can result in reduced PBDE load in treatment plant effluent.

Muskegon Lake sediment concentrations of BDE180 and BDE183 behaved differently than the congeners mentioned previously. These compounds are observed at relatively low concentrations in the uppermost strata, but BDE 180 concentrations tend to diminish abruptly at the 1993 and 1985 strata before increasing again in the 1983 and 1966 strata. Literature values for this congener in sediment samples are limited, likely due to the fact that BDE180 is not a substantial contributor to most commercial PBDE mixtures. BDE183 maintains a relatively stable concentration from the surface stratum to the 1995 stratum sample, at which point the concentration abruptly increases in the four lowest strata (1993 to 1966). This congener is a principal component of the OctaBDE mixture (Geller et al., 2007). Others have demonstrated that BDE183 levels in some aquatic organisms result from the debromination of higher brominated PBDEs (Yang et al., 2009).

BDE171 was selected for evaluation due to its concentration and frequency characteristics in core samples from both lakes. A pattern is difficult to discern in either lake, however, due to the random nature of its occurrence in sediment strata. Literature values for this BDE171 in any matrix are limited, likely due to its small contribution to commercial PBDE mixtures. Because of the randomness of BDE171 concentrations in the data, the qualitative identification of this compound received additional scrutiny. In all cases where it was detected, both the primary and secondary ion was present. However, chromatograms reveal increased baseline noise at the retention time of BDE171, which may contribute to increased uncertainty when evaluating this congener.

Methoxylated Polybrominated Diphenyl Ethers

Sediment samples from both lakes were analyzed for twelve methoxylated polybrominated diphenyl ethers (MeO-BDEs), (Appendix C). The analysis of White Lake sediments detected only one compound in each of three samples, all at low levels (<10 pg/g dw). An examination of Muskegon Lake sediments identified at least one of three primary MeO-BDE congeners in a majority of strata. Results for MeO-BDE analysis of both lakes are presented in Appendices I and J. Levels of total MeO-BDEs begin to appear in 1977, increase in concentration up to a peak in 2004 at a concentration of 115 pg/g, and drop to about half this level in the uppermost stratum (2006). A congener-specific plot reveals that the primary contributor to Muskegon Lake MeO-BDEs is 6MBDE47, which generally increased in concentration up to 2006, at which point the concentration of this congener in the upper layer was less than half the peak levels (Figure 11). The dominance of 6MBDE47 in the profile is not unexpected if one assumes that it is a metabolite or decomposition product of the parent material, BDE47, which appears as the most abundant congener in the total PBDE profile. The two other MeO-BDE congeners, 6MBDE85 and 3PMBDE68, both follow a similar trajectory. One anomaly in this trend is at the 2004 time point where only 6MBDE47 was detected at lesser concentrations than in strata either before or after it. Examination of the labeled injection standard recovery indicated reasonable instrument performance, however, since no labeled analog standards were available at the time of extraction, loss of analyte during preparation of this sample cannot be ruled out. The total MeO-BDE concentration profile in Muskegon Lake is noteworthy in that it differs from the total PBDE profile.

While total PBDEs generally peak in the early 1990's, the total MeO-BDEs appear in greatest concentration in the 2004 stratum. A survey of the Canadian arctic marine food web enumerated various MeO-PBDEs in marine biota, but detected none in marine sediments (Kelley et al., 2008).

When comparing the Parent PBDE/MeO-BDE concentration ratios (Table 5), only metabolites for which parent compounds existed in the analytical suite were evaluated. Comparisons were made in three representative strata, years 2006, 2004, and 1995, as these represent the maxima for 6MBDE47, 6MBDE85, and 5MBDE99, respectively. PBDE/MeO-BDE ratios in the upper sediments demonstrate a relatively greater concentration of MeO-BDE as compared to parent PBDEs, while in the 1995 sediment layer MeO-BDE concentration are appreciably lower. This disparate temporal trend in PBDE and MeO-BDE ratios was also observed in pike (*Esox lucius*) from Swedish waters, suggesting different sources (Kierkegaard et al., 2004). In sediment samples, the differing trends may be due to selective chemical or biological decomposition of the MeO-BDEs in sediment due to the chemically active methoxyl functional group present. Another possible reason for the lower ratio may be related to the hypothesis that these compounds are not anthropogenic in nature, but rather the natural byproducts of algal communities or other aquatic organisms (Teuten et al., 2005).

It is not clear why MeO-BDEs were consistently detected in Muskegon Lake but not in White Lake. It is possible that these compounds are natural byproducts of the pelagic or benthic fauna, and that the aquatic communities in the two lakes differ. Using radiocarbon analysis, Teuten et al. (2005) determined that MeO-BDEs found in the blubber of a beaked whale were not anthropogenic in nature, and were isotopically very

similar to a methoxybrominate found in the Pacific marine sponge *Phyllospongia foliascens*. Approximately thirty species of freshwater sponge exist in North America. Perhaps these methoxylated bromine compounds are metabolites of freshwater analogs of the marine sponges.

The total PBDE concentration profile in Muskegon Lake differs from that found in White Lake in the lower core strata, suggesting local sources influenced the total PBDE load in each lake. Similar concentrations of total PBDEs in later sections of both lakes (early 2000s to present) indicate that contributions from local sources have been reduced in recent years and the PBDE load is now dominated by regional inputs (i.e. atmospheric). In addition, when comparing select congeners, temporal shifts in congener patterns exist in both lakes. This result is consistent with a flux of PBDE source material and a likely flux in regional/local input influence. The concentration of both carbon and organic matter in each sample appears to be correlated with total PBDE concentrations. As strata analyte concentration increases, so does carbon and OM. One exception seems to be in the older sediments. This may be due to greatly reduced PBDE concentrations. Methoxylated PBDE concentration has little relationship to carbon and OM percentages. MeO-BDEs were detected most consistently in Muskegon Lake sediments, while only a few were observed in White Lake sediments. This has prevented a valid congener comparison between lakes. The reason for this difference is not known, but may be influenced by a biotic community unique to each lake.

Future work involving PBDEs and lake sediments may benefit from the inclusion of additional methoxylated PBDEs and hydroxylated PBDEs in the analytical suite. Past research has suggested that the MeO-BDEs may be natural products, while current

research has demonstrated that the hydroxylated species are likely derived via demethylation of naturally occurring MeO-PBDEs (Wan et al., 2009). Measurements of total bromine in core samples would allow for the development of a mass budget for bromine, clarifying the role of PBDEs and their metabolites in lentic and lotic systems.

TABLES

Table 1. Carbon/OM content as compared to analyte concentration.

White Lake			
Sample ID	Total PBDE Conc	Carbon %	Organic Matter %
WH1+2	2091	13.430	23.15
WH3+4	2376	13.640	23.5
WH5+6	2205	13.085	22.55
WH7+8	2426	13.640	23.5
WH9+10	2252	12.435	21.45
WH11+12	1638	12.335	21.3
WH13+14	749	12.710	21.9
WH15+16	644	12.020	20.7
WH17+18	723	11.820	20.4
WH19+20	537	11.650	20.1
WH21+22	454	10.995	18.95
WH23+24	764	11.180	19.3
WH25+26	734	10.830	18.65
WH27+28	1087	10.435	17.95
WH29+30	1369	13.280	22.9
WH31+32	1305	9.490	16.35
WH33+34	888	9.530	16.4
WH35+36	389	7.980	13.8
WH37+38	397	6.265	10.8
WH39+40	206	1.730	3.05
WH41+42	520	1.760	3.1
WH43+44	781	3.935	6.8

Table 1 (cont'd).

Muskegon Lake				
Sample ID	Total PBDE Conc	Total MeO-PBDE Conc	Carbon %	Organic Matter %
MU1+2	2050	53.02	10.460	18.05
MU3+4	2146	115.48	10.485	18.1
MU5+6	2676	73.74	11.060	19.05
MU7+8	2441	5.93	10.725	18.5
MU9+10	2896	38.58	10.265	17.7
MU11+12	2981	15.17	10.115	17.45
MU13+14	3414	33.14	10.055	17.35
MU15+16	3130	18.66	10.265	17.7
MU17+18	3883	11.01	10.660	18.35
MU19+20	2810	12.87	10.005	17.25
MU21+22	2739	10.85	10.005	17.25
MU23+24	2624	5.35	9.840	16.95
MU25+26	2338	7.58	9.765	16.85
MU27+28	2313	7.59	9.390	16.2
MU29+30	2029	3.57	9.485	16.35
MU31+32	2327	0.00	10.425	18
MU33+34	983	0.00	8.955	15.45
MU35+36	1348	0.00	9.265	15.95
MU37+38	1726	0.00	9.140	15.75
MU39+40	2585	0.00	8.770	15.15
MU41+42	2096	0.00	9.670	16.65

Table 2. Quality control sample spiking levels and recovery data (%).

Congener	UNS 52407 (pg/g)	Spike Amount (pg/g)	MS 52407 (pg/g)	% Rec	Spike Amount (pg/g)	MSD 52407 (pg/g)	% Rec	LCS 52407 (pg/g)	% Rec
BDE28	1.00	49.98	47.28	93	49.73	52.11	102	47.70	95
BDE47	23.96	49.98	71.86	96	49.73	180.41	313	74.50	149
BDE66	0.90	49.98	41.88	82	49.73	41.97	82	39.00	78
BDE100	5.19	49.98	48.98	88	49.73	64.74	119	48.70	97
BDE99	17.47	49.98	60.67	86	49.73	116.66	198	57.40	115
BDE85	0.60	49.98	45.98	91	49.73	47.44	94	48.20	96
BDE154	2.80	49.98	45.08	85	49.73	53.90	102	45.10	90
BDE153	3.49	49.98	44.78	83	49.73	56.89	107	46.90	94
BDE183	3.59	49.98	54.17	101	49.73	63.05	119	51.80	104
Congener	UNS 5807 (pg/g)	Spike Amount (pg/g)	MS 5807 (pg/g)	% Rec	Spike Amount (pg/g)	MSD 5807 (pg/g)	% Rec	LCS 5807 (pg/g)	% Rec
BDE28	0.00	49.95	50.05	100	49.43	48.34	98	47.10	94
BDE47	23.00	49.95	61.24	77	49.43	62.58	80	59.70	119
BDE66	0.79	49.95	39.06	77	49.43	43.01	85	44.70	89
BDE100	4.36	49.95	45.35	82	49.43	45.58	83	44.80	90
BDE99	16.06	49.95	57.94	84	49.43	53.09	75	56.70	113
BDE85	0.40	49.95	50.25	100	49.43	46.27	93	52.20	104
BDE154	3.47	49.95	47.25	88	49.43	48.44	91	48.30	97
BDE153	5.85	49.95	45.95	80	49.43	46.86	83	49.30	99
BDE183	7.64	49.95	53.85	93	49.43	55.96	98	57.80	116

Table 3. Total PBDE (Σ_{23}) concentration by sample (pg/g dry wt).

Sample	Year	Conc	Sample	Year	Conc
WH1+2	2006	2091	MU1+2	2006	2050
WH3+4	2004	2376	MU3+4	2004	2146
WH5+6	2002	2205	MU5+6	2002	2676
WH7+8	1999	2426	MU7+8	2001	2441
WH9+10	1997	2252	MU9+10	1999	2896
WH11+12	1995	1638	MU11+12	1997	2981
WH13+14	1993	749	MU13+14	1995	3414
WH15+16	1990	644	MU15+16	1993	3130
WH17+18	1988	723	MU17+18	1991	3883
WH19+20	1985	537	MU19+20	1989	2810
WH21+22	1983	454	MU21+22	1987	2739
WH23+24	1980	764	MU23+24	1985	2624
WH25+26	1978	734	MU25+26	1983	2338
WH27+28	1976	1087	MU27+28	1981	2313
WH29+30	1973	1369	MU29+30	1979	2029
WH31+32	1971	1305	MU31+32	1977	2327
WH33+34	1966	888	MU33+34	1974	983
WH35+36	1949	389	MU35+36	1972	1348
WH37+38	1920	397	MU37+38	1970	1726
WH39+40	<1901	206	MU39+40	1968	2585
WH41+42	<1901	520	MU41+42	1966	2096
WH43+44	<1901	781			

Table 4. Select PBDE congener contributions in White and Muskegon lakes.

White Lake	
Congener Number	Percent Contribution to total
BDE47	28.5
BDE183	17.6
BDE99	16
BDE171	7.49
BDE49	4.62
BDE100	4.58
BDE180	2.37
Muskegon Lake	
Congener Number	Percent Contribution to total
BDE47	23.6
BDE99	15
BDE171	9.48
BDE180	9.37
BDE49	8.39
BDE183	7.91
BDE100	5.2

Table 5. Parent : Metabolite ratios in Muskegon Lake.

Muskegon Lake Parent:Metabolite Ratios			
PBDE:Metabolite	2006	2004	1995
BDE47:6MBDE47	16.4	7.1	64.7
BDE99:5MBDE99	N/A	N/A	82.0
BDE85:6MBDE85	1.3	1.0	2.3

Compared all parent/metabolite sets available. Only maximum values used.

Table 6. Method blank congener concentrations.

Congener	BLANK 52407	BLANK WH13-34	BLK 5807	MU23-42 BLK	MU1-22 BLK*
BDE28	< DL	2.63	< DL	3.16	29.49
BDE17	< DL	< DL	< DL	< DL	11.06
BDE30	< DL	< DL	< DL	< DL	< DL
BDE71	< DL	< DL	< DL	< DL	< DL
BDE49	5.27	3.16	< DL	2.63	46.87
BDE47	91.10	87.41	< DL	81.10	1332.81
BDE66	< DL	< DL	< DL	2.63	24.75
BDE77	< DL	< DL	< DL	< DL	< DL
BDE100	13.69	14.22	9.48	11.06	148.50
BDE119	2.11	1.05	< DL	< DL	< DL
BDE99	54.77	68.98	31.07	48.97	737.23
BDE85	2.11	4.74	2.63	2.11	28.44
BDE126	2.11	1.58	< DL	< DL	< DL
BDE154	10.53	10.53	6.32	7.90	63.19
BDE153	15.27	15.80	15.80	14.22	104.27
BDE139	< DL	1.58	1.58	0.53	5.79
BDE140	0.53	1.05	1.05	1.05	3.16
BDE138	2.63	2.63	< DL	1.05	10.01
BDE183	16.85	18.96	< DL	17.38	261.19
BDE184	< DL	< DL	< DL	< DL	7.90
BDE180	< DL	< DL	< DL	4.21	20.01
BDE191	1.05	1.05	< DL	< DL	25.80
BDE171	< DL	< DL	< DL	< DL	< DL

5-8 QC set also applies to samples WH 1+2 thru WH 11+12

5-24 QC set also applies to WH-35 to WH-44

* this blank lost during extraction and re-created during sample clean up

FIGURES

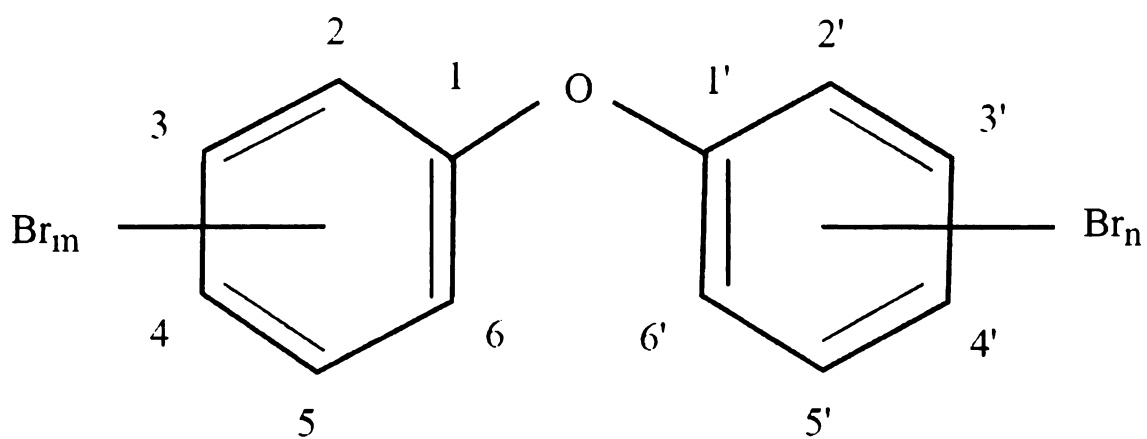


Figure 1. Generalized Structure of PBDEs (where $(m+n) = 2$ to 10 bromines)

BDE 47

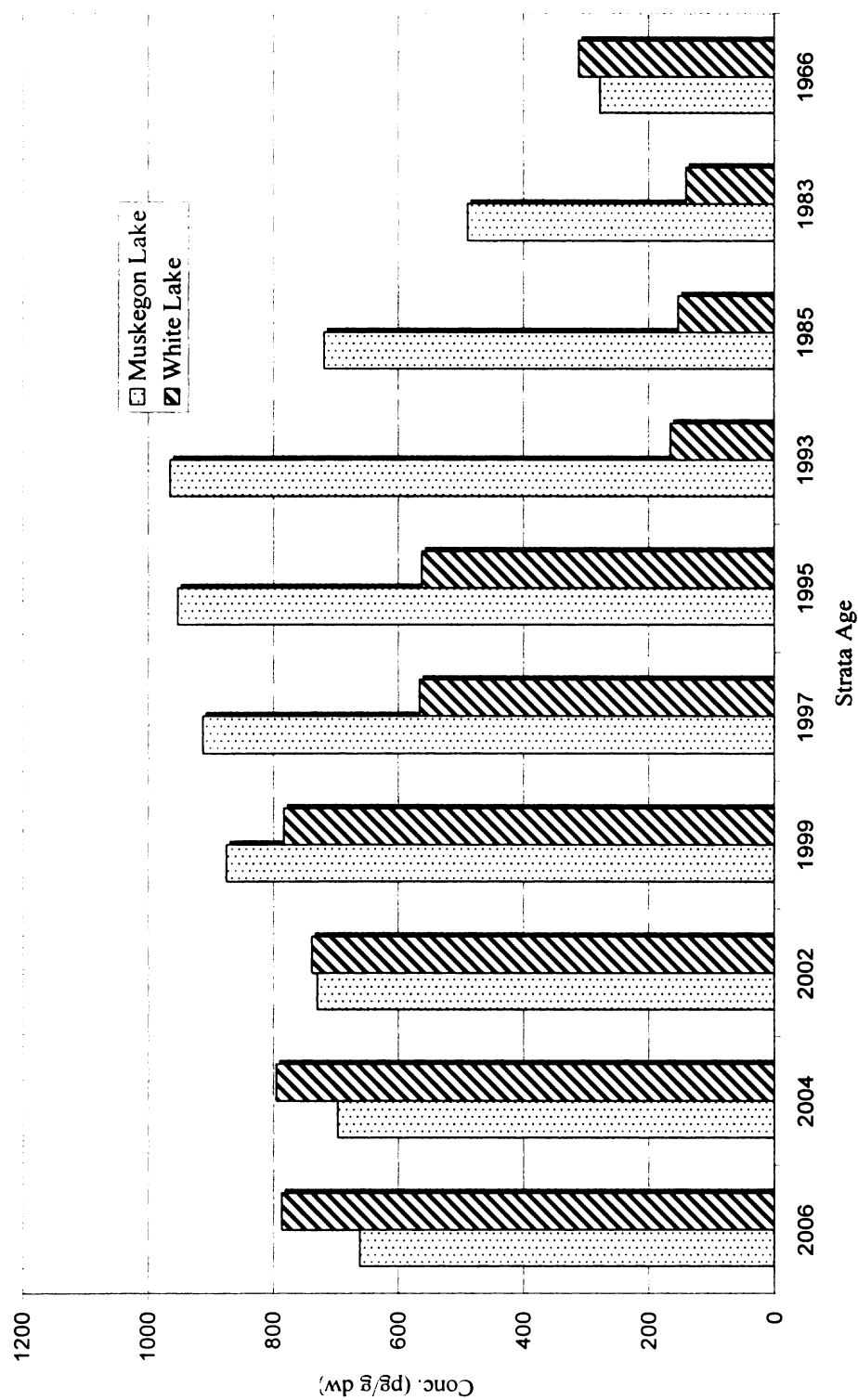


Figure 2. Comparison of select PBDE congeners in White and Muskegon Lakes.

BDE 99

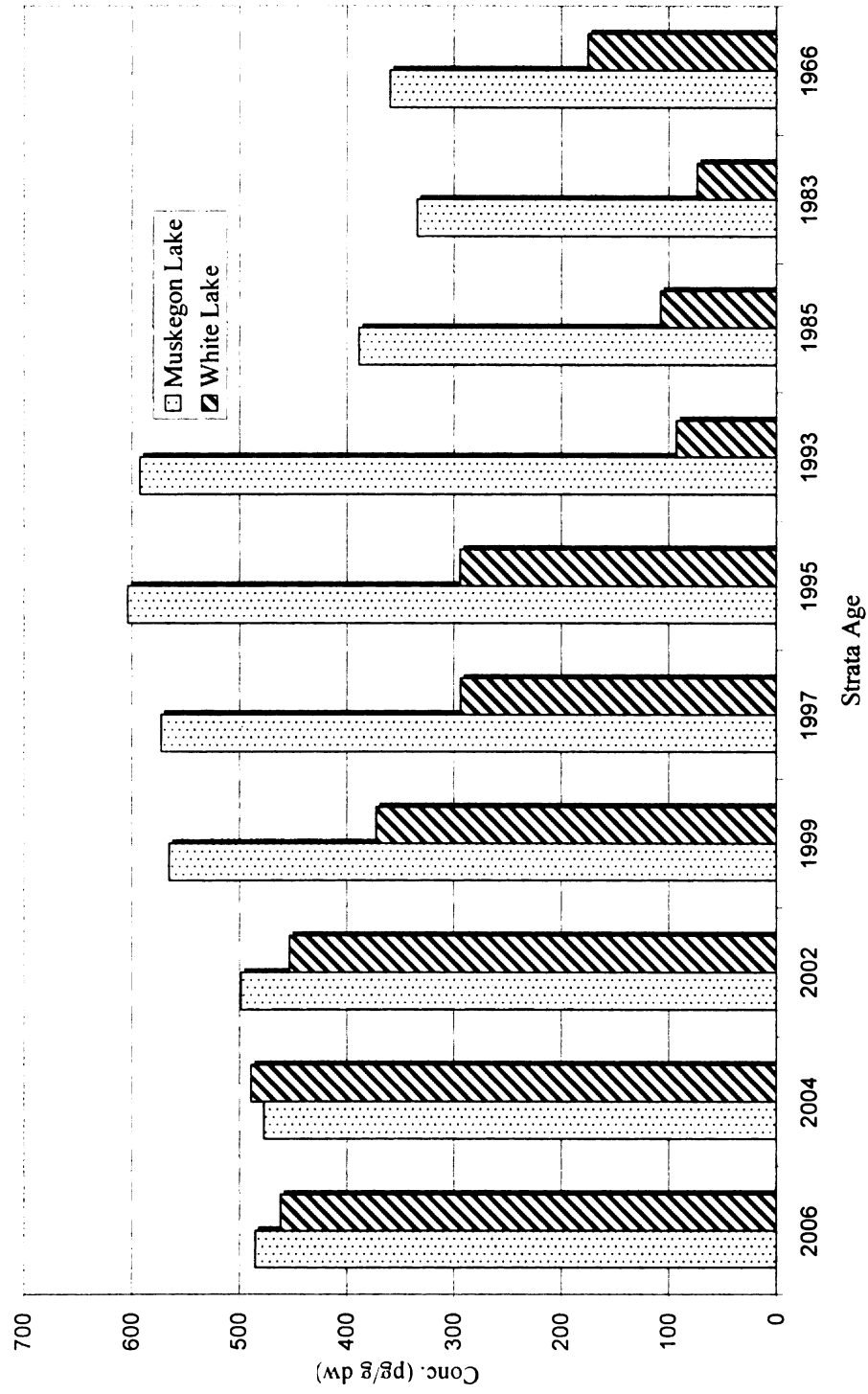


Figure 2 (cont'd).

BDE 183

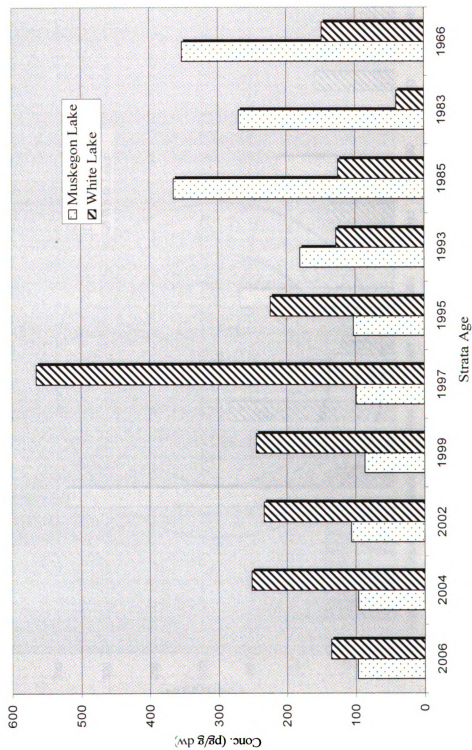


Figure 2 (cont'd).

BDE 171

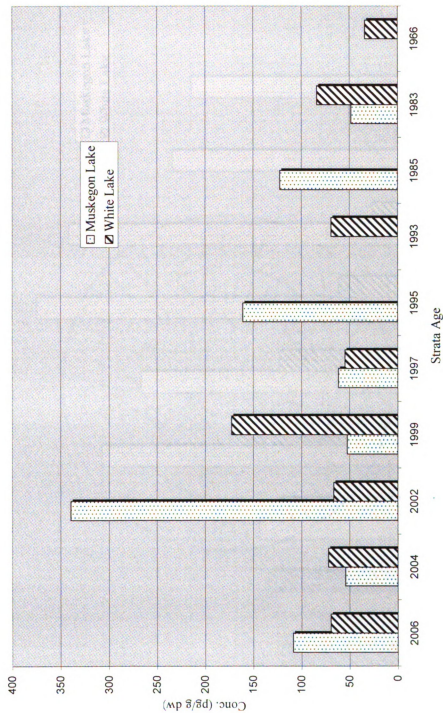


Figure 2 (cont d).

BDE 49

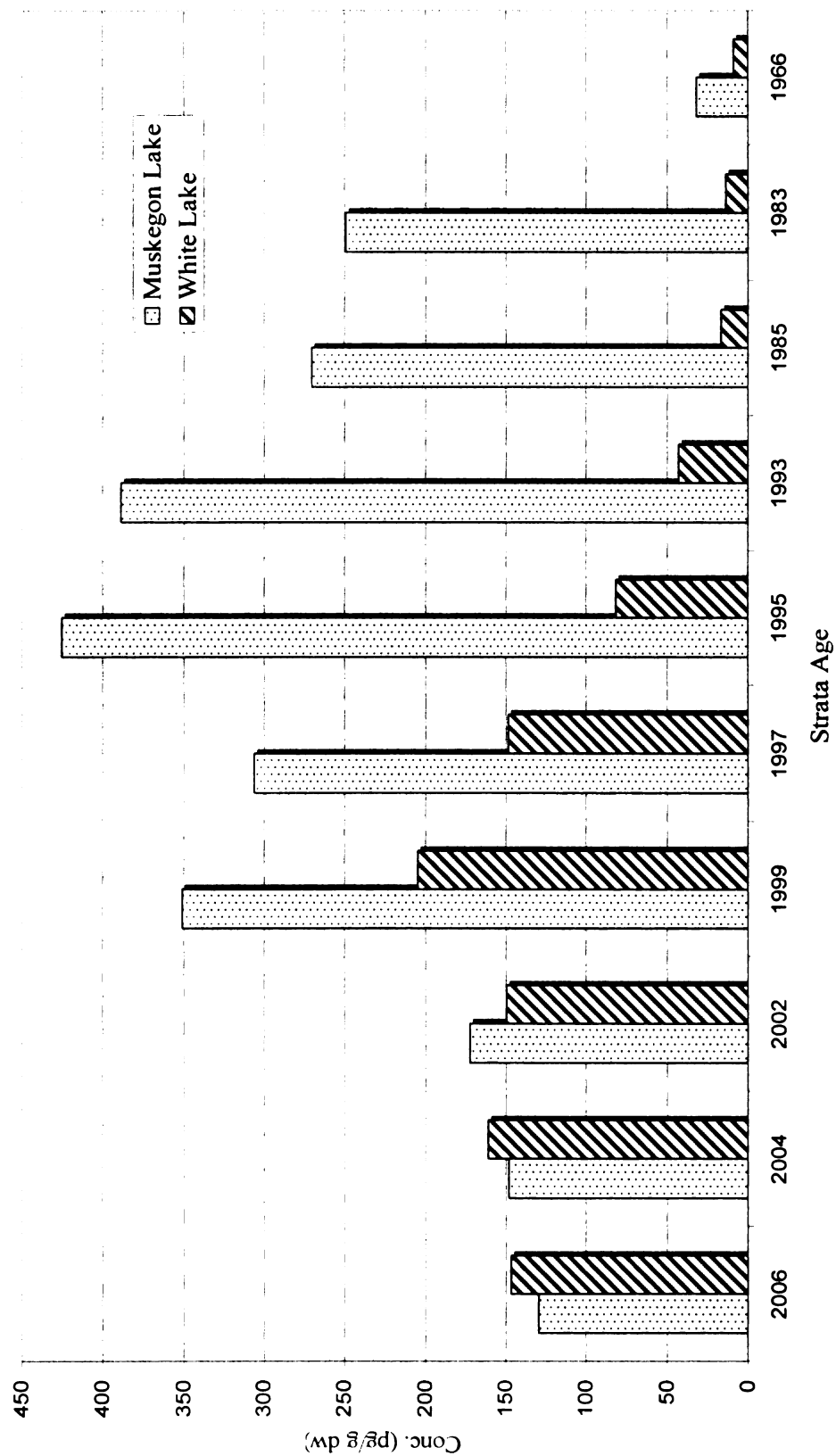


Figure 2 (cont'd).

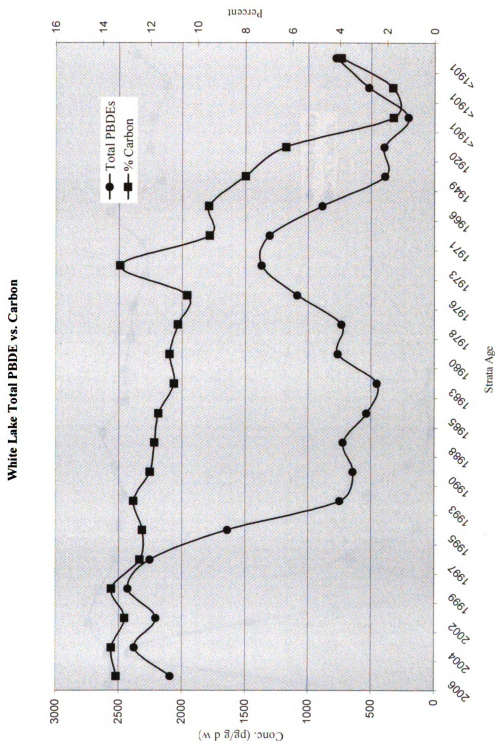


Figure 3. White Lake total PBDE and carbon comparison.

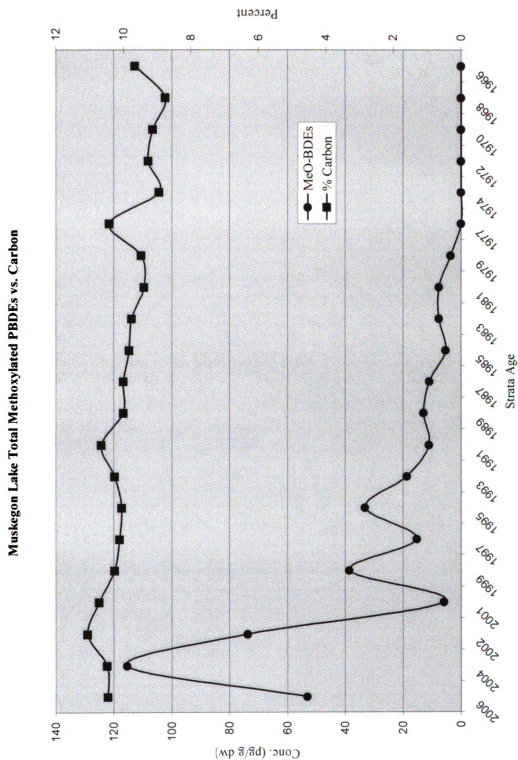


Figure 5. Muskegon Lake total Methoxylated PBDE and carbon comparisons.

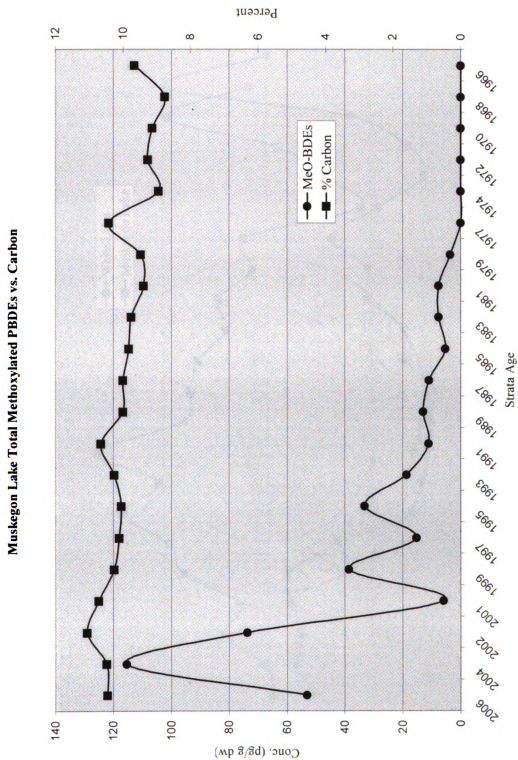
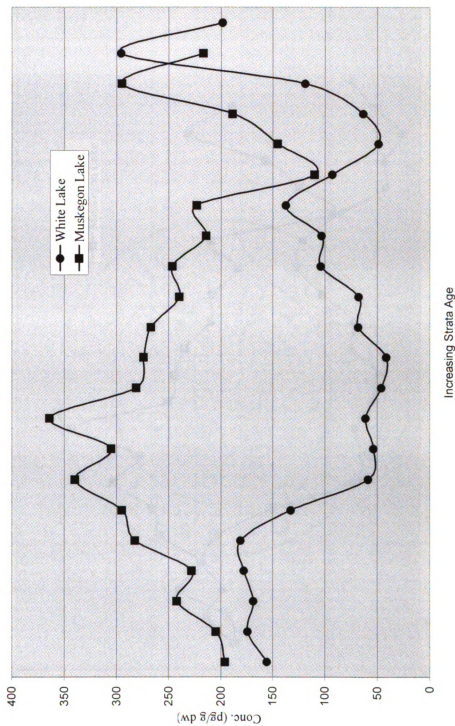
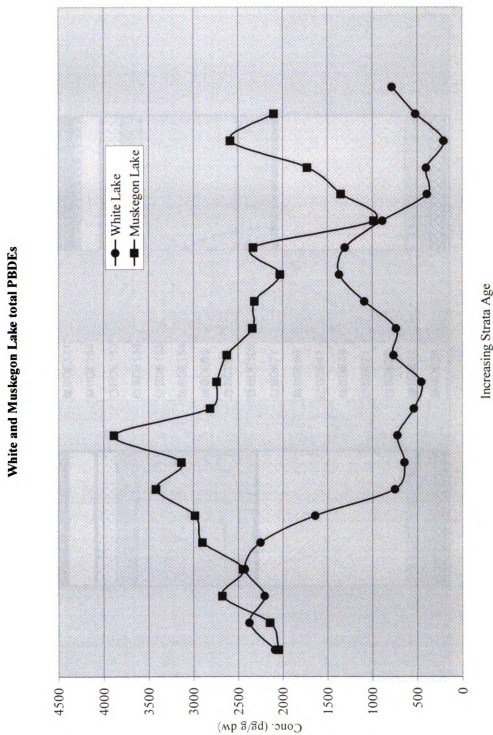


Figure 5. Muskegon Lake total Methoxylated PBDE and carbon comparison.

Carbon Normalized Total PBDEs in White and Muskegon Lakes





Uppermost Sediment Layer Congener Comparison

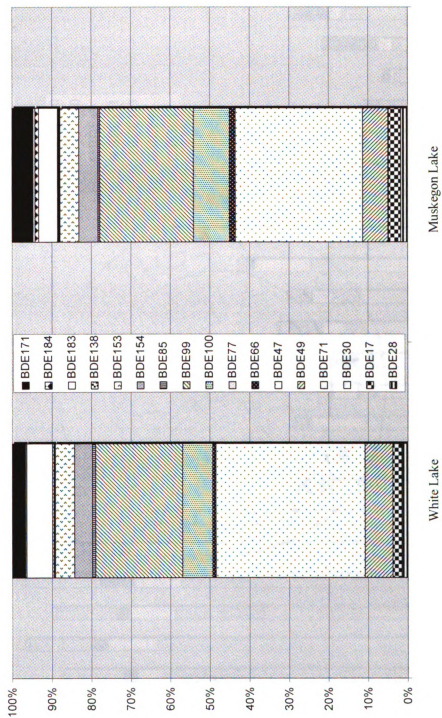


Figure 8. Uppermost sediment layer congener comparison .

Select White Lake PBDEs

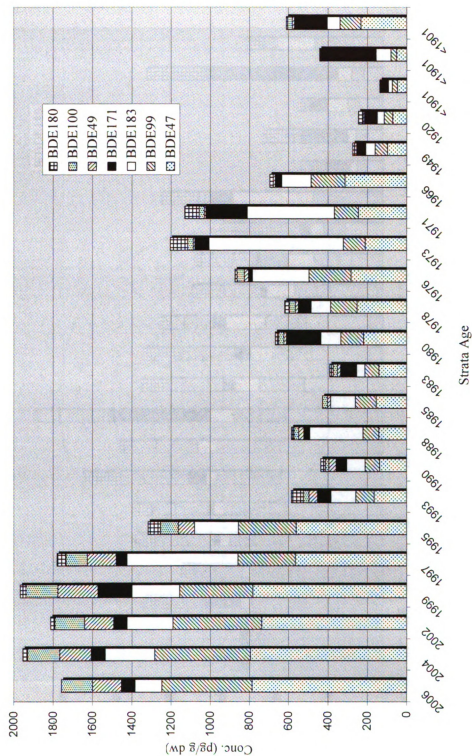


Figure 9. Select White Lake PBDEs.

Select Muskegon Lake PBDEs

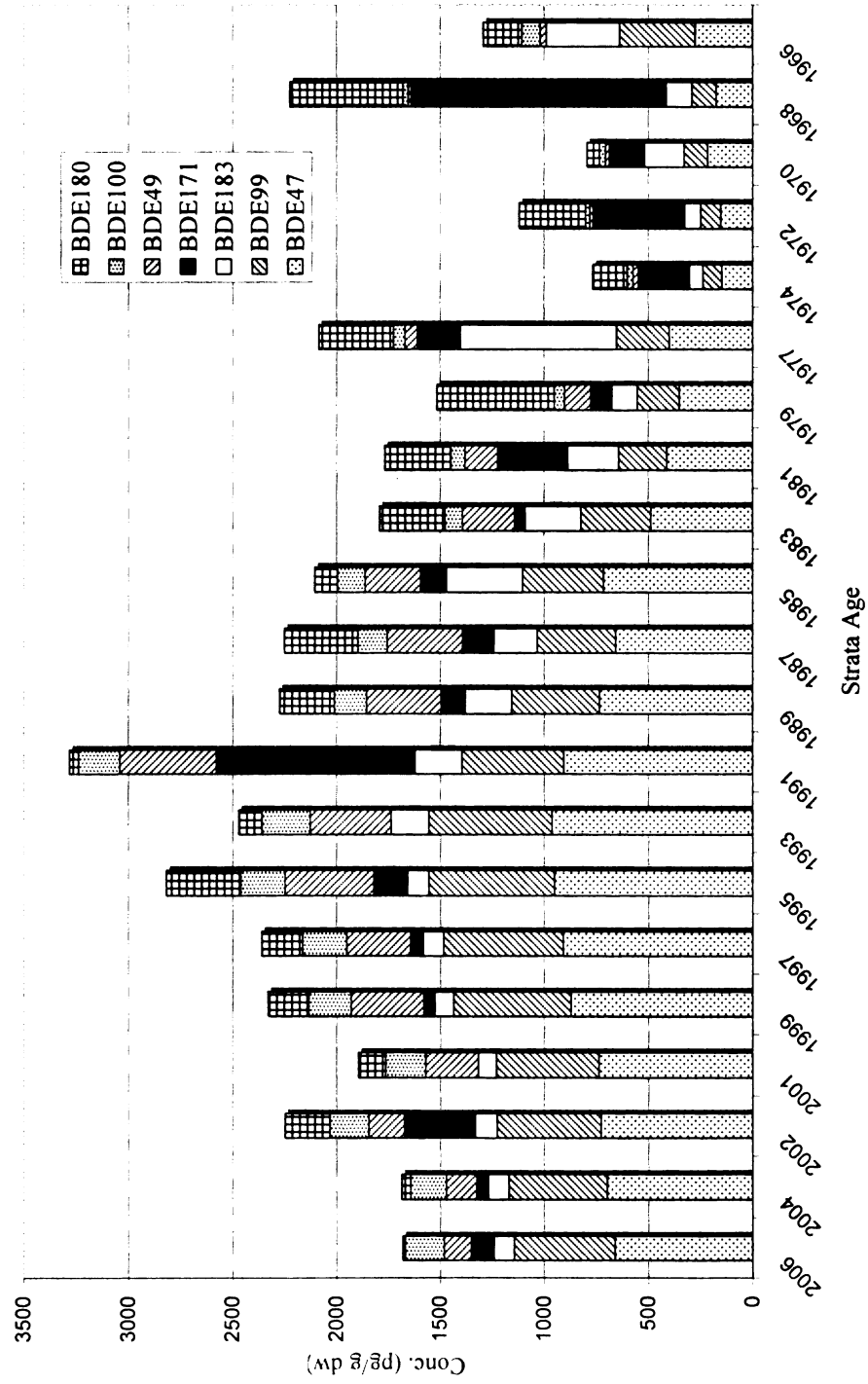


Figure 10. Select Muskegon Lake PBDEs.

Methoxylated PBDEs in Muskegon Lake

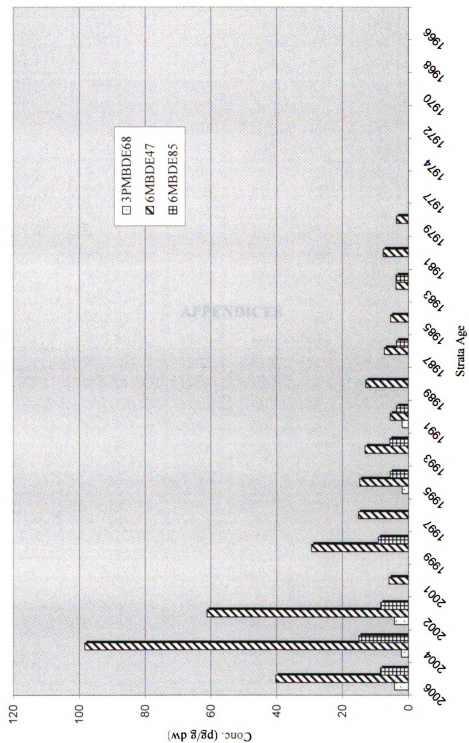


Figure 11. Methoxylated PBDEs in Muskegon Lake

APPENDICES

Appendix A. Sediment strata aging data for White and Muskegon Lakes.

White Lake	Year	Muskegon Lake	Year
WH 1+2	2006	MU 1+2	2006
WH 3+4	2004	MU 3+4	2004
WH 5+6	2002	MU 5+6	2002
WH 7+8	1999	MU 7+8	2001
WH 9+10	1997	MU 9+10	1999
WH 11+12	1995	MU 11+12	1997
WH 13+14	1993	MU 13+14	1995
WH 15+16	1990	MU 15+16	1993
WH 17+18	1988	MU 17+18	1991
WH 19+20	1985	MU 19+20	1989
WH 21+22	1983	MU 21+22	1987
WH 23+24	1980	MU 23+24	1985
WH 25+26	1978	MU 25+26	1983
WH 27+28	1976	MU 27+28	1981
WH 29+30	1973	MU 29+30	1979
WH 31+32	1971	MU 31+32	1977
WH 33+34	1966	MU 33+34	1974
WH 35+36	1949	MU 35+36	1972
WH 37+38	1920	MU 37+38	1970
WH 39+40	<1901	MU 39+40	1968
WH 41+42	<1901	MU 41+42	1966
WH 43+44	<1901		

Appendix B. Analytical instrument parameters for PBDE and MeO-PBDE analysis.

Primary Column	Agilent DB-5MS (30m x 0.25mm ID x 0.1 µm)	
Injection Port Type	Split/splitless-in splitless mode	
Injection Liner Type	Focus liner split/splitless	
Injection Volume	1 ul	
Injection Port Temperature	285°C	
Purge Flow	5 ml/min	
Purge On Time	2 min	
Carrier Gas	Helium	
Initial pressure	200 kpa	
Mode	Constant pressure	
Detector Temperature	285°C	
	<u>PBDE Analysis</u>	<u>MeO-PBDE Analysis</u>
Initial Temperature	110°C	150°C
Initial Hold	10.00 min	2.00 min
Ramp 1 Rate	25°C/min	2°C/min
Final Temperature 1	250°C	245°C
Hold Time 1	N/A	2.00 min
Ramp 2 Rate	1.5°C/min	30°C/min
Final Temperature 2	260°C	320°C
Hold Time 2	N/A	2 min
Ramp 3 Rate	25°C/min	N/A
Final Temperature 3	323°C	N/A
Hold Time 3	15 min	N/A

Appendix C. Analyte IUPAC names, CAS numbers, and calibration standard concentrations.

B/Z Number	IUPAC Name	CAS Number	Cal Conc (ng/ml)
BDE17	2,2',4-Tribromodiphenyl ether	147217-75-2	0.25, 1, 5, 20
BDE28	2,4,4'-Tribromodiphenyl ether	41318-75-6	0.25, 1, 5, 20
BDE30	2,4,6-Tribromodiphenyl ether	155999-95-4	0.25, 1, 5, 20
BDE47	2,2',4,4'-Tetrabromodiphenyl ether	5436-43-1	0.5, 2, 10, 40
BDE49	2,2',4,5'-Tetrabromodiphenyl ether	243982-82-3	0.5, 2, 10, 40
BDE66	2,3',4,4'-Tetrabromodiphenyl ether	189084-61-5	0.5, 2, 10, 40
BDE71	2,3',4',6-Tetrabromodiphenyl ether	189084-62-6	0.5, 2, 10, 40
BDE77	3,3',4,4'-Tetrabromodiphenyl ether	93703-48-1	0.5, 2, 10, 40
BDE85	2,2',3,4,4'-Pentabromodiphenyl ether	182346-21-0	0.5, 2, 10, 40
BDE99	2,2',4,4',5-Pentabromodiphenyl ether	60348-60-9	0.5, 2, 10, 40
BDE100	2,2',4,4',6-Pentabromodiphenyl ether	189084-64-8	0.5, 2, 10, 40
BDE119	2,3',4,4',6-Pentabromodiphenyl ether	189084-66-0	0.5, 2, 10, 40
BDE126	3,3',4,4',5-Pentabromodiphenyl ether	366791-32-4	0.5, 2, 10, 40
BDE138	2,2',3,4,4',5'-Hexabromodiphenyl ether	182677-30-1	0.5, 2, 10, 40
BDE139	2,2',3,4,4',6-Hexabromodiphenyl ether	N/A	0.5, 2, 10, 40
BDE140	2,2',3,4,4',6'-Hexabromodiphenyl ether	243982-83-4	0.5, 2, 10, 40
BDE153	2,2',4,4',5,5'-Hexabromodiphenyl ether	68631-49-2	0.5, 2, 10, 40
BDE154	2,2',4,4',5,6'-Hexabromodiphenyl ether	207122-15-4	0.5, 2, 10, 40
BDE171	2,2',3,3',4,4',6-Heptabromodiphenyl ether	N/A	1, 4, 20, 80
BDE180	2,2',3,4,4',5,5'-Heptabromodiphenyl ether	N/A	1, 4, 20, 80
BDE183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	207122-16-5	1, 4, 20, 80
BDE184	2,2',3,4,4',6,6'-Heptabromodiphenyl ether	N/A	1, 4, 20, 80
BDE191	2,3,3',4,4',5',6-Heptabromodiphenyl ether	N/A	1, 4, 20, 80

Appendix C (cont'd).

B/Z Number	IUPAC Name	CAS Number	Cal Conc (ng/ml)
4MBDE17	4'-Methoxy-2,2',4-Tribromodiphenyl ether	N/A	1, 4, 20, 80, 400
6MBDE17	6'-Methoxy-2,2',4-Tribromodiphenyl ether	N/A	1, 4, 20, 80, 400
5MBDE47	5-Methoxy-2,2',4,4'-Tetrabromodiphenyl ether	N/A	1, 4, 20, 80, 400
6MBDE47	6-Methoxy-2,2',4,4'-Tetrabromodiphenyl ether	N/A	1, 4, 20, 80, 400
4PMBDE49	4'-Methoxy-2,2',4,5'-Tetrabromodiphenyl ether	N/A	1, 4, 20, 80, 400
3PMBDE68	3'-Methoxy-2,3',4,5'-Tetrabromodiphenyl ether	N/A	1, 4, 20, 80, 400
6MBDE85	6-Methoxy-2,2',3,4,4'-Pentabromodiphenyl ether	N/A	1, 4, 20, 80, 400
6MBDE90	6-Methoxy-2,2',3,4',5-Pentabromodiphenyl ether	N/A	1, 4, 20, 80, 400
5MBDE99	5-Methoxy-2,2',4,4',5-Pentabromodiphenyl ether	N/A	1, 4, 20, 80, 400
5MBDE100	5-Methoxy-2,2',4,4',6-Pentabromodiphenyl ether	N/A	1, 4, 20, 80, 400
4MBDE101	4-Methoxy-2,2',4,5,5'-Pentabromodiphenyl ether	N/A	1, 4, 20, 80, 400
4MBDE103	4-Methoxy-2,2',4,5',6-Pentabromodiphenyl ether	N/A	1, 4, 20, 80, 400

Appendix D. ¹³C Labeled analog recovery (%) in White and Muskegon Lake samples

Congener	WH1+2	WH3+4	WH5+6	WH7+8	WH9+10	WH11+12	WH13+14	WH15+16
BDE138L INJ	191	113	92	104	143	106	111	142
BDE28L	18	40	50	36	31	27	43	27
BDE47L	16	48	62	36	37	28	48	29
BDE100L	17	52	64	36	37	27	48	30
BDE99L	19	53	64	40	40	31	52	33
BDE154L	12	32	38	26	23	20	30	20
BDE153L	14	32	37	26	23	20	31	20
BDE183L	12	28	32	19	16	13	22	17
BDE139L CUP	17	14	17	24	17	31	17	15
Congener	WH17+18	WH19+20	WH21+22	WH23+24	WH25+26	WH27+28	WH29+30	
BDE138L INJ	148	128	135	98	83	104	70	
BDE28L	26	40	34	35	42	34	48	
BDE47L	28	44	42	41	54	30	60	
BDE100L	29	46	43	43	54	40	59	
BDE99L	31	50	45	46	58	41	65	
BDE154L	18	28	26	25	34	25	34	
BDE153L	18	30	27	26	37	27	38	
BDE183L	15	23	23	24	33	24	38	
BDE139L CUP	19	20	19	25	33	30	30	

Appendix D (cont'd).

Congener	WH31+32	WH33+34	WH35+36	WH37+38	WH39+40	WH41+42	WH43+44
BDE138L INJ	83	92	90	90	112	108	90
BDE28L	33	22	27	34	22	27	40
BDE47L	46	34	41	48	35	38	46
BDE100L	49	0	0	0	0	38	50
BDE99L	51	41	51	54	44	45	50
BDE154L	27	22	28	30	26	28	26
BDE153L	28	23	28	31	28	29	26
BDE183L	10	28	30	33	26	26	26
BDE139L CUP	30	34	30	25	35	31	25
Congener	MU1+2	MU3+4	MU5+6	MU7+8	MU9+10	MU11+12	MU13+14
BDE138L INJ	53	49	40	42	28	35	33
BDE28L	35	36	48	36	73	57	59
BDE47L	58	62	66	64	70	70	59
BDE100L	68	74	79	82	106	85	89
BDE99L	66	74	73	77	96	75	80
BDE154L	34	39	36	34	44	35	40
BDE153L	34	37	34	30	40	32	36
BDE183L	27	28	24	23	27	22	25
BDE139L CUP	22	27	25	25	32	25	30

Appendix D (cont'd).

Congener	MU15+16	MU17+18	MU19+20	MU21+22	MU23+24	MU25+26	MU27+28
BDE138L INJ	32	32	22	29	35	22	23
BDE28L	59	47	87	63	36	51	49
BDE47L	77	54	98	71	42	55	59
BDE100L	92	68	111	82	50	70	70
BDE99L	84	64	102	76	48	59	66
BDE154L	40	28	46	34	24	32	29
BDE153L	35	25	40	30	21	29	25
BDE183L	27	18	27	21	16	20	20
BDE139L CUP	31	29	32	25	37	35	30
Congener	MU29+30	MU31+32	MU33+34	MU35+36	MU37+38	MU39+40	MU41+42
BDE138L INJ	14	16	15	12	17	33	13
BDE28L	80	60	43	58	42	14	38
BDE47L	87	66	46	68	47	16	45
BDE100L	99	86	57	74	52	20	49
BDE99L	89	70	58	74	54	23	53
BDE154L	41	35	27	34	25	10	27
BDE153L	38	31	23	31	23	8	25
BDE183L	26	24	18	22	15	8	17
BDE139L CUP	42	36	36	40	33	29	36

Appendix D (cont'd).

Congener	BLANK 5807	BLANK MU23-42	BLANK MU1-22 *	LCS 5807	UNS 5807	MS 5807	MSD 5807
BDE138L INJ	156	167	134	189	143	148	175
BDE28L	18	28	32	20	25	33	26
BDE47L	NR	30	33	20	28	40	25
BDE100L	18	28	39	20	29	43	28
BDE99L	20	30	36	20	30	44	32
BDE154L	18	27	29	18	26	38	27
BDE153L	18	28	26	19	25	40	29
BDE183L	0	21	15	15	17	30	22
BDE139L CUP	33	35	33	37	36	46	39
Congener	BLANK 52407	BLANK WHI3-34	LCS 52407	UNS 52407	MS 52407	MSD 52407	
BDE138L INJ	128	135	131	163	113	136	
BDE28L	24	27	31	43	57	19	
BDE47L	25	27	27	40	50	15	
BDE100L	24	26	23	40	48	14	
BDE99L	25	29	26	46	53	16	
BDE154L	22	26	22	39	39	12	
BDE153L	23	26	22	39	37	12	
BDE183L	19	21	16	28	26	10	
BDE139L CUP	41	39	37	40	39	41	

CUP = Labeled Clean Up Standard

INJ = Labeled Injection Standard

NR = Not Recovered

Appendix E. PBDE and MeO-PBDE analysis: Calibration verification standard recoveries (%).

CONGENER	PBDE Analysis			
	SEQUENCE ID			
	PATR-5	PATR-5A	PATR-5B	PATR-5C
BDE138L INJ	143	160	250	517
BDE28	104	86	4	84
BDE28L	126	126	256	73
BDE17	94	74	4	78
BDE30	112	102	0	102
BDE47L	116	114	13	68
BDE71	95	98	1	90
BDE49	94	92	15	82
BDE47	93	93	111	81
BDE66	85	85	4	75
BDE77	94	88	0	79
BDE100L	118	111	15	84
BDE100	89	89	27	81
BDE119	85	85	0	73
BDE99L	112	105	15	79
BDE99	86	89	89	79
BDE85	82	86	0	78
BDE126	86	92	0	88
BDE154L	108	107	14	101
BDE154	95	97	17	88
BDE153L	103	100	13	98
BDE153	92	94	26	86
BDE139	992	93	1	87
BDE140	86	90	1	86
BDE138	94	94	6	89
BDE183L	110	107	4	108
BDE183	98	101	36	96
BDE184	89	94	3	84
BDE180	84	89	9	81
BDE191	69	79	3	71
BDE171	69	82	19	75
BDE139L CUP	100	98	36	97

Appendix E (cont'd).

MeO-PBDE Analysis				
	POSITION IN SEQUENCE			
Congener	1ST	2ND	3RD	4TH
BDE138L INJ	105	0	249	364
6MBDE17	85	0	55	52
4MBDE17	90	0	60	60
3PMBDE68	87	0	69	29
6MBDE47	90	0	72	35
5MBDE47	99	0	76	34
4PMBDE49	91	0	71	33
6MBDE90	90	0	69	74
5MBDE100	90	0	84	73
4MBDE103	101	0	84	77
5MBDE99	93	0	84	80
4MBDE101	85	0	84	81
6MBDE85	80	0	76	73

CUP = Labeled Clean Up standard

INJ = Labeled Injection standard

Appendix F. White and Muskegon Lake sample percent moisture.

Sample	%	Sample	%
MU1+2	81.17	WH1+2	87.96
MU3+4	81.49	WH3+4	84.79
MU5+6	81.12	WH5+6	83.61
MU7+8	79.83	WH7+8	84.66
MU9+10	78.48	WH9+10	85.25
MU11+12	79.12	WH11+12	86.09
MU13+14	78.45	WH13+14	86.02
MU15+16	78.96	WH15+16	85.19
MU17+18	78.71	WH17+18	85.65
MU19+20	78.28	WH19+20	86.33
MU21+22	78.01	WH21+22	87.05
MU23+24	77.83	WH23+24	86.72
MU25+26	79.08	WH25+26	88.47
MU27+28	79.28	WH27+28	88.33
MU29+30	77.68	WH29+30	87.97
MU31+32	79.31	WH31+32	86.30
MU33+34	79.91	WH33+34	87.05
MU35+36	81.13	WH35+36	85.32
MU37+38	80.09	WH37+38	79.53
MU39+40	78.28	WH39+40	60.60
MU41+42	80.14	WH41+42	59.73
		WH43+44	72.26

Appendix G. PBDE congener concentration data for Muskegon Lake (pg/g dry wt).

Congener	MU1+2	MU3+4	MU5+6	MU7+8	MU9+10	MU11+12	MU13+14
BDE28	35.52	43.84	46.35	61.80	73.48	72.51	69.04
BDE17	63.10	78.59	76.38	124.10	103.79	124.17	142.69
BDE30	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE71	3.71	<DL	4.74	<DL	6.43	2.84	5.52
BDE49	129.37	148.09	172.24	251.17	350.86	306.16	425.32
BDE47	662.25	697.14	729.52	740.67	874.86	912.80	953.28
BDE66	28.10	28.87	23.70	24.23	45.92	35.07	46.49
BDE77	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE100	188.23	172.68	184.88	191.35	202.07	212.80	215.42
BDE119	<DL	<DL	<DL	3.96	<DL	2.84	<DL
BDE99	485.15	476.88	498.29	493.45	564.87	572.51	603.91
BDE85	10.60	15.50	7.90	8.41	13.32	12.32	12.89
BDE126	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE154	99.15	93.02	102.19	109.77	135.48	131.28	127.96
BDE153	98.62	118.15	104.82	135.97	137.77	135.07	145.91
BDE139	3.18	4.28	8.43	5.93	3.67	8.53	2.76
BDE140	4.24	10.69	4.21	3.46	6.89	<DL	5.06
BDE138	5.30	19.25	15.80	16.32	18.83	13.74	<DL
BDE183	97.03	96.23	106.40	85.54	86.34	98.58	102.65
BDE184	17.50	8.55	29.50	54.88	22.50	86.26	40.51
BDE180	10.07	41.17	214.38	130.04	196.10	192.42	354.43
BDE191	<DL	39.56	6.32	<DL	<DL	<DL	<DL
BDE171	108.70	54.00	339.74	<DL	52.35	61.14	160.64
Σ_{23}	2049.84	2146.48	2675.80	2441.04	2895.52	2981.04	3414.50

Appendix G (cont'd).

Congener	MU15+16	MU17+18	MU19+20	MU21+22	MU23+24	MU25+26	MU27+28
BDE28	72.31	69.72	61.14	55.58	49.50	25.59	24.19
BDE17	168.42	176.15	142.96	130.14	112.82	69.67	56.91
BDE30	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE71	4.67	4.13	4.60	2.71	4.46	8.06	4.27
BDE49	388.62	462.84	358.54	362.86	270.68	249.29	155.56
BDE47	964.31	908.26	736.84	658.38	718.39	490.05	412.14
BDE66	33.59	37.61	29.42	26.21	28.54	17.54	13.75
BDE77	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE100	232.80	198.17	153.53	144.15	129.32	89.57	67.35
BDE119	<DL	<DL	<DL	<DL	2.68	<DL	2.37
BDE99	592.49	488.53	420.59	377.32	388.85	334.12	228.60
BDE85	10.26	5.96	6.89	5.42	9.36	10.43	<DL
BDE126	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE154	145.56	123.85	117.67	111.61	99.44	78.20	67.82
BDE153	167.02	155.05	133.76	121.10	115.94	93.36	119.52
BDE139	<DL	8.72	9.65	9.04	8.47	12.80	16.13
BDE140	<DL	<DL	<DL	<DL	8.92	<DL	0.00
BDE138	17.73	<DL	34.93	28.92	30.77	36.49	32.72
BDE183	180.55	225.23	224.78	208.77	364.77	269.67	249.94
BDE184	41.05	<DL	<DL	<DL	51.28	99.05	<DL
BDE180	111.03	41.74	258.33	348.85	107.47	311.37	317.29
BDE191	<DL	22.48	<DL	<DL	<DL	94.79	210.58
BDE171	<DL	954.13	116.75	147.76	122.19	48.34	334.36
Σ_{23}	3130.39	3882.57	2810.39	2738.82	2623.86	2338.39	2313.49

Appendix G (cont'd).

Congener	MU29+30	MU31+32	MU33+34	MU35+36	MU37+38	MU39+40	MU41+42
BDE28	18.30	18.19	14.33	4.22	5.01	<DL	<DL
BDE17	51.32	13.88	13.34	8.44	8.51	8.25	23.46
BDE30	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE71	3.57	<DL	<DL	<DL	<DL	2.75	<DL
BDE49	126.28	59.34	27.67	15.83	16.53	15.12	31.95
BDE47	350.29	401.05	149.74	154.58	217.88	175.90	277.08
BDE66	14.73	10.53	7.41	6.33	4.01	3.66	9.49
BDE77	<DL	<DL	<DL	3.69	<DL	<DL	<DL
BDE100	51.32	55.99	23.72	22.69	31.56	26.57	86.37
BDE119	2.23	<DL	<DL	<DL	<DL	<DL	<DL
BDE99	203.93	253.17	89.94	97.07	109.19	114.52	359.96
BDE85	<DL	13.40	<DL	<DL	<DL	10.99	<DL
BDE126	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE154	45.52	45.47	19.77	16.35	28.05	14.66	70.89
BDE153	74.97	91.41	21.25	27.43	53.09	34.81	89.37
BDE139	20.97	4.79	18.29	<DL	38.07	35.73	<DL
BDE140	10.71	0.00	23.72	<DL	21.54	<DL	37.94
BDE138	29.45	28.72	<DL	<DL	<DL	26.11	13.48
BDE183	123.16	749.46	64.25	74.91	191.33	124.14	352.47
BDE184	<DL	<DL	<DL	39.04	482.34	37.56	504.24
BDE180	564.48	358.94	167.04	314.96	61.11	542.83	182.73
BDE191	238.73	15.31	98.34	123.45	288.00	187.36	56.91
BDE171	98.62	207.71	244.63	439.46	169.80	1223.55	<DL
Σ_{23}	2028.56	2327.35	983.44	1348.46	1726.02	2584.52	2096.36

Appendix H. PBDE congener concentration data for White Lake (pg/g dry wt).

Congener	WH1+2	WH3+4	WH5+6	WH7+8	WH9+10	WH11+12	WH13+14	WH15+16
BDE28	33.00	40.43	37.52	38.75	27.00	27.90	12.78	13.45
BDE17	46.20	73.04	67.78	80.72	64.12	38.63	18.47	18.15
BDE30	<DL	<DL	<DL	<DL	<DL	<DL	<DL	74.62
BDE71	<DL	<DL	<DL	<DL	<DL	<DL	0.71	0.67
BDE49	146.86	161.07	149.47	204.71	148.50	81.55	42.61	34.96
BDE47	787.13	795.57	738.28	783.34	565.64	562.23	164.77	135.80
BDE66	18.98	24.78	23.00	29.71	15.52	15.74	3.55	8.74
BDE77	<DL	8.48	7.87	1.94	1.35	7.87	<DL	0.67
BDE100	157.59	162.37	150.68	161.45	108.00	90.84	28.41	18.15
BDE119	<DL	<DL	<DL	1.94	<DL	2.86	2.13	1.34
BDE99	461.22	488.43	453.25	371.97	293.62	294.71	92.33	73.95
BDE85	18.15	15.65	14.52	10.33	8.77	6.44	5.68	2.69
BDE126	<DL	<DL	<DL	3.87	<DL	<DL	<DL	<DL
BDE154	94.88	85.43	79.27	86.54	86.40	67.95	29.83	20.84
BDE153	99.83	123.25	114.37	107.20	231.52	105.87	38.35	30.25
BDE139	3.30	<DL	<DL	<DL	<DL	2.86	<DL	<DL
BDE140	4.95	8.48	7.87	6.46	<DL	5.72	4.26	3.36
BDE138	7.43	10.43	9.68	10.98	12.82	8.58	9.23	4.71
BDE183	136.14	251.71	233.59	244.75	564.97	223.89	127.84	94.79
BDE184	<DL	31.30	29.05	75.56	23.62	14.31	12.07	9.41
BDE180	<DL	23.48	21.79	29.06	45.22	62.95	61.08	24.20
BDE191	5.78	<DL	<DL	4.52	<DL	17.17	25.57	18.82
BDE171	69.31	71.73	66.57	172.42	54.67	<DL	68.89	54.45
Σ_{23}	2090.76	2375.61	2204.54	2426.22	2251.77	1638.05	748.58	644.03

Appendix H (cont'd).

Congener	WH17+18	WH19+20	WH21+22	WH23+24	WH25+26	WH27+28	WH29+30	WH31+32
BDE28	11.09	7.28	10.78	13.48	18.10	21.36	12.45	31.01
BDE17	12.48	7.28	8.47	9.73	15.52	17.94	14.94	27.41
BDE30	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE71	1.39	<DL	<DL	2.25	2.59	2.56	2.49	1.44
BDE49	26.34	16.75	13.86	14.23	16.38	22.21	9.96	8.65
BDE47	140.03	152.95	140.11	218.64	250.86	281.08	209.96	245.22
BDE66	4.85	<DL	<DL	<DL	<DL	21.36	5.81	<DL
BDE77	<DL	<DL	<DL	<DL	<DL	<DL	2.49	5.77
BDE100	22.88	26.22	21.56	24.71	30.17	36.74	27.39	27.41
BDE119	1.39	0.73	<DL	<DL	<DL	<DL	<DL	<DL
BDE99	81.80	107.79	73.13	116.06	134.48	215.29	111.20	120.45
BDE85	2.77	4.37	3.08	5.99	7.76	11.96	7.47	5.77
BDE126	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
BDE154	22.88	22.58	10.78	14.98	18.10	35.88	19.09	38.23
BDE153	47.83	41.51	20.79	26.21	26.72	55.53	42.32	47.60
BDE139	<DL	<DL	<DL	2.25	1.72	<DL	4.15	<DL
BDE140	2.77	7.28	2.31	3.74	3.45	5.13	8.30	3.61
BDE138	<DL	5.83	<DL	<DL	3.45	<DL	3.32	13.70
BDE183	270.36	124.54	40.03	100.34	100.86	289.62	685.48	446.45
BDE184	30.50	4.37	4.62	16.47	17.24	18.80	34.02	<DL
BDE180	12.48	<DL	16.94	18.72	22.41	10.25	90.46	73.57
BDE191	<DL	7.28	3.85	<DL	<DL	22.21	7.47	<DL
BDE171	31.20	<DL	83.91	175.96	64.66	18.80	70.54	209.16
Σ_{23}	723.05	536.78	454.20	763.76	734.48	1086.72	1369.29	1305.45

Appendix H (cont'd).

Congener	WH33+34	WH35+36	WH37+38	WH39+40	WH41+42	WH43+44
BDE28	21.40	37.84	15.97	13.67	9.65	16.44
BDE17	31.33	14.19	48.86	17.21	16.58	39.67
BDE30	<DL	<DL	<DL	<DL	4.21	21.80
BDE71	1.53	<DL	<DL	<DL	<DL	<DL
BDE49	9.17	4.05	6.29	2.02	2.97	10.01
BDE47	311.81	97.97	71.60	48.34	52.45	231.24
BDE66	<DL	4.05	<DL	<DL	<DL	<DL
BDE77	<DL	<DL	28.06	15.44	11.63	22.16
BDE100	<DL	<DL	<DL	<DL	5.20	23.59
BDE119	<DL	<DL	<DL	<DL	<DL	0.36
BDE99	175.01	61.49	44.03	25.31	27.96	107.58
BDE85	8.41	2.70	<DL	2.02	<DL	<DL
BDE126	<DL	2.03	<DL	0.00	1.24	<DL
BDE154	48.91	15.54	20.32	5.82	7.67	20.01
BDE153	56.55	18.24	15.97	8.86	14.10	26.80
BDE139	<DL	<DL	<DL	0.76	2.23	1.07
BDE140	15.28	8.78	4.35	2.02	4.45	5.36
BDE138	8.41	12.84	9.19	0.00	2.72	2.50
BDE183	148.26	49.32	34.83	19.99	76.45	63.62
BDE184	<DL	<DL	5.32	4.05	2.23	10.72
BDE180	18.34	17.57	23.71	1.52	<DL	7.51
BDE191	<DL	<DL	4.35	<DL	<DL	1.79
BDE171	33.63	41.89	64.34	38.72	278.33	168.33
Σ_{23}	888.04	388.51	397.19	205.77	520.04	780.56

Appendix I. PBDE metabolite congener concentration data for Muskegon Lake (pg/g dry wt).

Congener	MU1+2	MU3+4	MU5+6	MU7+8	MU9+10	MU11+12	MU13+14
6MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
3PMBDE68	4.24	2.14	4.21	< DL	< DL	< DL	1.84
6MBDE47	40.30	98.37	61.10	5.93	29.39	15.17	14.73
5MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4PMBDE49	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE90	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE100	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE103	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE99	< DL	< DL	< DL	< DL	< DL	< DL	7.36
4MBDE101	< DL	< DL	< DL	< DL	< DL	< DL	3.68
6MBDE85	8.48	14.97	8.43	< DL	9.18	< DL	5.52
Σ_{12}	53.02	115.48	73.74	5.93	38.58	15.17	33.14

Appendix I (cont'd).

Congener	MU15+16	MU17+18	MU19+20	MU21+22	MU23+24	MU25+26	MU27+28
6MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
3PMBDE68	< DL	1.83	< DL	< DL	< DL	< DL	< DL
6MBDE47	13.06	5.50	12.87	7.23	5.35	3.79	7.59
5MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4PMBDE49	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE90	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE100	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE103	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE99	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE101	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE85	5.60	3.67	< DL	3.62	< DL	3.79	< DL
Σ_{12}	18.66	11.01	12.87	10.85	5.35	7.58	7.59

Appendix I (cont'd).

Congener	MU29+30	MU31+32	MU33+34	MU35+36	MU37+38	MU39+40	MU41+42
6MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
3PMBDE68	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE47	3.57	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4PMBDE49	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE90	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE100	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE103	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE99	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE101	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE85	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Σ_{12}	3.57	< DL	< DL	< DL	< DL	< DL	< DL

Appendix J. PBDE metabolite congener concentration data for White Lake (pg/g dry wt).

Congener	WH1+2	WH3+4	WH5+6	WH7+8	WH9+10	WH11+12	WH13+14
6MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
3PMBDE68	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE47	< DL	< DL	< DL	2.58	< DL	< DL	< DL
5MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4PMBDE49	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE90	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE100	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE103	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE99	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE101	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE85	9.90	< DL	< DL	< DL	< DL	< DL	< DL
Σ_{12}	9.90	< DL	< DL	2.58	< DL	< DL	< DL

Appendix J (cont'd).

Congener	WH15+16	WH17+18	WH19+20	WH21+22	WH23+24	WH25+26	WH27+28
6MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL
3PMBDE68	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4PMBDE49	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE90	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE100	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE103	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE99	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE101	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE85	< DL	< DL	< DL	< DL	< DL	< DL	< DL
Σ_{12}	< DL	< DL	< DL	< DL	< DL	< DL	< DL

Appendix J (cont'd).

Congener	WH29+30	WH31+32	WH33+34	WH35+36	WH37+38	WH39+40	WH41+42	WH43+44
6MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE17	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
3PMBDE68	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE47	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4PMBDE49	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE90	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE100	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE103	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
5MBDE99	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
4MBDE101	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL
6MBDE85	< DL	< DL	< DL	< DL	< DL	< DL	< DL	1.43
Σ_{12}	< DL	< DL	< DL	< DL	< DL	< DL	< DL	1.43

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