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Contaminant dynamics and trophic ecology of Lake Huron's lower pelagic food web

Lauren Liese Di Pierdomenico University of Windsor

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Contaminant dynamics and trophic ecology of Lake Huron's lower pelagic food web

By

Lauren L. Di Pierdomenico

A Thesis Submitted to the Faculty of Graduate Studies through the Great Lakes Institute for Environmental Research in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario, Canada

2016

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Contaminant dynamics and trophic ecology of Lake Huron's lower pelagic food web

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ABSTRACT

This study investigated Lake Huron's lower pelagic food web for regional heterogeneity using contaminant and energy dynamics. Recently, Lake Huron experienced a regime shift which has been characterized by changes in species dominance, reduced abundances, and top predator energy dynamics. The upper trophic levels of the offshore food web have been well investigated and as such, this study focused on the primary consumers (zooplankton, *Mysis, Dreissenid* mussels) and secondary consumers (*Coregonus hoyi, Osmerus mordax, Neogobius melanostomus*). Due to the well studied nature of polychlorinated biphenyls (PCBs) and mercury (Hg) in aquatic systems, these were utilized in this study as tracers to investigate trophic level dynamics andregional variability among Lake Huron's three basins. Gut content data and stable isotope analysis were also used as a means of examining foraging behaviour. Additionally, the condition of the lower trophic level organisms was investigated using lipid content andenergy density. Primary consumers revealed strong homogeneity in trophic level, PCB and Hg contents, and energy densities among and within basins of Lake Huron. However, secondary consumers revealed strong differences in energy densities, PCB and Hg accumulation patterns, and trophic levels among and within basins. Isotope data demonstrated nearshore tracking of resources in the North Channel, while both PCB and Hg data revealedhigh variability in bioaccumulation dynamics among the basins. This research concluded that the trophic shift in Lake Huron is primarily a bottom up process but ecological responses vary among the basins.

iv

DEDICATION

To my younger sister, Emily. This would not have been possible without your support and encouragement. I will forever be grateful.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure 1.1: Lake Huron, basins are as follows: (i) Main Basin, (ii) Georgian Bay, (iii) North Channel. Sampling locations are indicated by a red dot. Image adapted from Ryder 2013 .. 4 **Figure 2.1**: 2011-2012 Main Basin zooplankton composition for (A) April, n=1, (B) May, n=2, (C) June, n=7, (D) July, n=1, (E) August, n=4 and (F) September, n=1 33

Figure 2.3:North Channel zooplankton composition for July 2011-2012, n=3............... 34

Figure 2.4: Mean δ^{13} C signatures (‰) in the lower food web of (A) Main Basin, (B) Georgian Bay, and (C) North Channel. The dashed line represents the pelagic-littoral point, in which values favouring the more positive side are considered littoral and those favouring the more negative side are considered pelagic. Error bars indicate ± 1 SE .. 35

Figure 2.5: Mean $\delta^{15}N$ signatures (%) in the lower food web of (A) Main Basin, (B) Georgian Bay, and (C) North Channel. Error bars indicate ± 1 SE 36

Figure 2.6: Carbon and nitrogen isotopic niche and standard ellipse areas for (A) Main Basin, (B) Georgian Bay, and (C) North Channel. Species included here are representative of the lower food web and include zooplankton (black), *Mysis* (red), *Dreissenid* mussels (green), rainbow smelt (dark blue), bloater chub (light blue), round goby (purple), and deepwater sculpin (yellow)... 37

Figure 2.7: Mean dry weight energy densities (kJ/g) of the lower trophic food web amongst the basins of Lake Huron. The white, light grey, and dark grey bars correspond to the Main Basin, Georgian Bay, and North Channel, respectively. Error bars indicate ± 1 SE... 38

Figure 3.1: Discriminant function ordinations of Lake Huron bloater chub (*Coregonus hoyi*) collected from the Main Basin (\diamond), Georgian Bay (\square) and the North Channel (\triangle). Ordinations were completed using (A) fish stable isotope (δ^{13} C & δ^{15} N) values and proportional (% of ΣPCB) concentrations for 32 PCB congeners or (B) solely PCB congener proportional concentrations... 62

Figure 3.2: Discriminant function ordinations of Lake Huron rainbow smelt (*Osmerus mordax*) collected from the Main Basin (\diamond), Georgian Bay (\square) and the North Channel (\triangle). Ordinations were completed using (A) fish stable isotope ($\delta^{13}C \& \delta^{15}N$) values and proportional (% of ΣPCB) concentrations for 29 PCB congeners or (B) solely PCB congener proportional concentrations... 63

Figure 3.3: Mean lipid content (%) of the lower trophic food web amongst the basins of Lake Huron. The white, light grey, and dark grey bars correspond to the Main Basin, Georgian Bay, and North Channel, respectively. Error bars indicate ± 1 SE 64 **Figure 3.4:** Mean wet weight Hg concentrations (ng/g) for Lake Huron's lower trophic level species. The Main Basin is indicated in white, Georgian Bay in light grey, and the North Channel is represented by dark grey. Error bars indicate ± 1 SE 65 **Figure 3.5:** Mean lipid corrected PCB 180 concentrations (ng/g) for the species occupying the lower trophic level of Lake Huron. The Main Basin, Georgian Bay and the North Channel are represented as follows: white, light grey, and dark grey. Error bars indicate \pm 1 SE.. 66 **Figure 3.6:** Wet weight Hg concentrations (ng/g) in relationship to δ ¹⁵N (‰) of the lower food web within Lake Huron's basins: Main Basin (\diamond), Georgian Bay (\blacksquare), North Channel ()... 67 **Figure 3.7:** Lipid corrected PCB 180 concentrations (ng/g) in relationship to $\delta^{15}N$ (‰) of the lower food web within Lake Huron's basins: Main Basin (\diamond), Georgian Bay (\blacksquare), North Channel () .. 68 **Figure 3.8:** Mean biomagnification factors (BMF) of lipid corrected PCB 180 between various predators and prey items among Lake Huron's basins. (A) BMF predator: zooplankton and (B) BMF predator: *Mysis*. The predators included are as follows: rainbow smelt (white), bloater chub (light grey), round goby (dark grey), and deepwater sculpin (black) ... 69 **Figure 3.9:** Mean biomagnification factors (BMF) of wet weight Hg between various predators and prey items among Lake Huron's basins. (A) BMF predator: zooplankton and (B) BMF predator: *Mysis*. The predators included are as follows: rainbow smelt (white), bloater chub (light grey), round goby (dark grey), and deepwater sculpin (black) .. 70

LIST OF APPENDICES

LIST OF ABBREVIATIONS/SYMBOLS

- ANCOVA analysis of covariance
- ANOVA analysis of variance
- BMF biomagnification factor
- DMA-80 Direct mercury analyzer
- EtOH ethanol
- GC-ECD gas chromatography with electron capture detector
- GIT gastrointestinal tract
- GLIER Great Lakes Institute for Environmental Research
- GLWQA Great Lakes Water Quality Agreement

Hg – mercury

- K_{ow} octanol-water partition coefficient
- LC PCB 180 lipid corrected PCB 180
- MeHg methylmercury
- NSS nearshore shunt
- OMNR Ontario Ministry of Natural Resources
- Pa Pascal
- PCB polychlorinated biphenyl
- POP persistent organic pollutant
- SE standard error
- SIBER stable isotope Bayesian ellipses in R
- $TL_{\text{CONSUMER}} -$ trophic level
- δ^{13} C ratio of $^{13}C/^{12}$ C, carbon stable isotope signature
- δ^{15} N ratio of 15 N/ 14 N, nitrogen stable isotope signature

NOMENCLATURE

Alosa pseudoharengus – alewife *Coregonus clupeaformis –* lake whitefish *Coregonus hoyi* – bloater chub *Dreissena polymorpha –* zebra mussel *Dreissena bugensis –* quagga mussel *Myoxocephalus thompsonii* – deepwater sculpin *Mysis diluviana -* mysis *Neogobius melanostomus* – round goby *Osmerus mordax* – rainbow smelt *Petromyzon marinus –* sea lamprey *Salvelinus namaycush* – lake trout

CHAPTER 1:

GENERAL INTRODUCTION

1.1 INTRODUCTION

Lake Huron is the second largest of the five Great Lakes (Barbiero et al. 2009) and is composed of three basins with differing physical characteristics (Figure 1.1). The most central portion of the lake is called the Main Basin. To the east of this and separated by the Bruce Peninsula lies the second basin, Georgian Bay (Berst et al. 1973). The third basin, known as the North Channel, is positioned north of the Main and is separated by Drummond, Cockburn, and Manitoulin islands (Berst et al. 1973). This system receives water from two other Great Lakes, Superior and Michigan. Water from Lake Michigan is fed into the Main Basin via the Straits of Mackinac (Berst et al. 1973). Water from Lake Superior flows through the St. Mary's River into the North Channel from which it can take two paths. The first moves water directly into the Main Basin using Detour, False Detour and Mississagi Channels. The second route feeds water into Georgian Bay using the waterways around Little Current. Once in Georgian Bay, the water can flow through the Main Channel, which is situated between Manitoulin Island and the Bruce Peninsula; from there, it is carried into the Main Basin (Sly et al. 1988).

Of the basins, the Main Basin is the largest in both surface area and volume (40 512 km^2) and 2 790 km³), followed by Georgian Bay (15 108 km² and 660 km³), and lastly the North Channel (3 950 km² and 90km³) (DesJardine et al. 1995; Sly et al. 1988; EPA 2015). A similar pattern is observed when considering maximum depth of each basin: 229m, 165m, and 85m (Sly et al. 1988; EPA 2015). Beyond differences in surface area and volume, the three basins of Lake Huron differ in their geological formations. Georgian Bay and the North Channel lie on the Canadian Shield. Here, the geologic composition consists of granite, gneisses, metavolcanic, and metasedimentary rock from the Precambrian Period (Gillespie et al. 2008). Alternatively, the Main Basin occupies a depression of soft sedimentary rock originating from the Paleozoic time frame (Gillespie et al. 2008). The Bruce Peninsula and the islands which divide the North Channel from the Main Basin are made of Silurian Period dolomites and limestones (Gillespie et al. 2008).

Lake Huron is a system which in the last century has experienced numerous perturbations and various stressors. Many of these events have been attributed to invasive species, habitat destruction, and overfishing (Barbiero et al. 2009), leading to changes in the food web. After the 1920s, Lake Huron's food web was altered by the invasion of rainbow smelt

(*Osmerus mordax*) and alewife (*Alosa pseudoharengus*) (Roseman et al. 2009). Soon after, during the 1960s, lake trout (*Salvelinus namaycush*) and lake whitefish (*Coregonus clupeaformis*) experienced a significant decline in abundances resulting in the near extirpation of lake trout from Lake Huron (Barbiero et al. 2009). It was during this same time frame that the parasitic sea lamprey (*Petromyzon marinus*) invaded the lake; it is suggested that the lamprey bear at least partial responsibility for the abundance declines of lake trout (Roseman et al. 2009). In an effort to maintain the upper level of the food web, stocking the lake with salmonids was initiated in the 1970s. Additional aid in supporting the lake's health came in 1972 with the implementation of the Great Lakes Water Quality Agreement (GLWQA). The GLWQA was successful at fulfilling its purpose and resulted in the reduction of both contaminant and nutrient loading into the lakes (Dobiesz et al. 2005). During the 1990s however, Lake Huron's food web was again altered by the invasion of zebra mussels (*Dreissena polymorpha*), quagga mussels (*Dreissena bugensis*) and the round goby (*Neogobius melanostomus*). The continuous filter feeding nature of these mussels coupled with the decrease in nutrient loading caused an increase in water clarity (Bunnell et al. 2014). Furthermore in 2003, the population of alewife crashed and a significant decline was observed in the abundance of cladocerans (Barbiero et al. 2011). Today, Lake Huron is an ultra-oligotrophic lake (Pothoven et al. 2013) with relatively low species abundances occurring throughout the food web (Barbiero et al. 2009).

This study will investigate trophic ecology and contaminant tropho-dynamics of Lake Huron's lower pelagic food web. Here, the focus will not be on Lake Huron as a single limnological system, but will consider it from the spatial perspective of its three basins – the Main Basin, Georgian Bay, and the North Channel (Figure 1.1). The existence of basin-specific differences within the upper trophic levels of Lake Huron's food web was revealed by Abma et al. 2015 and Paterson et al. 2016. This study examines the lower trophic levels to determine if basin-specific bioaccumulation trends revealed by the aforementioned studies hold true for the primary and secondary consumers of the food web. Stable isotopes and gut content analysis will be utilized to provide insight into the foraging behaviours of the prey fish community. This data coupled with energy and contaminant dynamics will provide critical information as to what is occurring in the lower trophic levels of the food web. The hypotheses of this study have been established to anticipate lakewide spatial homogeneity. More specifically, Chapter 2 will examine the following hypotheses: (1) The diet and condition of the forage fish is consistent across the basins and (2) Energy density of organisms occupying the second and third trophic

levels of Lake Huron is constant across the basins. Chapter 3 hypotheses are as follows: (1) Assuming physiochemical properties alone regulate bioaccumulation, it is predicted that PCB and Hg concentrations are similar amongst the primary and secondary consumers throughout the three basins of Lake Huron and (2) Similarly, it is predicted that BMFs between the forage fish and its prey will be consistent across the three basins. By considering these hypotheses this study will provide information as to whether the trophic collapse in Lake Huron is common to all basins.

Figure 1.1: Lake Huron, basins are as follows: (i) Main Basin, (ii) Georgian Bay, (iii) North Channel. Sampling locations are indicated by a red dot. Image adapted from Ryder 2013.

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CHAPTER 2:

THE ZOOPLANKTON COMMUNITY AND THE FORAGING STRATEGIES OF PREY FISH COMMUNITIES IN LAKE HURON

2.1 INTRODUCTION

Food web structure can be controlled through either the top-down or the bottom-up approaches (McQueen et al. 1986). A food web undergoing top-down control is regulated by predation, and the effects tend to alternate between consecutive trophic levels (Pothoven et al. 2013). For example, the declining forage fish populations in Lake Huron should have resulted in a predation release on the zooplankton community, thereby increasing the zooplankton abundance. However, abundances of zooplankton and forage fish in Lake Huron are both declining and remain low (Bunnell et al. 2014), providing support for a bottom-up controlled food web. This latter type of food web is regulated by resource availability (Pothoven et al. 2013). The invasion of *Dreissenid* mussels in Lake Huron is thought to have resulted in the sequestering of nutrients and energy in the littoral environment, resulting in what is known as the Nearshore Shunt or the NSS (Hecky et al. 2004). During the 2000s, the *Dreissenid* mussels continued to proliferate and began colonizing deeper into areas which were previously unoccupied. The reduction in nutrient flow to the offshore environment caused a decrease in primary production, from 100 g C m⁻² y⁻¹ in the 1970s (Vollenweider et al. 1974) to 32 g C m⁻² y⁻¹ in 2011-2012 (Ryder 2013), potentially contributing to Lake Huron's ultra-oligotrophic state. As a result of this oligotrophication, zooplankton biomass has declined (Barbiero et al. 2009). Pelagic species rely on the resources in the offshore environment and subsequently have experienced declines in their biomass and energy densities (Paterson et al. 2014). These reductions in energy densities at successive trophic levels provide further evidence for a bottom-up controlled food web.

The composition of the zooplankton community is influenced by both extrinsic and intrinsic factors. Forage fish diet preferences can influence the zooplankton relative abundances and size distribution (Barbiero et al. 2009). Forage fish prefer to consume larger individuals resulting in a possible transition of the zooplankton community towards a smaller body size (Barbiero et al. 2009). Furthermore, the vulnerability of zooplankton to predation is also influenced by swimming ability, or in other words the ability to evade a predator. In relation to Lake Huron's zooplankton community, the predation risk associated with forage fish from greatest to least, is as follows: cladocerans, cyclopoid copepods, calanoid copepods (Barbiero et

al. 2009). Temporal trends associated with zooplankton abundances are characterized by a spring increase, followed by a summer decline that is possibly linked to predation by forage fish (Pothoven et al. 2013).

Zooplankton and *Mysis* are typical prey items found in the diet of forage fish, such as rainbow smelt (*Osmerus mordax*). Zooplankton tend to be less energy rich than other prey organisms such as *Mysis* and *Diporeia* (Bunnell et al. 2011). Therefore, to achieve the same caloric intake that would be garnered from the consumption of *Mysis*, forage fish must consume a greater proportion of zooplankton (Bunnell et al. 2011). Herein lies the problem, *Mysis* also share zooplankton as a food source. Additionally detracting from available energy for forage fish, the energy density of *Mysis* has declined in tandem with the zooplankton abundance decline (Mida Hinderer et al. 2012). In addition to the reduced abundances and energy densities, *Mysis* are difficult to capture as they exhibit diel vertical migration to minimize predation by forage fish. The aforementioned conditions in Lake Huron and behavioural characteristics of *Mysis* can lead to a high foraging cost for the prey fish, potentially providing a situation in which energy spent foraging will not be compensated (Pothoven et al. 2011).

2.2 OBJECTIVES

Lake Huron's lower trophic level has rarely been studied. Furthermore, many studies use only the Main Basin to represent Lake Huron (Roseman et al. 2009, Barbiero et al. 2012, Bunnell et al. 2012) instead of delving into its three basins. This chapter will examine the temporal and spatial characteristics of the zooplankton community of Lake Huron and investigate the foraging behaviours of the prey fish amongst the three basins. Stomach contents, stable isotopes and energy densities will be used to determine the feeding strategies of the lower trophic levels of Lake Huron including zooplankton, *Dreissenid* mussels (bulk *Dreissena bugensis* and *Dreissena polymorpha*), *Mysis* (*Mysis diluviana*), and forage fish: rainbow smelt (*Osmerus mordax*), bloater chub (*Coregonus hoyi*), round goby (*Neogobius melanostomus*) and deepwater sculpin (*Myoxocephalus thompsonii*). With use of the formerly stated analyses and species the following hypotheses will be scrutinized:

- 1) The diet and condition of the forage fish is consistent across the basins (Figure 1.1).
- 2) Energy density of organisms occupying the second and third trophic levels of Lake Huron is constant across the basins.

2.3 METHODOLOGY

Detailed collection information, including site and date, as well as the number of samples used per analysis can be found in Appendix A.

2.3.1 – Zooplankton Collection

Samples were collected approximately 2-6 km offshore via two consecutively vertical tows, using a 64 µm mesh plankton net, 1 metre in diameter and 8 metres long. One of the tows was transferred into a hexane-rinsed glass jar and frozen at approximately -25°C, while the other was preserved in 95% EtOH. The frozen samples were used for contaminant and stable isotope analysis and were stored at the Great Lakes Institute for Environmental Research (GLIER).

2.3.2 –Dreissenid Mussel Collection

Dreissenid mussel samples were collected by the Ontario Ministry of Natural Resources (OMNR) and Haffner lab personnel. A benthic sled was utilized for the samples collected by the OMNR. The samples collected by Haffner lab personal were by-catch from gill nets used in the capture of forage fish. Whole mussels were stored in plastic bags and placed on ice until arrival at the GLIER facility, where they were stored at -25°C until processing. Processing of the *Dreissenid* mussels involved shucking and storing bulk quantity in hexane-rinsed metal tins at approximately -25°C.

2.3.3 – Mysis Collection

Mysis samples were collected by Environment Canada using a benthic sled and stored at -25°C in hexane-rinsed metal tins at the GLIER facility.

2.3.4 – Forage Fish Collection

Rainbow smelt, round goby and bloater chub were identified and collected by the Upper Great Lakes Management Unit of the OMNR as part their annual Index Netting Program. Fish were caught using gill nets set overnight, which consisted of multiple panels of differing lengths and mesh sizes. Specifically, a 15m panel/32mm mesh, a 25m panel/38mm mesh, followed by 7 panels each 50m with an assortment of mesh sizes (51mm, 64mm, 76mm, 89mm, 102mm, 114mm, 127mm). Deepwater sculpin were captured and identified by Environment Canada using a benthic trawl net.

After capture, fish were sealed into food grade plastic bags and stored at the GLIER facility at approximately -25°C, until processing. During processing, the fish were thawed and

the following physiological data was collected: body mass (g), total length (cm), fork length (cm) and standard length (cm). Following dissection, sex of each individual was noted alongside the weight (g) of the gonads and that of the liver (g). The stomach was removed and stored in glass scintillation vials at -25°C for later gut content analysis. The fish were ground into whole body homogenates with use of a commercial high speed blender. The homogenates, weighing up to 35g, were then transferred into a hexane-rinsed metal tin for storage at approximately -25°C.

2.3.5 – Zooplankton Species Composition

Zooplankton composition analysis was performed on the samples preserved in 95% EtOH. Composition was determined by observing approximately 1mL of sample on a gridded Petri plate. With use of a light microscope, 100 individuals were counted and broadly categorized into the following: *Daphnia spp*., *Bosmina spp*., Calanoid copepod spp., Cyclopoid copepod spp., *Bythotrephes longimanus*, and *Holopedium gibberum.* Each sample was analyzed in triplicate.

2.3.6 – Gut Content Analysis

Upon analysis, stomachs were thawed then opened using surgical scissors. The contents of each stomach were rinsed using distilled water into a gridded Petri dish where a light microscope was used to categorize and count the contents. Gut content data are presented on a mean proportion basis. Therefore for each dietary item, a percentage was calculated to represent its proportion of the whole stomach contents. The mean value for the stomach proportions of each species was derived from these calculations.

$$
\text{(eq. 2.1)} \qquad \text{\% prey item} = \left(\frac{\text{nprey item}}{\text{ntotal prey items}}\right) * 100
$$

2.3.7 – Stable Isotope Analysis

Stable carbon isotope analysis was used to determine an organism's carbon source. $\delta^{13}C$ considers the change in the ratio of ${}^{13}C/{}^{12}C$. A more positive $\delta^{13}C$ is indicative of a littoral feeding strategy, which relies on algae and detritus. A more negative δ^{13} C indicates a pelagic feeding organism that relies on phytoplankton as its carbon source (Post 2002). δ^{13} C is calculated in relation to a standard and expressed in units of parts per thousand (‰). In the following equation, *R* represents the ratio of ${}^{13}C/{}^{12}C$ (Peterson et al. 1987).

$$
\text{(eq.2.2)} \qquad \delta^{13} \text{C} = \left[\left(\frac{R_{\text{SAMPLE}}}{R_{\text{STANDARD}}} \right) - 1 \right] * 1000
$$

Trophic position was quantified through the use of nitrogen stable isotopes. This utilized the change in the ratio of $^{15}N/^{14}N$, producing a $\delta^{15}N$ value for each organism. $\delta^{15}N$ was calculated by the same equation used for δ^{13} C, where *R* represents the ratio of $^{15}N/^{14}N$ (Peterson et al. 1987).

$$
\text{(eq.2.3)} \qquad \delta^{15} \text{N} = \left[\left(\frac{R_{\text{SAMPLE}}}{R_{\text{STANDARD}}} \right) - 1 \right] * 1000
$$

Due to a difference in elimination rates (i.e. ^{15}N is slower), ^{15}N enrichment occurs between a consumer and its diet. This enrichment, known as the δ^{15} N trophic enrichment factor, is approximately 3.4‰ (Post 2002). However, this can vary considerably based on feeding strategy. $\delta^{15}N$ of an organism was used to determine trophic position (equation 2.4), and has been adapted from Fisk et al. 2001. Trophic position was determined by establishing a baseline where zooplankton was assigned the trophic level of 2 and its δ^{15} N value ($δ$ ¹⁵N_{ZOOPLANKTON}) was used to adjust that of the consumer ($δ$ ¹⁵N_{CONSUMER}). The value of 3.4 ‰ is representative of the trophic enrichment factor, and δ^{15} N of the organism of interest is denoted by $\delta^{15}N_{\text{CONSUMER}}$.

$$
\text{(eq.2.4)} \qquad \qquad TL_{\text{CONSUMER}} = 2 + \frac{(\delta^{15} \text{N}_{\text{CONSUMER}} - \delta^{15} \text{N}_{\text{ZOOPLANKTON}})}{3.4}
$$

The process used for stable isotope analysis is detailed in Dennard et al. 2009. Briefly, a small aliquot of sample was freeze-dried for 48 hours and then ground using a mortar and pestle. Next, the sample was lipid extracted by adding 2mL of 2:1 chloroform: methanol solution, followed by 24 hours in a 37°C water bath. The sample was then centrifuged for 5 minutes, following which the chloroform: methanol solution was decanted. Another 2mL of chloroform: methanol solution was added, then centrifugation and decanting was repeated. The samples were allowed to air dry for 48 hours.

The amount of sample needed for isotope analysis was dependent on species and was as follows: 600-800μg for zooplankton/*Dreissenid* mussels/*Mysis*, and 400-600μg for forage fish. The appropriate weight was measured into tin capsules, folded and placed into individual wells in a microtiter plate. The 13 C and 15 N values of the samples were determined using an Elemental Analyzer (Costech Analytical Technologies, Valencia, CA, USA) coupled to a Delta V Isotope Ratio Mass Spectrometer (Thermo Scientific, San Jose, CA, USA). Carbon and nitrogen stable isotopes were quantified using three certified commercially produced standards: NIST 1577c, USGS 41, and Urea IVA 33802174. Two additional standards, Tilapia (in-house) and USGS 40 (commercially produced) were used to check for accuracy.

2.3.8 – Energy Density

Examining energy density within a food web allows understanding of how trophic levels respond to changes in energy flow within a system. Energy density (caloric value, kJ/g) can be used to investigate the health of an individual and predict its capacity for survival and reproduction (Breck 2008). Using a mass-balance approach energy density was determined, and is based on the composition of the organism in terms of lipids, protein, ash, and water (Paterson et al 2009).

The equations used to analyze the energy density of organism are found in Table B.1 of Appendix B (G. Paterson, personal communication, 11 December 2015). Energy density was calculated by first measuring the percentage of both lipids and moisture in a sample. First, lipid extraction was performed via the process outlined in Daley et al 2009. Briefly, the sample was combined with sodium sulfate and funneled into a glass microextraction column containing 15 mL of a 1:1 v/v dichloromethane: hexane solution and allowed to sit for 1 hour. The columns were eluted using an additional 10mL of the 1:1 solution. The samples were concentrated using a rotoevaporator and then diluted to 10mL using hexane. To determine lipid content, 1mL of the 10mL solution was removed and dried for 1 hour at 110°C for gravimetric lipid determination. The percentage of moisture in a sample was determined gravimetrically by placing a known amount of sample into an oven at 110°C for 24 hours. After the percentage of lipid and moisture was determined, the values were transformed into a lipid mass and water mass. Water content is negligible in terms of caloric content, however was needed to determine protein mass of the organism. A fraction of the organism is made up of minerals which do not possess a caloric value. This is known as the ash content and was also required to aide in the determination of protein content. By using the masses of lipid, water, and ash, the amount of protein within the organism was calculated. With the lipid and protein mass determined, fish tissue energy values of 9.02 kcal and 4.27 kcal respectively, were used to derive the lipid and protein mass energy content (Merrill et al. 1973). The total energy content of the organism was determined by adding the lipid and protein energy content values (Paterson et al 2009). Finally, energy density was calculated by taking into account the mass of the organism. In this study dry weight energy density was used and required that the water mass first be subtracted from the organism's weight before calculating energy density.

The calculation for energy density of zooplankton, *Mysis*, and *Dreissenid* mussels varied slightly from the above method for fish. The equations unique to this method are found in Table

B.2 of Appendix B (G. Paterson, personal communication, 11 December 2015). Due to the lack of sample availability, not all samples were measured for moisture percentage. However, moisture contents for zooplankton samples in this study were estimated where results were absent. This was done using existing data describing the relationship between lipid and moisture contents for zooplankton samples collected by GLIER researchers for this study, Lake Erie (K.G. Drouillard, unpublished data), and for multiple North American lakes (Houde et al. 2008) The mass of both lipids and moisture were calculated using the same approach described for fish. A dry mass measurement was calculated by subtracting the moisture mass from the organism's mass – this value was subsequently used in determining ash mass. A random value within the range of $11.5 \pm 2.4\%$ was used, as was described for ash content of crustacean zooplankton by Kiørboe 2013. The dry mass and the percentage of ash was then utilized to quantify ash mass. From this point forward the process for determining energy density in zooplankton, *Mysis*, and *Dreissenid* mussels was the same as it is in fish, see above.

2.3.9 – Data Analysis

All statistical analyses were performed using IBM SPSS 22. Analysis of variance (ANOVA) was used to calculate mean differences for δ^{13} C and δ^{15} N stable isotope data with and among the basins. Before the ANOVAs were conducted, Levene's tests were performed to determine whether means would be compared using a standard ANOVA (homogenous variance between means) or a Welch's ANOVA (heterogeneous variance between means). Individual species where n<3 were excluded from within-basin analysis. Accordingly, the means of these species were analyzed using independent samples t-tests to determine significance.

Isotopic niche ellipses were produced using stable isotope data in conjunction with the R package SIBER (Stable Isotope Bayesian Ellipses in R) (Jackson et al. 2011). These ellipses indicate the area in which 40% of the data pertaining to a species is located. This analysis was used to visualize areas of niche overlap (Jackson et al. 2011).

2.4 RESULTS

2.4.1 – Zooplankton Composition

The Main Basin of Lake Huron was the only basin in which a temporal comparison (April – September) regarding the zooplankton community composition was possible. The dominant zooplankton in the Main Basin throughout this collection period were calanoid copepods, with the highest abundance at 87% in May and the lowest abundance at 49% in September (Figure

2.1). Secondary to calanoid, *Bosmina* abundances ranged from 0% in May and extended upward to 45% during the month of September (Figure 2.1). The only other zooplankton with significant biomass during the collection period were cyclopoid copepods, which ranged between 6%-13% abundance and were present in each month of the collection period (Figure 2.1)*.*

Similar to the Main Basin, the dominant type of zooplankton in Georgian Bay were calanoid copepods, with highest abundances in June (93%) and lowest in August (75%), followed by *Bosmina*, with an abundance range of 1%-12% *(*Figure 2.2). Again, only the cyclopoid copepods presented notable numbers with relative abundances ranging from 5% in June to 11% in August (Figure 2.2).

Consistent with the observations made in the other 2 basins of Lake Huron the dominant zooplankton in the North Channel was the calanoid copepod (71%) (Figure 2.3). Secondary to calanoid, the most abundant type of zooplankton was the cyclopoid copepods (17%), followed by *Bosmina* (12%) (Figure 2.3).

2.4.2 – Forage fish gut contents

Bloater chub (*Coregonus hoyi*) diet differed among the basins (Table 2.1)*.* In the Main Basin, the primary prey item was zooplankton (85.4 %) followed by *Mysis* (10%). Georgian Bay bloaters chiefly consumed *Mysis* (77.6%) followed by zooplankton (11.5%)*.* The bloater chubs in the North Channel exhibited a more diverse eating strategy, with zooplankton being the main prey item (44.7%) followed by veliger larvae (19.2%). It is important to note that the energy-rich prey item *Mysis* was present in all diets, however at differing proportions.

Rainbow smelt (*Osmerus mordax*) also exhibited different diets among basins (Table 2.1). The primary prey item across all basins was zooplankton: 65.4% (Main Basin), 42.5% (Georgian Bay), and 46.4% (North Channel). For rainbow smelt, the second most consumed items was as follows: Main Basin = detritus (26.9%), Georgian Bay = *Mysis* (27.5%), and North Channel = unspecified fly larvae (35.8%). Unlike bloaters chubs, *Mysis* was notably absent from the Main Basin diet composition of rainbow smelt.

A comparison amongst all 3 basins could not be made for deepwater sculpin (*Myoxocephalus thompsonii*) (Table 2.2) and round goby (*Neogobius melanostomus*) (Table 2.3) due to the lack of gut content data. In the Main Basin, deepwater sculpin primarily consumed detritus (56.5%), followed by *Mysis* (17.2%). Additionally, across both the Main Basin and Georgian Bay the round goby preferred *Dreissenid* mussels as their primary food source (70%; 100%, respectively).

2.4.3 – Carbon and Nitrogen Stable Isotopes

The δ^{13} C signatures for the lower food web of Lake Huron are illustrated in Figure 2.4. A δ^{13} C value of -23‰ (indicated in Figure 2.4 by a dashed line) was used to aide in the categorization of a species into a littoral or pelagic feeding style (Paterson et al. 2013). Figure 2.4 illustrates a consistency in the round goby's foraging behaviour throughout the lake as it tracked a littoral carbon source. In comparison to the round goby, zooplankton and *Dreissenid* mussels, in all basins, were relying on a pelagic carbon source. However it was not possible to statistically assess North Channel zooplankton, as well as the *Dreissenid* mussels in both the Main Basin and the North Channel, due to a small sample size, n=2. Similarly, dependency on offshore carbon was observed for *Mysis* in the Main Basin and Georgian Bay; however North Channel *Mysis* do not show as strong of a pelagic carbon signature. Again, due to a small sample size, n=2, strong relations for Georgian Bay *Mysis* cannot be concluded. Akin to the North Channel *Mysis*, rainbow smelt in this same basin exhibit a different carbon signature than those of the Main Basin and Georgian Bay. In the North Channel, rainbow smelt demonstrated a strong littoral carbon signature (-20.5 \pm .27 ‰). However, the data points for rainbow smelt in the Main Basin and Georgian Bay tended to cluster around -24, suggesting that they may be encountering both nearshore and offshore carbon sources. This same pattern was also observed in bloater chub.

Trophic level was determined using δ^{15} N values substituted into Equation 2.4. The trophic levels of the Main Basin and the North Channel were found to be organized in the same manner; from highest to lowest trophic position as follows: rainbow smelt, bloater chub, *Mysis*, round goby, *Dreissenid* mussels, and zooplankton (Table 2.4 and Figure 2.5). The trophic organization for Georgian Bay however, was as follows: bloater chub, rainbow smelt, round goby, *Mysis*, zooplankton, and *Dreissenid* mussels (Table 2.4 and Figure 2.5).

2.4.4 – Across Basin Analysis of Carbon and Nitrogen Stable Isotopes

Appendix C contains the mean δ^{13} C and δ^{15} N values for all species (Tables C.1 and C.2) as well as mean difference values across the basins (Table C.3 and C.4). *Dreissenid* mussels could not be compared across basins due to a lack of samples.

Zooplankton

Due to a lack of samples, the North Channel zooplankton was excluded from the following analyses. An independent samples t-test was used to compare means between the δ^{13} C values of zooplankton in the Main Basin and those in Georgian Bay, Figure 2.4. This test

revealed no significance amongst means of these basins, *p*>.05. The same analysis was used to compare the means for the $\delta^{15}N$ values between the same basins, which again revealed no significance amongst means, Figure 2.5.

Mysis

Due to a limited sample size (n=2), Georgian Bay was excluded from the following analyses. To compare δ^{13} C values of *Mysis* in the North Channel with those in the Main Basin, an independent samples t-test was used. The results of this test proved insignificant, with no notable differences, p >.05, Figure 2.4. Similarly the same test was used to analyze δ^{15} N values between the same basins and again this test revealed no significant differences, *p*>.05, Figure 2.5.

Round goby

An ANOVA was used to compare mean δ^{13} C values of round goby among Lake Huron's three basins, Figure 2.4. The results of the ANOVA were significant, *p*<.01. Furthermore, Tukey's post hoc analysis displayed a significant difference between the North Channel and Main Basin, where North Channel round gobies displayed a higher δ^{13} C value, p <.01. Round gobies in the North Channel displayed a greater average δ^{13} C values than their Georgian Bay counterparts, p <.01. No significant differences in δ^{13} C values were observed in round goby between the Main Basin and Georgian Bay, *p*>.05.

Mean δ^{15} N values for round gobies amongst the basins were compared using an ANOVA, *p*<.05, Figure 2.5. A Tukey's post hoc revealed a significant difference between means of the North Channel and the Main Basin, where the average $\delta^{15}N$ value of round gobies in the North Channel were greater, p <.05. No other significant relations were observed in the $\delta^{15}N$ values of round gobies amongst the other basins.

Rainbow smelt

Differences amongst the δ^{13} C values of rainbow smelt across the basins were determined using a Welch's ANOVA, *p*<.01, Figure 2.4. A Games-Howell post hoc test revealed significant differences between the δ^{13} C values of the North Channel and the Main Basin, where the North Channel displayed a stronger littoral signature with a significantly higher mean difference δ ¹³C value, *p*<.01. A similar relationship was also observed between the North Channel and Georgian Bay, where again the North Channel rainbow smelt showed a significantly higher mean difference value, *p*<.01.

An ANOVA was used to determine the significance between δ^{15} N values of rainbow smelt amongst the basins, $p<0.01$, Figure 2.5. Using a Tukey's post hoc test, the mean $\delta^{15}N$ value for North Channel rainbow smelt was determined to be significantly different from that of the Main Basin, $p<0.1$. No other significant relations were observed among the basins. Bloater chub

A Welch's ANOVA was used to compare the δ^{13} C values of bloater chub among the basins, *p*<.01, Figure 2.4. Significance among the basins was determined using a Games-Howell post hoc test and are as follows: Georgian Bay were significantly greater than Main Basin (*p*<.01), the North Channel were significantly greater from the Main Basin (*p*<.01) and lastly, the North Channel showed significantly elevated δ^{13} C values from those fish observed in Georgian Bay (*p*<.01).

An ANOVA was performed for the δ^{15} N values of bloater chubs amongst the three basins, p < .01, Figure 2.5. A Tukey's post hoc analysis of bloater chub δ^{15} N values revealed the following results: Georgian Bay showed higher significant differences from the Main Basin (*p*< .01), Georgian Bay fish also showed higher significant differences from the North Channel (*p*<.01), and the North Channel differed from the Main Basin (*p*< .01).

2.4.5 – Within Basin Analysis of Carbon and Nitrogen Stable Isotopes

The mean δ^{13} C and δ^{15} N values can be found in Appendix C, Tables C.1 and C.2. The mean differences within the three basins are detailed in Appendix C in Tables C.5 – C.10. *Dreissenid* mussels were excluded from the analyses in the Main Basin and North Channel due to a small sample size. For the same reason, *Mysis* were excluded from the Georgian Bay analyses and zooplankton were excluded from the North Channel analyses.

Main Basin

A Welsh's ANOVA was used to analyze the differences between mean δ^{13} C values, *p*<.01, Figure 2.4 and 2.6. Games-Howell post hoc analyses revealed that the round goby maintained greater average δ^{13} C values compared to the following species: zooplankton (p <.01), *Mysis* (p <.01), rainbow smelt (p <.01), bloater chub (p <.01), and deepwater sculpin (p <.01). These post hoc analyses also determined that rainbow smelt maintained higher mean $\delta^{13}C$ values compared to the following: zooplankton (*p*<.01), *Mysis* (*p*<.01), and deepwater sculpin (p <.01). Furthermore, these analyses showed bloater chubs to display higher average $\delta^{13}C$ values compared to zooplankton (p <.01) and *Mysis* (p <.05). Lastly, the Games-Howell post hoc

test revealed that deepwater sculpin had a greater mean δ^{13} C value compared to that of zooplankton, *p*<.01.

A Welch's ANOVA was also used to test for differences between the δ^{15} N values of these species within the Main Basin *p*<.01, Figures 2.5 and 2.6. Games-Howell post hoc analyses showed that deepwater sculpin displayed significantly higher $\delta^{15}N$ means compared to the following species: zooplankton (*p*<.01), rainbow smelt (*p*<.01), bloater chub (*p*<.01), and round goby (*p*<.01). The Games-Howell post hoc tests also revealed that bloater chubs displayed significantly higher means compared to both zooplankton (*p*<.01) and round goby (*p*<.01). In addition, these post-hoc analyses showed that rainbow smelt displayed larger average $\delta^{15}N$ values than zooplankton (*p*<.01), and round goby (*p*<.01). Lastly, these tests determined *Mysis* to possess significantly higher mean δ^{15} N values than zooplankton (*p*<.01).

Georgian Bay

An ANOVA was used to compare means of the δ^{13} C values for Georgian Bay species, *p*<.01, Figures 2.4 and 2.6. Tukey's post hoc tests found the round goby to maintain significantly higher mean δ ¹³C values, compared to those of zooplankton (*p*<.01), *Dreissenid* mussels (p <.01), rainbow smelt (p <.01), and bloater chub (p <.01). These post hocs also revealed rainbow smelt to display significantly greater mean δ^{13} C values compared to those of zooplankton (*p*<.01) and *Dreissenid* mussels (*p*<.01). Lastly, the Tukey's post hoc analysis showed that bloater chubs possessed significantly higher average δ^{13} C values compared to zooplankton, *p*<.01.

A Welsh's ANOVA was used to compare means for the δ^{15} N values across the species in Georgian Bay, *p*<.01, Figures 2.5 and 2.6. Games-Howell post hoc tests determined that bloater chubs showed significantly higher $\delta^{15}N$ mean values when compared to those of the subsequent species: zooplankton (*p*<.05), *Dreissenid* mussels (*p*<.01), rainbow smelt (*p*<.01), and round goby (*p*<.01). Post hoc tests also showed that rainbow smelt maintained significantly higher mean values for δ¹⁵N compared to that of zooplankton (*p*<.05), *Dreissenid* mussels (*p*<.01), and round goby (p <.01). Finally, the same post hoc test revealed round goby $\delta^{15}N$ mean values to be significantly higher than those of *Dreissenid* mussels, *p*<.01.

North Channel

An ANOVA was used to evaluate the differences among the δ^{13} C values of the species within the North Channel, $p<0.01$, Figures 2.4 and 2.6. Tukey's post hoc analysis revealed significantly higher δ ¹³C mean values for round goby, compared to *Mysis* (*p*<.01), rainbow smelt

(*p*<.01), and bloater chub (*p*<.01). Tukey's post hoc test also showed that bloater chubs possessed a significantly higher mean δ¹³C value compared to *Mysis*, *p*<.01. Lastly, this same post hoc analysis determined that rainbow smelt more often displayed significantly higher average δ^{13} C values than *Mysis*, *p*<.01.

An ANOVA revealed insignificant differences between mean δ^{15} N values for all studied species in the North Channel, *p*>.05, Figures 2.5 and 2.6.

2.4.6 – Across Basins Analysis of Energy Density

Mean energy densities for each species (Table D.1) as well as mean difference values across the basins (Table D.2) are summarized in Appendix D.

Zooplankton

An ANOVA was used to test for significant mean difference between the energy density values for zooplankton among the three basins, Figure 2.7. The ANOVA revealed insignificant results, *p*>.05.

Dreissenid Mussels

North Channel *Dreissenid* mussels were excluded from the following analysis due to poor sample availability. The mean energy density of individuals in the Main Basin and Georgian Bay were compared using an independent samples t-test, Figure 2.7. This test showed no significant mean difference, *p*>.05.

Mysis

Georgian Bay *Mysis* were excluded from the following analysis due to insufficient sample size. An independent samples t-test was used to compare mean energy densities of *Mysis* located in the Main Basin and the North Channel, Figure 2.7. No significant mean difference between these two basins was found, *p*>.05.

Round Goby

An ANOVA was used to analyze the energy density of round goby amongst the basins, Figure 2.7. This analysis revealed insignificant results, *p*>.05.

Rainbow Smelt

A Welch's ANOVA was used to compare energy density means of rainbow smelt across the different basins, *p*<.05, Figure 2.7. The Games-Howell post hoc test showed a significantly higher mean difference in the North Channel compared to rainbow smelt in Georgian Bay, *p*<.01. Post hoc analyses similarly revealed a greater mean difference in energy densities of rainbow smelt in the Main Basin versus Georgian Bay, *p*<.01.

Bloater Chub

A Welch's ANOVA was conducted to analyze the energy densities of bloater chub among the basins, *p*<.01, Figure 2.7. The Games-Howell post hoc revealed that the North Channel had a greater mean difference compared to the Main Basin (*p*<.01) and Georgian Bay (*p*<.01). This post hoc test also showed that Georgian Bay has a significantly larger mean difference than the Main Basin, *p*<.05.

2.4.7 – Within Basin Analysis of Energy Density

Appendix D contains mean energy density values (Table D.1) and mean differences of the species within each basin (Tables D.3 – D.5).

Main Basin

A Welch's ANOVA was used to analyze the mean energy densities for species within the Main Basin, p <.05, Figure 2.7. The Games-Howell post hoc analyses showed that zooplankton (*p*<.01), *Mysis* (*p*<.05)*, Dreissenid* mussels (*p*<.01), and rainbow smelt (*p*<.05) all had a greater mean difference than deepwater sculpin. No other significance was found.

Georgian Bay

For the following analysis *Mysis* were excluded due to low sample number. Energy density values for the species within Georgian Bay were tested for significant difference using a Welch's ANOVA, $p<01$, Figure 2.7. The Games-Howell post hoc test revealed that bloater chub had a significantly higher mean difference than zooplankton (*p*<.05), *Dreissenid* mussels (*p*<.01), rainbow smelt (p <.01), and round goby (p <.01). Post hoc also revealed a significantly greater mean difference between *Dreissenid* mussels and the following: rainbow smelt (*p*<.01) and round goby (*p*<.01). Lastly, post hoc analyses showed that zooplankton had a significantly larger mean difference than rainbow smelt (*p*<.01) and round goby (*p*<.01).

North Channel

For the following analysis *Dreissenid* mussels were excluded due to insufficient sample size. An ANOVA was used analyze the energy densities of the species within the North Channel, p <.01, Figure 2.7. Tukey's post hoc revealed that bloater chub have a significantly greater mean difference than zooplankton (*p*<.01), *Mysis* (*p*<.01), rainbow smelt (*p*<.01) and round goby (*p*<.01). This post hoc also showed that rainbow smelt had a significantly larger mean difference than round goby, *p*<.01. Lastly, the Tukey's test showed that *Mysis* had a significantly greater mean difference than round goby, *p*<.01.

2.5 DISCUSSION

The results of this study indicated that there was significant spatial heterogeneity occurring among Lake Huron's three basins in terms of nutrient and energy flow. Furthermore, this heterogeneity differs amongst the trends in the secondary consumers (round goby, rainbow smelt, bloater chub) versus the primary consumers (zooplankton, *Dreissenid* mussels).

The Lake Huron zooplankton community composition remained consistent across the basin and was dominated by calanoid copepods, Figures $2.1 - 2.3$. This was in agreement with what was observed by Bunnell et al. 2011 and the 2010 State of Lake Huron Report (Riley 2013). The productivity of a lake can influence the configuration of a zooplankton community. As such, the oligotrophic nature of Lake Huron promotes the presence of calanoid copepods, as was confirmed in this study (Bunnell et al. 2011). In addition, the increase in *Bosmina* as the season progressed was consistently observed regionally (with the exception of the North Channel due to a lack of sample availability). This seasonal increase in cladoceran biomass was also noted by Bunnell et al. 2011, and is likely due to the reproductive life history of the organism (Balcer et al. 1984).

Examination of gut contents can provide a glimpse into an organism's diet and aid in understanding a species foraging strategies. Stomach contents for two of the four fish species used in this study—bloater chub and rainbow smelt—were analyzed across all three basins, Table 2.1. Bloater chub and rainbow smelt are both pelagic species which occupy the hypolimnion (Evans et al. 1987; Clemens et al. 2009; O'Brien et al. 2012), and exhibit diel vertical migration to track food resources (Evans et al. 1987; TeWinkel et al. 1999; Rooney et al. 2009; Harford et al 2012). Given this common habitat utilization strategy, an overlap in prey items between the two species was observed and confirmed through their reliance on zooplankton, with the exception of Georgian Bay bloater chub. It is important to note the absence of *Diporeia* in the gut contents of these two species. *Diporeia* is a key energetically-rich dietary item for both bloater chub and rainbow smelt (Barbiero et al. 2011) which has undergone a significant decline in its abundances beginning in 2003 (Nalepa et al. 2007). In comparison to *Diporeia,* zooplankton are smaller in size and less energy-rich. Due to this dissimilarity more zooplankton would have to be consumed to achieve the same energy intake. In addition to Lake Huron's decline in zooplankton biomass (Barbiero et al. 2009), further complication arises as the dominant zooplankton (calanoid copepod) are known to be efficient predator evaders (Barbiero
et al. 2009). As forage fish rely more heavily on zooplankton, the time spent foraging increases, potentially exerting more energy.

The gut contents of two additional secondary consumers – round goby and deepwater sculpin – were also examined, Tables 2.2 – 2.3. However, a complete spatial analysis could not be performed due to a lack of available samples. Round gobies differ from bloater chub and rainbow smelt in that they occupy a more littoral habitat, preferring rocky substrates (Schaeffer et al. 2005). Due to the contrast in preferred habitat, a dietary variation between these species was expected. This study showed that *Dreissenid* mussels were the dominant prey item of the round goby amongst the basins, Table 2.3. This is likely due to the preferred nearshore habitat of the *Dreissenid* mussels, as it provides the hard surface which they require for attachment (Hecky et al. 2004). The coexistence of these two organisms allow for the formation of a strong predator-prey relationship. In contrast to the habitats of the former species, deepwater sculpin reside in the profundal zone (O'Brien et al. 2009). The gut contents of this species revealed a reliance on detritus, Table 2.1. This is somewhat unexpected as sculpin are known to prey upon *Diporeia* and *Mysis* (Pothoven et al. 2011). As previously mentioned, *Diporeia* abundances have declined in Lake Huron (Nalepa et al. 2007); as such, there has been a reduction in the availability of this valuable energy-rich prey item. In addition to this decrease, *Mysis* move throughout the water column daily whereas deepwater sculpin do not (O'Brien et al. 2009). This possibly further restricts sculpin access to this prey item. Given the proximity of sculpin to the lake's bottom, where particulates settle, detritus may be a main dietary item when preferred prey is not available.

Carbon stable isotopes are useful to determine the foraging strategy in an aquatic environment. An organism possessing an enriched δ^{13} C value indicates littoral foraging habitats, whereas a relatively depleted δ^{13} C value indicates foraging in the offshore region (Post 2002). In this study, a δ^{13} C value of -23‰ was used as a way to denote pelagic foraging from littoral, herein referred to as the pelagic-littoral line, Figure 2.4 (Paterson et al. 2013). Uniformity was observed in the δ^{13} C signature of the primary consumers. Across all species and regardless of basin, the primary consumers had the most pelagic δ^{13} C values. Spatially, species residing in the North Channel have the most enriched δ^{13} C values, Figure 2.4.C. This is likely a function of basin morphology as the North Channel is shallower and narrower in comparison to the other basins. As a result organisms living in this region would have increased access to the nearshore environment, subsequently increasing their littoral carbon signature. In terms of the $\delta^{13}C$

signatures of individual species, rainbow smelt and bloater chub demonstrated enriched values, hovering just below the pelagic-littoral line or favouring a littoral isotope signature. As previously mentioned these two species are typically pelagic-dwelling. The littoral signature observed for rainbow smelt and bloater chub are thought to be due to the declining abundances of key dietary items, such as *Diporeia* (Nalepa et al. 2007; Barbiero et al. 2011) and the subsequent need for pelagic fish to utilize the nearshore zone under conditions of reduced abundances of pelagic prey species. This movement towards shore would explain the positive shift in their δ^{13} C signature (Turschak et al. 2014). Dietary data in this study has shown that rainbow smelt and bloater chub mainly consumed zooplankton, Table 2.1. Conversely, zooplankton in all three basins showed a distinct pelagic signature (Main Basin = -26.7 ± 0.39‰, Georgian Bay = -27.4 \pm 0.31‰, North Channel = -27.29‰). It is possible for this difference in δ^{13} C signature is an artefact of our offshore zooplankton sampling methods, as previously described; without nearshore zooplankton samples by which to compare their signatures, it is unknown whether the lake zone from which the sampled zooplankton primarily reside will significantly affect their signatures. Round goby exhibited a strong littoral signature throughout the lake which was expected as this species occupies nearshore habitats (Main Basin = -20.62 \pm 0.43‰, Georgian Bay = -21.42 ± 0.71‰, North Channel = -17.03 ± 0.41 ‰) (Schaeffer et al. 2005). In contrast to the round goby, *Dreissenid* mussels displayed a stronger pelagic δ¹³C signature (Main Basin = -27.00 ‰, Georgian Bay = -26.00 ± 0.37‰, North Channel = -27.58 ‰). In this study, *Dreissenid* mussels were found as the dominant prey item of the round goby, Table 2.3. There are two possible explanations for this finding. Firstly, *Dreissenid* mussels may be over-represented in the gut contents as their shells take longer to digest than other invertebrates (Kionka et al. 1972; Brush et al. 2012). Alternatively, this observation could simply be due to differences in collection sites from which these two species were sampled, as some of the *Dreissenid* mussel samples were by-catch off of the gill nets used from forage fish collection.

Nitrogen stable isotopes are a way by which to inspect the regional trophic structure of Lake Huron's lower food web. Uniformity in δ^{15} N signatures of Main Basin and North Channel lower food webs was found (Figures 2.5.A and 2.5.C), however this did not extend to Georgian Bay (Figure 2.5.B). δ^{15} N data discrepancies within and amongst the basins continued to appear when trophic level was calculated, Table 2.4. This calculation revealed that some predators occupy a greater than one predicted trophic level above their prey (according to dietary data). A possible explanation for the inflated differences between predator and prey trophic positions is

that there may be dietary items which were not considered in our analysis. This study was designed mainly for among-basin comparisons and as such, data collection was not focused on establishing strong within-basin associations. This key feature of our study's design could reasonably limit the preciseness of trophic level calculation. An alternative explanation for the magnified predator-prey trophic level values is stress and food limitations. Under pressure, an organism may have to sustain themselves through use of their own energy reserves. Accordingly, the organism can utilize their tissues to access body protein for sustenance. As this process occurs, ^{14}N becomes depleted resulting in an increase of ^{15}N which leads to enrichment of the δ^{15} N signature in the organism (Hobson et al. 1993; Doucett et al. 1999; Cherel et al. 2005). Additional discrepancies observed in the δ^{15} N signatures for species such as the deepwater sculpin and *Dreissenid* mussels could be a result of an enriched ¹⁵N pool existing at the bottom of the lake. The microbial community located in this zone metabolizes the particulate which settles out of the water column. The metabolism of this matter results in a depletion of 14 N causing the formation of an enriched 15 N area at the lake bottom (Vander Zanden et al. 1999). Organisms accessing this pool would generate an overinflated $\delta^{15}N$ signature.

The isotopic niche of a species can be determined utilizing carbon and nitrogen stable isotope data, Figure 2.6. Across all three basins there was a consistent overlap in isotopic niche between bloater chub and rainbow smelt. As indicated by gut content analysis, these species appear to be competing for resources, Table 2.1. The effects of interspecific competition can be explored by way of energy content.

Energy density analysis provides information regarding the condition of an organism, allowing for a more in-depth analysis of the organism's survival and reproductive capabilities (Breck 2008). In Lake Huron, the energy densities of primary consumers as well as the round goby were conserved lakewide, Figure 2.7. Furthermore, the energy content was uniform across these primary consumers. Contrarily, examination of the secondary consumers revealed regional heterogeneity. These differences, in conjunction with the trophic level discrepancies previously discussed (Table 2.4), offer support that ecological processes vary regionally in Lake Huron. Analysis of energy content within each basin yielded unexpected results, Figure 2.7. The Main Basin's lower food web displayed similar energy values across all species. Given the similarity in energy densities between predator and prey items, along with the aforementioned irregularities in trophic levels, limited food resource availability is feasible. These discrepancies

continued into the lower food webs of Georgian Bay and the North Channel, where some prey species have energy contents that was consistent with or greater than that of their predators. An interesting observation can be made for these two system's food webs in terms of the condition of native versus invasive species. The energy density of bloater chub residing in the previously mentioned regions was greater than all other species. This corresponds with bloater chub maintaining the highest or shared highest calculated trophic level, Table 2.4. As observed in the dietary data and isotopic niches, bloater chub and rainbow smelt had overlapping resource use (Table 2.1 and Figure 2.6). The energy density value of bloater chub in these two basins provides support that the native bloater chub is out-competing the non-native rainbow smelt in a resource limited system. For instance, Georgian Bay *Dreissenid* mussels and zooplankton—the main dietary items of rainbow smelt and round goby respectively—possessed a greater energy density than that of their predators. In the North Channel the energy content of rainbow smelt was consistent with zooplankton, its main prey item. Based on these observations, the native species of Lake Huron appear to be faring better than their non-native counterparts.

The objective of this research was to investigate the possibility of regional heterogeneity in Lake Huron's ecological processes using fish diet and energy density as indicators. Fromthe information gathered, part of this study's hypotheses hold true – forage fish diets were consistent across the three basins. However, the energy density and subsequently thecondition of the forage fish were not spatially maintained. Significant findings from this study included thelack of food resources and the absence of energy-rich prey items such as *Diporeia.* Additionally, the results of this research suggested that primary consumers in the lower food web remained indifferent, however basin-specific differences began to emerge at the level of the secondary consumer.

2.6 References

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Table 2.1: Mean diet items of bloater chub (*Coregonus hoyi*) and rainbow smelt (*Osmerus mordax*) in the 3 basins of Lake Huron.

-*Note:* The values represent the mean percentage of each prey item of the total stomach contents of an individual. The total number of individuals which had an empty stomach is presented as a value over the total number of individuals sampled.

| Prey Item | Main Basin |
|--------------------------|------------|
| Chironomidae | 0.4 |
| Diporeia | |
| Diptera | |
| Dixidae | |
| Mysis | 17.2 |
| Odonata | 8.3 |
| Unspecified larval flies | |
| Veliger | 3.2 |
| Zooplankton | 14.4 |
| Detritus | 56.5 |
| Empty | 12/36 |

Table 2.2: Mean diet items of deepwater sculpin (*Myoxocephalus thompsonii*) in the Main Basin.

Note: The values represent the mean percentage of each prey item of the total stomach contents of an individual. The total number of individuals which had an empty stomach is presented as a value over the total number of individuals sampled.

Table 2.3: Mean stomach content for round goby (*Neogobius melanostomus*) in the Main Basin and Georgian Bay.

Note: Each dietary item is in presented in term of items average proportion of that item found in individual stomachs. The total number of individuals which had an empty stomach is presented as a value over the total number of individuals sampled.

Table 2.4: Trophic levels of species among the 3 basins of Lake Huron.

Figure 2.1: 2011-2012 Main Basin zooplankton composition for (A) April, n=1, (B) May, n=2, (C) June, n=7, (D) July, n=1, (E) August, n=4 and (F) September, n=1.

Figure 2.2: Georgian Bay zooplankton composition for (A) June 2011, n=1 and (B) August 2011- 2012, n=6.

Figure 2.3:North Channel zooplankton composition for July 2011-2012, n=3.

Figure 2.4: Mean δ¹³C signatures (‰) in the lower food web of (A) Main Basin, (B) Georgian Bay, and (C) North Channel. The dashed line represents the pelagic-littoral point, in which values favouring the more positive side are considered littoral and those favouring the more negative side are considered pelagic. Error bars indicate \pm 1 SE.

Figure 2.5: Mean δ^{15} N signatures (%) in the lower food web of (A) Main Basin, (B) Georgian Bay, and (C) North Channel. Error bars indicate \pm 1 SE.

Figure 2.6: Carbon and nitrogen isotopic niche and standard ellipse areas for (A) Main Basin, (B) Georgian Bay, and (C) North Channel. Species included here are representative of the lower food web and include zooplankton (black), *Mysis* (red), *Dreissenid* mussels (green), rainbow smelt (dark blue), bloater chub (light blue), round goby (purple), and deepwater sculpin (yellow).

Figure 2.7: Mean dry weight energy densities (kJ/g) of the lower trophic food web amongst the basins of Lake Huron. The white, light grey, and dark grey bars correspond to the Main Basin, Georgian Bay, and North Channel, respectively. Error bars indicate ± 1 SE.

CHAPTER 3:

CONTAMINANT DYNAMICS OF LAKE HURON'S LOWER TROPHIC LEVELS

3.1 INTRODUCTION

Environmental contaminants can be a useful tool to understand how an ecosystem is functioning and its response to perturbations. Pollutants can be used as ecological tracers; often when studying contaminants the pollutants used in this context are those whose physiochemical properties – including how they interact with biological tissues – are well understood. When considering the effect of an environmental contaminant on an aquatic system, two keys processes must be considered – bioaccumulation and biomagnification. Bioaccumulation occurs when the concentration of the contaminant in an organism exceeds that which is found in the surrounding medium (Mackay et al. 2000). That is, the rate of chemical uptake through water and food exceeds the chemical elimination rates via the water, metabolism, and feces (Gobas et al. 1999). Biomagnification occurs when the concentration of a chemical in an organism surpasses that which is found in the food consumed – thus the rate and amount of chemical accumulation is related to the organism's trophic position (Mackay et al. 2000). As such, top predators tend to have the highest concentrations of environmental contaminants. This process can be studied using biomagnification factors (BMFs) to examine the relationship between the consumer and its dietary items. More specifically, BMFs consider the concentration of the chemical in the predator, $[C]_{PREDATOR}$, to that in the prey, $[C]_{PRFY}$ (Mackay et al. 2000).

$$
(eq.3.1) \t\t\t\tBMF = \frac{[C]_{PREDATOR}}{[C]_{PREV}}
$$

One commonly studied group of environmental contaminants are polychlorinated biphenyls (PCBs). PCBs are synthetic organic compounds composed of two phenyl rings, each having five sites for chlorine atoms to attach (Safe 1994). Differences in the placement and number of chlorine atoms on the biphenyl structure gives rise to 209 variations known as congeners (Hawker et al. 1988). It is the degree of chlorination and placement of these chlorine atoms that dictates the physicochemical properties of each PCB congener. These compounds were once synthesized for industrial purposes, as they are chemically stable, resist degradation, possess a high boiling point, and are non-combustible (Safe 1994). The very properties which make PCBs industrially beneficial are also those which make them an environmental concern. This is due to the hydrophobic nature of PCBs and subsequent potential to bioaccumulate in aquatic food webs such that chemical fugacity increases with trophic level (Hawker et al. 1988). Fugacity

refers to the pressure of a chemical to leave its present medium for another; in other words, it represents the chemical's potential to 'escape' a phase (Gobas et al.1999). This potential is measured as a pressure (Pascal, Pa) and is the pressure exerted by the chemical to partition from one form of media to another (Gobas et al. 2015).

Dietary uptake of a chemical is related to changes in fugacity in the gastrointestinal tract (GIT). As the contents of the intestines move through the GIT the organism absorbs the lipids into its system. The decline in lipids corresponds to a decrease in the medium's capacity to hold the chemical. This results in an increase in the chemical's fugacity and therefore an increase in pressure. As such, it becomes more favourable for the chemical to partition through the intestinal wall and into the organism (Gobas et al.1999). Only some PCB congeners are able to be eliminated from the organism based on the degree of chlorination and hydrophobicity. These congeners possess a low octanol-water partition coefficient (K_{ow}) , typically with a value less than 5 (Mackay et al. 2000; Nfon et al. 2008). The outcome of increased chlorination and hydrophobicity is a decline in the organism's ability to eliminate the chemical. As such, PCB congeners with a log K_{ow} greater than 6.5 tend to persist within a fish (McLeod et al. 2015).

Another environmental contaminant of interest is mercury (Hg). In the environment, Hg originates from both natural and anthropogenic sources and, like PCBs, has the ability to bioaccumulate and biomagnify. Through different speciation processes, Hg is able to move through an aquatic system from sediment into the food web, and through volatilization at the water's surface, is able to enter into the atmosphere (Ullrich et al. 2001). This allows for atmospheric transportation and deposition into other areas leading to what is known as the global Hg cycle (Boening 2000). Of the various forms, methylmercury (MeHg) is of interest because it undergoes food web bioaccumulation; possibly due to its hydrophobicity and its resistance to degradation (Stein et al. 1996). Although the process is not fully understood, MeHg moves into an organism and is thought to be stored primarily in muscle tissue (Stein et al. 1996).

3.2 OBJECTIVES

Given the extensive knowledge of these environmental contaminants, PCBs and Hg were selected as contaminant tracers for this study. This chapter examined the contaminant tropho-dynamics of PCB and Hg in Lake Huron's lower trophic levels with emphasis on amongstbasin comparisons (Figure 1.1). Mercury and PCB concentrations, along with lipid content, were

used to assess the BMFs of the primary and secondary consumers in the lower food web of Lake Huron's three basins. The primary consumers included: zooplankton, *Dreissenid* mussels (bulk *Dreissena bugensis* and *Dreissena polymorpha)*, *Mysis* (*Mysis diluviana*), and the secondary consumers included: rainbow smelt (*Osmerus mordax*), bloater chub (*Coregonus hoyi*), round goby (*Neogobius melanostomus*) and deepwater sculpin (*Myoxocephalus thompsonii*). By using these species and the previously stated measures, the following hypotheses were examined:

- 1) Assuming physiochemical properties alone regulate bioaccumulation, it is predicted that PCB and Hg concentrations are similar amongst the primary and secondary consumers throughout the three basins of Lake Huron.
- 2) Similarly, it is predicted that BMFs between the forage fish and its prey will be consistent across the three basins.

3.3 METHODOLOGY

Detailed collection information pertaining to site and date is located in Appendix A, Table A.1.

3.3.1 – Zooplankton Collection

Samples were collected using two successive vertical tows roughly 2 to 6 km offshore (net dimensions: 64µm mesh, 1 m diameter, 8m length). One of the tows was transferred into a hexane-rinsed glass jar, while the other was preserved in 95% EtOH. Upon return to the Great Lakes Institute for Environmental Research (GLIER), the unpreserved sample was frozen at -25°C for use in stable isotope and contaminant analysis.

3.3.2 –Dreissenid Mussel Collection

Samples were collected using a benthic sled by the Ontario Ministry of Natural Resources (OMNR). Additionally, samples were collected by Haffner lab personnel from aggregations on the gill nets used to catch forage fish. Samples were stored at -25°C at the GLIER facility until they could be processed, whereupon they were shucked and deposited into hexane-rinsed tins for re-freezing and storage at -25°C.

3.3.3 – Mysis Collection

Collection of *Mysis* samples was performed by Environment Canada using a benthic sled. These samples were stored at the GLIER facility in hexane-rinsed tins at -25°C.

3.3.4 – Forage Fish Collection

Collection and identification of rainbow smelt, round goby, and bloater chub was carried out by the Upper Great Lakes Management Unit of the OMNR using gill nets. The gill nets were

set overnight and consisted of several sections of varying lengths and mesh sizes: 15m x 32mm mesh, 25m x 38mm mesh, followed by 7 sections of 50m corresponding to various mesh sizes 51mm/64mm/76mm/89mm/102mm/114mm/127mm. Using a benthic trawl net, Environment Canada collected and identified the deepwater sculpin.

The forage fish were transferred into food grade plastic bags and transported back to the GLIER facility on dry ice, upon which they were stored at -25°C. Processing of the forage fish included the collection of physiological data (body mass, total length, fork length, standard length), dissection to determine sex, and weighing of the liver and gonads. During this time, the stomach was removed and stored for gut content analysis. Next, with use of a commercial high speed blender, the fish was ground into a whole body homogenate and, up to approximately 35g, was stored at -25°C in a hexane-rinsed tin.

3.3.5 – Stable Isotope Analysis

Trophic niche of an organism can be determined through use of carbon and nitrogen stable isotopes. Carbon stable isotope analysis uses the fractionation between $^{13}C/^{12}C$ ($\delta^{13}C$) to determine an organism's source of primary production and ultimately which area of the lake the organism is utilizing (Post 2002; Foley et al. 2014). Alternatively, the nitrogen stable isotope analysis is used to determine an organism's trophic position by examining the change in the proportion of $^{15}N/^{14}N$, denoted as $\delta^{15}N$ (Post 2002).

The technique used to prepare samples for $\delta^{15}N$ and $\delta^{13}C$ quantification can be found in Dennard et al. 2009. Briefly, a small amount of sample was freeze-dried for 48 hours after which it underwent lipid extraction. Lipids were removed from the sample by adding 2:1 chloroform: methanol solution followed by 24 hour incubation in a 37°C water bath. After 24 hours the sample was centrifuged and the chloroform: methanol solution was poured off. Another aliquot of the chloroform: methanol solution was added, the sample was then vortexed followed by centrifugation. Again, the chloroform: methanol was decanted and the sample was allowed to dry for 48 hours.

An Elemental Analyzer (Costech Analytical Technologies; Valencia, CA, USA) coupled to a Delta V Isotope Ratio Mass Spectrometer (Thermo Scientific; San Jose, CA, USA) was used to quantify carbon and nitrogen stable isotope signatures. The species being analyzed dictated the amount of sample required and was as follows: 600-800μg zooplankton/*Dreissenid* mussels/*Mysis*; 400-600μg forage fish. Three commercially produced standards were utilized in the calculation of carbon and nitrogen stable isotopes and are as follows: NIST 1577c, USGS 41,

and Urea IVA 33802174. In addition to these, two other standards – Tilapia (in-house) and USGS 40 (commercial)—were used to assess accuracy.

3.3.6 – PCB Extraction and Analysis

The procedure used for PCB extraction varied depending on the species: microextraction and long-column extraction. Species such as zooplankton required a larger amount of sample to be extracted in order for PCBs to be observed in detectable amounts. The primary difference between the two procedures is the quantity of extraction solvents required to perform the extraction. *Mysis, Dreissenid* mussels and forage fish samples were able to be extracted using 0.5-1.0g and as such underwent 'microextraction', using fewer solvents. Zooplankton samples underwent long-column extraction which required a larger amount of chemicals, as well as 2.0-6.0g of sample depending on availability. Subsequently, different glassware was needed to accommodate the increased materials.

The process used for PCB microextraction is detailed in Daley et al. 2009. Briefly, glass microextraction columns are prepared using a small amount of glass wool and 15.0mL of 1:1 dichloromethane: hexane solution. A small amount of sample, 0.5-1.0g, is ground into 15.0g of sodium sulfate and funneled into a prepared microextraction column. This was followed by the addition of 10.0mL of 1:1 dichloromethane: hexane solution. The columns were then spiked with 50μL of PCB 34 to act as an internal recovery standard, and allowed to sit for one hour. The columns were then eluted with an additional 15.0mL of the 1:1 solution into a flat bottom flask. The samples were concentrated using a rotoevaporator and then diluted to 10.0mL using hexane.

The procedure for long-column extraction is described in Lazar et al 1992. Correspondingly, 500.0mL reservoir glass chromatography columns were prepared using glass wool and 25.0mL of 1:1 dichloromethane: hexane solution. A desired amount of sample was added to 30.0g of sodium sulfate, ground using a mortar and pestle, and deposited into the column using an additional 25.0mL of the 1:1 solution. Each column was then spiked with 100µL of PCB 34 and allowed to sit of 1 hour. The columns were then eluted with an additional 250.0mL of the 1:1 solution. The resultant extract was then concentrated using a rotoevaporator followed by dilution to 10.0mL using hexane.

Following extraction, both of the above methods proceeded as follows. The amount of lipids in the sample was quantified by removing 1.0mL of the 10.0mL solution and drying it at 110°C for gravimetric lipid determination. The samples then underwent florisil chromatography.

In this process, 6.0g of florisil was added to a 200mL glass chromatography column containing hexane and topped with 2.0cm of sodium sulfate. The samples were then added to the column and eluted with 60.0mL of hexane. The eluent was concentrated via rotoevaporation and diluted to 1.0mL using iso-octane. The resultant extracts were sealed in a gas autosampler vial. PCB analysis was then performed using gas chromatography coupled to an electron capture detector (GC-ECD) on Agilent 6890 GC System (Agilent Technologies; Santa Clara, CA, USA). Each batch of six samples was extracted with two standards: blank and in-house quality control reference homogenate (Detroit River carp). The reference homogenate was compared, on an individual PCB congener basis, to the GLIER laboratory database values. The results were within two standard deviations. Recovery of the internal standard (PCB 34) averaged 80.91 ± 0.88% (standard error). The samples were not recovery corrected.

3.3.7 – Mercury Analysis

Mercury was quantified using a Direct Mercury Analyzer (DMA-80) (Milestone Inc.; Sorisole, BG, Italy). This process is detailed fully in Haynes et al. 2006. Briefly, Hg was quantified by placing a small amount of sample (i.e. 0.200g zooplankton/*Mysis*/*Dreissenid* mussels, 0.150g forage fish) in a nickel boat for automatic combustion and analysis. Each batch of thirty-two samples was analyzed with four in-house quality control standards. These standards included W-CntVg (0.1 mg/L), BT-Cnt2M-Spk (0.1 mg/kg), BT-Dorm3 (0.4 mg/kg), and BT-Dolt4 (2.58 mg/kg). Analyses of in-house quality control samples were within 91 \pm 9% (standard deviation) of the mean laboratory database values for these materials

3.3.8 – Data Analysis

All ANOVAs, ANCOVAs, and independents samples t-tests in this study were completed using IBM SPSS 22. Levene's test was conducted before the ANOVAs were performed. This served to determine if the means would be compared using a standard ANOVA (homogenous variance between means) or a Welch's ANOVA (heterogeneous variance between means). Discriminant functions analysis is a multivariate approach which utilized stable carbon and nitrogen isotopes along with the proportional concentrations (% of ΣPCB) of 32 PCB congeners to determine the potential basin-specific patterns in PCB congener bioaccumulation for rainbow smelt and bloater chub. Similar to Paterson et al. 2016, PCB 180 was chosen in this study to be investigated due to its high hydrophobicity, log K_{ow} = 7.36 (Hawker et al. 1988). Linear regressions were performed using log_{10} transformed data (i.e. wet weight Hg and lipid corrected

PCB 180 concentrations). These regressions were used to describe the relationship between contaminant concentrations and δ^{15} N values.

3.4 RESULTS

3.4.1 – Discriminant Functions

The following analyses included only rainbow smelt and bloater chub, as the remaining species' samples sizes were not sufficient for the robustness of the measure. Discriminant function analyses for both rainbow smelt and bloater chub were performed in all three basins using: 1) the proportional concentration of 32 PCB congeners of the sum total (Figures 3.1.B and 3.2.B) and 2) A combination of carbon and nitrogen stable isotope data with 32 PCB congeners concentrations by proportion (Figures 3.1.A and 3.2.A).

3.4.2 – Across Basins Analysis of Lipid Content

Lipid content means and mean differences are summarized in Appendix E.

Zooplankton

A Welch's ANOVA of the mean lipid content of zooplankton among the basins revealed no significance, *p>*.05, Figure 3.3.

Dreissenid mussels

North Channel mussels were excluded from the following analysis due to insufficient sample size. An independent samples t-test indicates insignificant mean difference in lipid content between mussels in the Main Basin and Georgian Bay, *p*>.05, Figure 3.3.

Mysis

Due to low sample numbers Georgian Bay *Mysis* were excluded from the following analysis. An independent samples t-test revealed no significant mean difference between Main Basin and North Channel *Mysis*, *p*>.05, Figure 3.3.

Round goby

An ANOVA was used to test for significant mean differences in the mean lipid content of round goby among the basins, $p<0.01$, Figure 3.3. A Tukey's post hoc analysis showed that Main Basin round goby have a significantly greater mean difference in lipid content than those located in Georgian Bay (*p*<.01) and the North Channel (*p*<.01).

Rainbow smelt

A Welch's ANOVA was used to examine rainbow smelt lipid content for regional significance, *p*<.01, Figure 3.3. A Games-Howell post hoc test revealed that rainbow smelt in the Main Basin (*p*<.01) and North Channel (*p*<.01) had a significantly larger mean difference than those located in Georgian Bay.

Bloater chub

A Welch's ANOVA was used to test for significant mean difference of bloater chub lipid content among the basins, *p*<.01, Figure 3.3. The Games-Howell post hoc analysis showed that North Channel bloater chub have a significantly greater mean difference than their counterparts in the Main Basin (*p*<.01) and Georgian Bay (*p*<.01).

3.4.3 – Within Basin Analysis of Lipid Content

Appendix E contains the means and mean differences of the lipid content data.

Main Basin

A Welch's ANOVA was used to test for significance mean difference of the lipid content values for the species within the Main Basin, *p*<.01, Figure 3.3. The Games-Howell post hoc analysis revealed that deepwater sculpin had a significantly higher mean difference than zooplankton (*p*<.01), *Mysis* (*p*<.01), *Dreissenid* mussels (*p*<.01), round goby (*p*<.01), rainbow smelt (*p*<.01) and bloater chub (*p*<.01). That same post hoc test showed that round goby has a significantly higher mean difference than zooplankton (*p*<.01), *Dreissenid* mussels (*p*<.05), rainbow smelt (p <.01) and bloater chub (p <.01). Lastly, the Games-Howell test showed that rainbow smelt's mean lipid content was significant higher than zooplankton (*p*<.01).

Georgian Bay

Mysis were excluded from this analysis due to sample availability. A Welch's ANOVA was used to test for significant mean differences in the lipid content of the Georgian Bay species, p<.01, Figure 3.3. Games-Howell post hoc analysis revealed that round goby (*p*<.05) and bloater chub (*p*<.01) had significantly greater mean differences than rainbow smelt.

North Channel

Dreissenid mussels were excluded from this analysis due to low sample numbers. An ANOVA was used to test for significant mean differences in the lipid content of the North Channel species, *p*<.01, Figure 3.3. A Tukey's post hoc test revealed that bloater chub have a significantly higher mean difference than zooplankton (*p*<.01), *Mysis* (*p*<.01), rainbow smelt (*p*<.01) and round goby (*p*<.01).

3.4.4 – Across Basins Analysis of Hg Content

The means and mean difference values for Hg content is located in Appendix F.

Zooplankton

Due to sample availability, North Channel zooplankton were excluded from this analysis. An independent samples t-test indicated no significance mean difference between Main Basin and Georgian Bay zooplankton, *p*>.05, Figure 3.4.

Dreissenid mussels

North Channel *Dreissenid* mussels were excluded from the following analysis due to sample availability. An independent samples t-test revealed an insignificant mean difference between Main Basin *Dreissenid* mussels and their Georgian Bay counterparts, *p*>.05, Figure 3.4. *Mysis*

Georgian Bay *Mysis* were excluded from following analysis due to low sample numbers. The mean difference between *Mysis* in the Main Basin and the North Channel were explored using an independent samples t-test. No significant mean difference was indicated by this analysis, *p*>.05, Figure 3.4

Round goby

An ANOVA showed that there is no significant mean difference in round goby Hg content throughout the basins, *p*>.05, Figure 3.4.

Rainbow smelt

A Welch's ANOVA was used to indicate significant mean difference in Hg concentrations of rainbow smelt across the basins, *p*<.01, Figure 3.4. The Games-Howell post hoc test revealed that Main Basin (*p*<.01) and North Channel (*p*<.01) rainbow smelt had a significantly greater mean difference than their Georgian Bay counterparts.

Bloater chub

A Welch's ANOVA was used to test the bloater chub Hg content for significant mean differences, *p*<.01, Figure 3.4. The Games-Howell post hoc test indicated that Georgian Bay bloater chub have a greater mean difference than those in the Main Basin (*p*<.01) and the North Channel (*p*<.05).

3.4.5 – Within Basin Analysis of Hg Content

Appendix F contains the mean values and mean differences for Hg content.

Main Basin

A Welch's ANOVA was used to examine Hg content for significant mean differences within the species in the Main Basin (*p*<.01). The Games-Howell post hoc test revealed that deepwater sculpin had a significantly greater mean difference than zooplankton (*p*<.01),*Mysis* (*p*<.01), *Dreissenid* mussels (*p*<.01), and round goby (*p*<.01). The same post hoc testalso demonstrated that rainbow smelt had a significantly larger mean difference than zooplankton (*p*<.01), *Mysis* (*p*<.05), *Dreissenid* mussels (*p*<.05), and round goby (*p*<.01). Finally, the Games-Howell test showed that bloater chub had a significantly greater mean differencethan zooplankton (*p*<.01), *Mysis* (*p*<.05), *Dreissenid* mussels (*p*<.05), and round goby(*p*<.05).

Georgian Bay

Mysis were excluded from the following analysis due to limited sample size. AWelch's ANOVA was used to inspect the Hg content of the species in Georgian Bay, (*p*<.01). TheGames-Howell post hoc test indicated that bloater chub had a significantly greater meandifference than zooplankton (*p*<.01), *Dreissenid* mussels (*p*<.01), rainbow smelt (*p*<.01) and roundgoby (*p*<.01).

North Channel

Due to a lack of sample availability, zooplankton and *Dreissenid* mussels were excluded from the following analysis. Hg content of species in the North Channel were tested formean differences using a Welch's ANOVA, (*p*<.01). The Games-Howell post hoc revealed that the bloater chub had a significantly larger mean difference than *Mysis* (*p*<.01), rainbow smelt (*p*<.05), and round goby (*p*<.01). Additionally the same post hoc test showed that rainbow smelt had a significantly greater mean difference than both *Mysis* (*p*<.01) round goby, (*p*<.01).

3.4.6 – Across Basins Analysis of Lipid Corrected PCB 180 Content

Appendix G contains the lipid corrected PCB 180 mean values of the species as well as the mean differences for the below analyses.

Zooplankton

An ANOVA revealed no significant mean differences in the lipid corrected PCB 180 concentration among the basins, *p*>.05, Figure 3.5.

Dreissenid mussels

North Channel mussels were excluded from the following analysis due to a lack of sample. An independent samples t-test showed that the Main Basin *Dreissenid* mussels had a significantly greater mean difference than their Georgian Bay counterparts, *p*<.05, Figure 3.5. *Mysis*

Due to sample availability, Georgian Bay *Mysis* were excluded from the following analysis. An independent samples t-test revealed no significant mean difference between *Mysis* in the Main Basin and those in the North Channel, *p*>.05, Figure 3.5.

Round goby

An ANOVA demonstrate a lack of significant mean difference across the basins for round goby, *p*>.05, Figure 3.5.

Rainbow smelt

A Welch's ANOVA revealed significance in the mean differences of rainbow smelt across the basins, p<.01, Figure 3.5. The Games-Howell post hoc analysis showed that both the Main Basin (*p*<.01) and Georgian Bay (*p*<.05) rainbow smelt had a significantly greater mean difference than those located in the North Channel, Figure 3.5.

Bloater chub

A Welch's ANOVA was used to test for significance mean difference of bloater chub across the basins, *p*<.01, Figure 3.5. The Games-Howell post hoc test showed that bloater chubs located in the Main Basin (*p*<.01) and Georgian Bay (*p*<.01) both had a significantly greater mean difference than their North Channel counterparts, Figure 3.5.

3.4.7 – Within Basin Analysis of Lipid Corrected PCB 180 Content

Mean lipid corrected PCB 180 content mean and mean difference values for the following can be found in Appendix G.

Main Basin

A Welch's ANOVA was used to assess for significant mean differences amongst the species in the Main Basin, *p*<.01, Figure 3.5. The Games-Howell post hoc analysis showed that deepwater sculpin had a significantly greater mean difference than zooplankton (*p*<.01), *Mysis* (*p*<.05), *Dreissenid* mussels (*p*<.01), and rainbow smelt (*p*<.05). The same post hoc test showed that rainbow smelt had a significantly higher mean difference than both zooplankton (*p*<.01) and *Dreissenid* mussels (*p*<.01). Lastly, the Games-Howell showed that bloater chub had a significantly larger mean difference than zooplankton (*p*<.01) and *Dreissenid* mussels (*p*<.01). Georgian Bay

The following analysis excluded *Mysis* do to a lack of sample availability. A Welch's ANOVA revealed significance in mean difference of the species located in Georgian Bay, *p*<.01, Figure 3.5. The Games-Howell post hoc test showed that rainbow smelt had a higher significant mean difference than zooplankton (*p*<.05) and *Dreissenid* mussels (*p*<.05). Bloater chub also showed a significantly greater mean difference than zooplankton (*p*<.05) and *Dreissenid* mussels (*p*<.01).

North Channel

Dreissenid mussels were excluded from the following analysis due to insufficient sample size. An ANOVA was used to test for significance among the North Channel species' mean differences, *p*<.01, Figure 3.5. A Tukey's post hoc analysis revealed that *Mysis* had a significantly higher mean difference than zooplankton (p <.01), rainbow smelt (p <.01), and bloater chub (*p*<.01).

3.4.8 – Degree of Hg biomagnification within the lower trophic levels of Lake Huron:

A linear regression was performed on log_{10} -transformed wet weight Hg concentrations versus stable nitrogen data for the species in the lower trophic level s of Lake Huron (Figure 3.6). An analysis of covariance (ANCOVA) indicated regardless of basin, the lower food web biomagnified Hg at rates that are not significantly different (*p>*.05).

3.4.9 - Degree of PCB 180 biomagnification within the lower trophic levels of Lake Huron:

 $Log₁₀$ -transformed lipid corrected PCB 180 concentrations versus stable nitrogen data for the species in Lake Huron's lower food web underwent a linear regression (Figure 3.7). Regional heterogeneity was indicated using an ANCOVA (*p*<.05). The Bonferroni post-hoc analysis indicated that the lower food webs in Main Basin and Georgian Bay biomagnified PCB 180 at a significantly greater rate than what is found in the North Channel (*p*<.01, respectively).

3.4.10 – PCB Biomagnification Factors

The following PCB 180 BMF values were compared across and within Lake Huron's basins by considering mean values and the corresponding standard deviations.

3.4.10.1 - Across Basins Analysis of Lipid Corrected PCB 180 (LC PCB 180) BMF predator: zooplankton

• Round goby

There was similarity in the LC PCB 180 BMF_{round goby: zooplankton} values between the Main Basin – North Channel and Main Basin – Georgian Bay (Figure 3.8.A). Georgian Bay possessed the greatest LC PCB 180 BMF_{round goby: zooplankton} while the North Channel had the lowest.

Rainbow smelt

The LC PCB 180 BMF_{rainbow smelt: zooplankton} values were comparable across all three basins (Figure 3.8.A). This similarity occurred to a greater extent between Main Basin and Georgian Bay LC PCB 180 BMF_{rainbow smelt: zooplankton} values.

• Bloater chub

The LC PCB 180 BMF_{bloater chub: zooplankton} values in the Main Basin and Georgian Bay had a high degree of similarity and are both much greater compared to their North Channel counterparts (Figure 3.8.A).

3.4.10.2 – Within Basin Analysis of Lipid Corrected PCB 180 (LC PCB 180)BMF predator: zooplankton

Main Basin

In the Main Basin the LC PCB 180 BMF_{predator: zooplankton} values for the rainbow smelt and round goby were very similar. Bloater chub possessed the greatest BMF in this basin (Figure 3.8.A).

Georgian Bay

Georgian Bay rainbow smelt and round goby displayed some similarity in their LC PCB 180 BMF values. These species differed from the bloater chub such that the bloater had the greatest LC PCB 180 BMF in this basin (Figure 3.8.A).

North Channel

All species in this basin experienced comparable LC PCB 180 BMF predator: zooplankton values. There was a high amount of similarity in the LC PCB 180 BMF means and standard deviations of the rainbow smelt and bloater chub (Figure 3.8.A).

3.4.10.3 - Across Basins Analysis of Lipid Corrected PCB 180 BMFpredator: Mysis

• Round goby

The LC PCB 180 BMFround goby: *Mysis* values were comparable amongst the basins (Figure 3.8.B).

Rainbow smelt

Lakewide similarity was observed for the LC PCB 180 BMF_{rainbow smelt: *Mysis* values (Figure 3.8.B).}

• Bloater chub

The LC PCB 180 BMFbloater chub: *Mysis* values were comparable between the Main Basin and Georgian Bay. The lowest value was observed in the North Channel (Figure 3.8.B).

3.4.10.4 - Within Basin Analysis of Lipid Corrected PCB 180 BMF predator: Mysis

• Main Basin

In the Main Basin, rainbow smelt and round goby had very similar LC PCB 180 BMF_{predator: *Mysis*} values. In this basin, the greatest mean LC PCB 180 BMF_{predator: *Mysis* value belonged to the} bloater chub (Figure 3.8.B).

Georgian Bay

In Georgian Bay, the standard deviation could not be calculated for the mean LC PCB 180 BMFpredator: *Mysis* due to low *Mysis* sample availability. High variability existed between samples, with highest and lowest LC PCB 180 BMF corresponding to rainbow smelt and round goby, respectively (Figure 3.8.B).

• North Channel

All species demonstrated a high amount of similarly in LC PCB 180 BMFpredator: *Mysis* values for this basin (Figure 3.8.B).

3.4.11 – Hg Biomagnification Factors

The Hg BMFs were analyzed spatially throughout Lake Huron by observing the means and corresponding standard deviations.

3.4.11.1 - Across Basins Analysis of Hg BMF predator: zooplankton

• Round goby

A high degree of variability was observed in the Hg BMF_{round goby: zooplankton} values, in which the highest value occurred in the Main Basin and the lowest in Georgian Bay (Figure 3.9.A)

• Rainbow smelt

Throughout the three basins there was variability in the Hg BMF rainbow smelt: zooplankton, in which the highest mean value occurred in the North Channel and the lowest in Georgian Bay (Figure 3.9.A).

• Bloater chub

The Hg BMF rainbow smelt: zooplankton values were similar between the Main Basin and Georgian Bay. The North Channel mean Hg BMF rainbow smelt: zooplankton value was the highest (Figure 3.9.A).

3.4.11.2 – Within Basin Analysis of Hg BMF predator: zooplankton

Main Basin

There is a high amount of similarity in the mean Hg BMF predator: zooplankton Values for both rainbow smelt and bloater chub. The highest mean Hg BMF predator: zooplankton in this basin belonged to deepwater sculpin (Figure 3.9.A).

Georgian Bay

In this basin, bloater chub possessed the highest mean Hg BMF predator: zooplankton value. Rainbow smelt and round goby displayed much similarity in their Hg BMF predator: zooplankton values (Figure 3.9.A).

• North Channel

The mean Hg BMF predator: zooplankton values in this basin displayed a great deal of variability with the highest and lowest values possessed by bloater chub and round goby, respectively (Figure 3.9.A).

3.4.11.3 - Across Basins Analysis of Hg BMF predator: Mysis

• Round goby

There was similarity in the Hg BMFround goby: *Mysis* values between Main Basin – North Channel and the North Channel – Georgian Bay (Figure 3.9.B).

Rainbow smelt

The lowest Hg BMFrainbow smelt: *Mysis* value was found in Georgian Bay. The other two basins displayed a large amount of similarity between BMF values (Figure 3.9.B)

• Bloater chub

There was much variability in the Hg BMF_{bloater chub: *Mysis* values amongst the basins. The highest} value was in the North Channel and the lowest in Georgian Bay (Figure 3.9.B).

3.4.11.4 - Within Basin Analysis of Hg BMF predator: Mysis

Main Basin

The Hg BMFpredator: *Mysis* values for rainbow smelt and bloater chub in the Main Basin displayed a great amount of similarity. The mean Hg BMF_{predator: Mysis} values of the formerly mentioned species were comparable to those of deepwater sculpin and round goby. However there was no similarity in the BMF values of deepwater sculpin and round goby (Figure 3.9.B).

Georgian Bay

In Georgian Bay, bloater chub possessed the highest Hg BMF_{predator: *Mysis* value. The BMF values} for rainbow smelt and round goby were comparable (Figure 3.9.B).

North Channel

Rainbow smelt and round goby in the North Channel had similar Hg BMF_{predator: *Mysis* values. In} this basin, the bloater chub had the highest BMF (Figure 3.9.B).

3.5 DISCUSSION

Similar to the trophic level and energy density differences observed in Chapter 2 (Table 2.4 and Figure 2.7), this study showed that there were spatial variations throughout Lake Huron starting at the level of the secondary consumers – round goby, rainbow smelt, and bloater chub. In contrast to this, the forage base – zooplankton, *Dreissenid* mussels, *Mysis* – displayed homogeneity. Generally, each of these primary consumer species was not only consistent lakewide but displayed uniformity in relation to one another when considering Hg and PCB 180, Figures 3.4 – 3.5. Within and amongst the basins, these primary consumers did not show significant lipid content variation, Figure 3.3. Taking these factors into account, the quality of this forage base appeared to be constant throughout Lake Huron. Under these circumstances, one could expect to observe similar uniformity in these prey consumers. However, as previously noted by Paterson et al. 2016 and Abma et al. 2015, pollutant bioaccumulation patterns in lake trout top predators exhibit basin-specific profiles. This held true for the secondary consumers as well, Figures $3.1 - 3.2$.

Although the primary consumers display lakewide consistency in lipid content, this does not carry into the next trophic level, Figure 3.3. As such, regional variation in the secondary consumers becomes apparent. Main Basin round goby and North Channel bloater chub were theonly instances where forage fish species have significantly different lipid content than most ofthe prey items. Even within species, a trend does not emerge. The North Channel

and Main Basin rainbow smelt were equally greater than their Georgian Bay counterparts. Throughout thebasins, the Main Basin bloater chub and Georgian Bay round goby each have the lowest lipid content. Among all these variations, no consistent trend emerges. This continued into thecontaminant dynamics aspect when taking into account total wet weight Hg and lipid corrected PCB180 concentrations, Figures $3.4 - 3.5$. Some disparity between these two contaminants was expected astheir sequestering mediums differ. Although it was once thought that Hg is stored in lipids (Masonet al. 1995), today it is widely accepted that Hg is stored in protein (Ullrich et al. 2001) and PCBis stored in lipids (Gobas et al. 1999). Additional dissimilarity was expected as the PCBvalues presented here were lipid corrected, whereas a lack of moisture content meant that Hgvalues could not be lean dry weight corrected. Abma et al. 2015 reported that Lake Huron lake trout residing in the Main Basin had the highest Hg concentration. Conversely, this studyobserved Georgian Bay to have the greatest Hg concentration in the primary consumers and thebloater chub, Figure 3.4. Rainbow smelt and round goby having the highest mercury content were located in the Main Basin, although again not statistically significant, Figure 3.4. Paterson et al. 2016 analyzed totalPCB concentration and noted that the lake trout located in the Main Basin had the greatest concentration. Similar to their observation, this study observed the same trend across all species with the exception of the round goby, Figure 3.5. However, there was still variability in terms ofPCB 180 concentration in the other two basins, Figure 3.5. The bioaccumulation patterns of Hg and PCB 180 both within and amongst species showed great variation, Figures 3.4 – 3.5. Within each of the three forage fish species there was not an instance where the patterns of these two contaminants align – inother words, within a species the highest concentration of each respective contaminant was foundin different basins. Amongst the forage fish species, the only instance where consistencywas observed is between the bloater chub and rainbow smelt's PCB 180 concentrations, Figure 3.5(highest concentration in the Main Basin, lowest in the North Channel). When analyzing each basin individually, uniformity emerged in the Hg bioaccumulation trends in Georgian Bay and the North Channel, Figure 3.4. Here, bloater chub possessed the greatest concentrations and were significantly greater than rainbow smelt and round goby—both of which showed no significant difference. Additionally, the PCB 180 concentrations of all three forage fish species demonstrated no significant difference across the three basins, Figure 3.5. Besides these trends, high variability was observed in the patterns of Hg and PCB 180. In terms of both PCB 180 and Hgbiomagnification factors, the trends were

the same regardless of prey item, Figures 3.8 – 3.9. Although possessing visuallysimilar patterns, the BMFs calculated using zooplankton as the prey species yielded a greater value than those calculated using *Mysis.* This reduction when using *Mysis* as the prey item was a resultof *Mysis'* consumption of zooplankton (Bunnell et al. 2011). Although their differences arenot statistically significant, *Mysis* did constantly register a higher mean contaminant concentration. In terms of BMFs for both Hg and PCB 180, widespread variability was observed againboth amongst and within basins. BMF is simply a ratio between the predator's and its prey's contaminant concentrations. Hence, if the quality of prey is consistent lakewide, as implicatedin this study, then BMF values should correspond. However, this was notobserved.

The inconsistency of secondary consumer data supports the notion that regions within Lake Huron have different ecological processes occurring. Furthermore, such differences in ecological aspects are able to influence contaminant exposure (Paterson et al. 2016). The observation of these inconsistencies could be due to resource composition and limitations, as well as environmental stress and physiochemical aspects of a system (Abma et al. 2015).

According to Warner et al. 2009 and the Status and Trends of Pelagic Prey Fish in Lake Huron 2015 report (O'Brien et al. 2016), the forage fish community consists primarily of rainbow smelt and bloater chub. However, these studies showed that the composition of the aforementioned species varied by basin such that bloater chub dominated in the Main Basin while rainbow smelt was the principle forage fish in Georgian Bay and the North Channel (O'Brien et al. 2016; Warner et al. 2009). In addition to the varying composition, the density of forage fish differs amongst Lake Huron's three regions. Warner et al. 2009 reported the greatest forage fish biomass in the North Channel, and the lowest in the Main Basin. Lakewide forage fish biomass has been declining since 1998 with particularly low levels during the 2000s to present (O'Brien et al. 2016). In addition to the population decline, a reduction in key energy-rich dietary items – such as *Diporeia* – has also occurred (Nalepa et al. 2007). These factors, along with data presented in the previous chapter, imply a lack of available food resources. The uniformity of this limitation amongst the basins is unknown. The 2015 Status and Trends of Pelagic Prey Fishes in Lake Huron report notes that this lakewide forage fish biomass decline is not observed in the North Channel, where the biomass fluctuates with no overall trend (O'Brien et al. 2016). Given this and the previously mentioned differences in composition and biomass among the basins, it is reasonable to conclude that the degree of food resource limitation varies regionally. Lack of food resources can result in more time spent foraging without the guarantee that energy

acquired will offset the energy expended. This would result in a negative impact on growth and condition of the organism.

In addition to changes in the structure of the forage assemblage, environmental stress can have a large impact on the food web. Lake Huron is experiencing changes in its thermal structure as a result of warming surface waters. Lake Huron's littoral zones have also been observed as warming quicker as a result of more shallow water (Nguyen et al. 2014). Additionally, thermal stratification of Lake Huron has been altered such that the thermocline is becoming established earlier on in the growing season (Austin et al. 2007). One outcome of this change in temperature regime is a reduction in seasonal ice coverage. This decrease leads to increased absorption of solar radiation and continued warming (Austin et al. 2007; O'Reilly et al. 2015). As fish are ectotherms and are strongly influenced by their external environment this trend is problematic (Kao et al. 2015). Different fish have specific thermal guilds that are ideal for their growth and maintenance – as such temperature of the environment is influential in where they reside and forage. Climate change and the ensuing warming of Lake Huron will exert stress on fish which rely on cooler temperatures, subsequently impacting their growth (Kao et al. 2015). As observed in the stable carbon and nitrogen isotope data presented in the previous chapter (Figures 2.4 and 2.5), it appears that forage fish are moving into the littoral zone to forage. Living and foraging in areas out of an organism's thermal optima results in the expenditure of additional energy.

 Lake Huron's current state of resource limitation and increased water temperatures can impact growth of an organism, and thereby the behaviour of contaminants (Figures 3.1 and 3.2). The energy which an organism attains via prey consumption is divided across multiple factions including maintenance, growth, and reproduction (Arendt 1997). The conditions in which an organism is subjected can alter these energy allocations. For example, when resources are limited or energy expenditure is high (i.e. living out of thermal optima), the organism's growth rate slows and reproduction can be hindered. This in turn can affect contaminant dynamics through lack of growth dilution and maternal off loading. Resource limitation and warming water temperatures do not appear to be consistent in its lakewide effects. As such, the different basins may experience these ecological factors to different extents. For example, the forage fish biomass is greater in the North Channel, possibly indicating more food resource availability. At the same time however, the North Channel is the shallowest of the basins and
would be more susceptible to warming. Alternatively, the Main Basin would be in the opposite situation with less food resources and slower warming effects.

Conclusively, Lake Huron is a system under considerable strain from multiple factors. The regional and species heterogeneity across numerous factors led to a rejection of the hypotheses. This study provided evidence that the basins of Lake Huron are impacted by different ecological processes and highlighted the complexity of the Lake's ecosystem interactions.

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Figure 3.1: Discriminant function ordinations of Lake Huron bloater chub (*Coregonus hoyi*) collected from the Main Basin (\diamond), Georgian Bay (\Box) and the North Channel (\triangle). Ordinations were completed using (A) fish stable isotope (δ^{13} C & δ^{15} N) values and proportional (% of ΣPCB) concentrations for 32 PCB congeners or (B) solely PCB congener proportional concentrations.

Figure 3.2: Discriminant function ordinations of Lake Huron rainbow smelt (*Osmerus mordax*) collected from the Main Basin (\diamond), Georgian Bay (\Box) and the North Channel (\triangle). Ordinations were completed using (A) fish stable isotope (δ^{13} C & δ^{15} N) values and proportional (% of ΣPCB) concentrations for 29 PCB congeners or (B) solely PCB congener proportional concentrations.

Figure 3.3: Mean lipid content (%) of the lower trophic food web amongst the basins of Lake Huron. The white, light grey, and dark grey bars correspond to the Main Basin, Georgian Bay, and North Channel, respectively. Error bars indicate ± 1 SE.

Figure 3.4: Mean wet weight Hg concentrations (ng/g) for Lake Huron's lower trophic level species. The Main Basin is indicated in white, Georgian Bay in light grey, and the North Channel is represented by dark grey. Error bars indicate \pm 1 SE.

Figure 3.5: Mean lipid corrected PCB 180 concentrations (ng/g) for the species occupying the lower trophic level of Lake Huron. The Main Basin, Georgian Bay and the North Channel are represented as follows: white, light grey, and dark grey. Error bars indicate \pm 1 SE.

Figure 3.6: Wet weight Hg concentrations (ng/g) in relationship to δ¹⁵N (‰) of the lower food web within Lake Huron's basins: Main Basin (\diamondsuit) , Georgian Bay (\Box), North Channel (\blacktriangle).

Figure 3.7: Lipid corrected PCB 180 concentrations (ng/g) in relationship to δ^{15} N (‰) of the lower food web within Lake Huron's basins: Main Basin (\diamond), Georgian Bay (\blacksquare), North Channel (\triangle) .

Figure 3.8: Mean biomagnification factors (BMF) of lipid corrected PCB 180 between various predators and prey items among Lake Huron's basins. (A) BMF predator: zooplankton and (B) BMF predator: *Mysis*. The predators included are as follows: rainbow smelt (white), bloater

Figure 3.9: Mean biomagnification factors (BMF) of wet weight Hg between various predators and prey items among Lake Huron's basins. (A) BMF predator: zooplankton and (B) BMF predator: *Mysis*. The predators included are as follows: rainbow smelt (white), bloater chub (light grey), round goby (dark grey), and deepwater sculpin (black).

CHAPTER 4:

SUMMARY

4.1 SUMMARY

The objective of this thesis was to examine the possibility of regional heterogeneity in Lake Huron's lower food web. Chapter 2 explored the condition of lower food web organisms amongst the basins while assessing their diet and energy content. Chapter 3 focused on Hg and PCB 180 content within these species and whether the dynamics of these contaminants could provide insight into how material flows through a system. The culmination of this research showed that basin-specific differences were apparent at the level of the secondary consumers. The various measures considered here indicated that these variations were most likely a result of different ecological processes occurring within each basin.

Lake Huron is a stressed system with low primary production and declines in abundances across multiple trophic levels (Barbiero et al. 2009). Ecological tools, such as stomach contents and stable isotopes, were utilized to determine how these perturbations were affecting the lower trophic levels and whether these effects were regionally uniform. Chapter 2 revealed there is homogeneity in the primary consumers – zooplankton, *Mysis, Dreissenid* mussels – and indicated a lack of resources. Analysis of the zooplankton community showed regional consistency in composition with the primary zooplankton being calanoid copepods (Figures $2.1 - 2.3$) – which includes species that are relatively mobile and adept at predator avoidance (Barbiero et al. 2009). This, combined with the already low zooplankton abundances, indicated that organisms depending on zooplankton (bloater chub and rainbow smelt according to stomach content data, Table 2.1) might be expending a larger amount of energy to forage in a resource-limited environment for a prey item that is successful at escaping. Additional input from carbon stable isotopes demonstrated that typically pelagic-dwelling forage fish species appear to be using the nearshore zone, Figure 2.4. This contributed to evidence that resources maybe limited in pelagic waters. Energy density proved to be a useful tool to show that regional heterogeneity existed in secondary consumers – particularly, rainbow smelt and bloater chub, Figure 2.7. This highlighted the importance of energy density as an effective means to understanding how food webs react to perturbations. Using this measurement in future studies would provide a more cohesive look in how material flows in a system.

This regional heterogeneity was further explored in chapter 3 using contaminants. Particular contaminants can act as effective tracers for the exploration of food web dynamics.

71

The contaminants selected in this study were Hg and PCB 180, as they are not readily eliminated (Stein et al. 1996; Safe 1994). PCB 180 is acquired through dietary means as a result of its highly hydrophobic nature, log K_{OW} = 7.36 (Hawker et al. 1988). An organism's diet can be reflected in the amount of acquired contaminants and for that reason, contaminant levels can be used to indicate the condition of the individual (Paterson et al. 2006). An unexpected observation found here were the large amounts of variability in the two contaminants measured, without a recognizable spatial trend, Figures $3.4 - 3.5$. It is thought that again, this high amount of variability was due to differences in ecological processes amongst the basins. Utilizing contaminants as a tool for understanding ecosystem dynamics, as seen here, could be improved through correction of the mercury data. Mercury is lean dry weight corrected as opposed to the lipid correction PCB concentrations underwent (Li et al. 2015). This difference in correction methodology was because Hg sequesters in protein (Ullrich et al. 2001), and therefore moisture and lipid data were required to eliminate individual variability. In this study, sample availability hindered the collection of moisture data, and as such lean dry weight could not be calculated. Thus the inconsistency between the two contaminants in this study could be the result of individual variability in the Hg data.

As shown in chapters 2 and 3, Lake Huron's lower food web is being affected by different ecological processes. The spatial heterogeneity within Lake Huron became evident when considering the discriminant functions analysis for bloater chub and rainbow smelt using stable isotopes and sum PCB concentrations, Figures $3.1 - 3.2$. Here, the combination of ecological and contaminant measures provided powerful support that the ecology of food resources and subsequently contaminant assimilation differ substantially among Lake Huron's three basins for secondary consumers such as rainbow smelt and bloater chub. It is speculated that there are two factors which could be contributing to the observed regional heterogeneity – resource limitation and climate change. Resource limited environments and increased time spent foraging can leave species in an energy deficit. Foraging in the ever warming waters of Lake Huron (Nguyen et al. 2014) and seeking nearshore food resources, out of organisms' thermal optima, can result in disproportionate energy expenditure. The differences observed throughout Lake Huron could be due to a combination of the above and other ecological processes. Further research would be needed to confirm these inferences.

Several studies have concluded that the perturbations in Lake Huron are a function of bottom-up effects (Barbiero et al. 2011; Bunnell et al. 2014), yet this research indentified that

72

the effects of such phenomenon present at the level of the secondary consumers. The main prey for Lake Huron lake trout, a top predator, are rainbow smelt and round goby (Roseman et al. 2014). The data presented in this study indicated that these prey items may not be sufficient enough to sustain the species of the upper trophic levels. Little research has been done that focuses on Lake Huron's lower food web. Furthermore, most studies assume the Main Basin to be representative of the whole of Lake Huron. Collectively, the research presented here, and that of Abma et al. 2015 and Paterson et al. 2016, demonstrate that regional heterogeneity exists. Furthermore, this research provides strong evidence of basin-specific energy assimilation efficiencies amongst the Lake Huron forage fish – particularly rainbow smelt and bloater chub. These two species are active predators thus having a higher foraging cost. Given the spatial heterogeneity observed for these two species, it can be concluded that the cost of foraging varied spatially. This contrasts the results gathered for round goby, where no basinspecific differences were observed. The round goby preys upon sessile *Dreissenid* mussels and as such has a lower foraging cost than the other forage fish. Additionally, this research highlighted the effectiveness of combining energy density with contaminant dynamics to understand how material flows through an ecosystem and how such systems are interacting.

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APPENDIX A

Table A.1: Species collection information.

Table A.2: Number of samples per analysis of each species.

APPENDIX B

Table B.1: Equations used for the calculation of energy density in fish (G. Paterson, personal communication, 11 December 2015).

*Note: $Wt_{Organism}$ is the organism's total body weight in grams

Table B.2: Equations used for the calculation of energy density in zooplankton, *Mysis*, and *Dreissenid* mussels (G. Paterson, personal communication, 11 December 2015). *Note: Wt_{Organism} is the organism's total body weight in grams

No. Measure Equation
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 Equation
 Equation
 Equation
 Equation
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 Equation
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 EXPLAREANCE EXPLAREANCE
 EXPLAREANCE
 EXPLAREANCE $\left($ eq.B12) Dry Mass (g) $\left($ eq.B13) | Ash Mass $\left($ g) A $\overline{1}$

APPENDIX C

| Species | Main Basin | Georgian Bay | North Channel |
|---------------------------|-------------------|---------------------|----------------------|
| Zooplankton | $-26.70(1.50)$ | $-28.08(1.72)$ | -27.97 |
| Dreissenid mussels | -27.01 | $-26.02(.64)$ | -27.50 |
| Mysis | $-27.20(0.60)$ | -24.32 | $-26.32(1.43)$ |
| Round goby | $-20.62(1.35)$ | $-21.42(2.02)$ | -17.03 (.70) |
| Rainbow smelt | $-23.46(1.39)$ | $-23.40(0.80)$ | $-20.50(1.06)$ |
| Bloater chub | $-24.24(0.49)$ | $-23.50(0.88)$ | $-21.68(1.55)$ |
| Deepwater sculpin | $-24.59(0.48)$ | n/a | n/a |

Table C.1: Mean $\delta^{13}C$ (‰) for species amongst Lake Huron's 3 basins.

Note. The bracketed values indicate 1 standard deviation. The denotation 'n/a' indicates that samples were not collected for corresponding the species.

Note. The bracketed values indicate 1 standard deviation. The denotation 'n/a' indicates that samples were not collected for corresponding the species.

| Species | Basin Relationship | Mean difference (SE) | p value |
|----------------------|---------------------------|-----------------------------|---------|
| Zooplankton | Main - Georgian | 1.38(.80) | .10 |
| Mysis | Main - North | .89(.88) | .35 |
| Round goby | North – Main $*$ | 3.59(1.05) | .01 |
| | North - Georgian* | 4.39(1.08) | .00 |
| | Main - Georgian | .80(.76) | .56 |
| Rainbow smelt | North – Main $*$ | 2.97(.37) | .00 |
| | North - Georgian* | 2.90(.34) | .00 |
| | Georgian - Main | .06(.33) | .98 |
| Bloater chub | Georgian - Main* | .74(.20) | .00 |
| | North - Main * | 2.56(.35) | .00 |
| | North - Georgian* | 1.82(.37) | .00 |

Table C.3: Mean difference δ^{13} C for study species across Lake Huron's three basins.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples the following species were excluded: North Channel zooplankton, all *Dreissenid* mussels, and Georgian Bay *Mysis*.

Table C.4: Mean difference δ^{15} N for study species across Lake Huron's three basins.

| Species | Basin Relationship | Mean difference (SE) | p value | |
|----------------------|---------------------------|-----------------------------|---------|--|
| Zooplankton | Main - Georgian | 1.45(.86) | .11 | |
| Mysis | Main - North | .76(.69) | .31 | |
| Round goby | North – Main $*$ | 1.16(0.40) | .03 | |
| | North - Georgian | .77(0.42) | .19 | |
| | Georgian - Main | .39(.29) | .39 | |
| Rainbow smelt | North – Main $*$ | .80(.23) | .00 | |
| | North - Georgian | .57(.26) | .09 | |
| | Georgian - Main | .23(.23) | .58 | |
| Bloater chub | Georgian - Main* | 1.40(0.18) | .00 | |
| | Georgian - North* | .50(.16) | .01 | |
| | North – Main $*$ | .90(0.19) | .00 | |

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples the following species were excluded: North Channel zooplankton, all *Dreissenid* mussels, and Georgian Bay *Mysis*.

| Species | Relationship | Mean difference (SE) | p value |
|----------------------|---------------------|-----------------------------|---------|
| Zooplankton | Mysis | .50(.52) | .92 |
| Round goby | Zooplankton* | 6.08(.58) | .00. |
| | Mysis* | 6.58(.55) | .00 |
| | Rainbow smelt* | 2.84(.50) | .00 |
| | Bloater chub* | 3.62 (.44) | .00 |
| | Deepwater sculpin* | 3.97(0.43) | .00 |
| Rainbow smelt | Zooplankton* | 3.24(0.47) | .00 |
| | Mysis* | 3.74(0.43) | .00 |
| | Bloater chub | .78(.29) | .10 |
| | Deepwater sculpin* | 1.13(0.27) | .00 |
| Bloater chub | Zooplankton* | 2.46(0.41) | .00 |
| | Mysis* | 2.96(0.37) | .03 |
| | Deepwater sculpin | .35(.15) | .18 |
| Deepwater sculpin | Zooplankton* | 2.11(.40) | .00 |
| | Mysis | 2.61(.35) | .05 |

Table C.5: Mean difference δ^{13} C for species within the Main Basin.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples, *Dreissenid* mussels were excluded.

| Species | Relationship | Mean difference (SE) | p value |
|----------------------|----------------|-----------------------------|-----------|
| Mysis | Zooplankton* | 5.27(.68) | .01 |
| | Round goby | 1.12(.58) | .53 |
| Round goby | Zooplankton* | 4.15(.42) | .00 |
| Rainbow smelt | Zooplankton* | 5.66(.41) | .00 |
| | Mysis | .39(.57) | .97 |
| | Bloater chub | .28(.22) | .81 |
| | Round goby* | 1.51(.21) | .00 |
| Bloater chub | Zooplankton* | 5.38(0.43) | .00 |
| | Mysis | .11(.58) | 1.00 |
| | Round goby* | 1.23(.24) | .00 |
| Deepwater sculpin | Zooplankton* | 8.15(.40) | .00 |
| | Mysis | 2.89(.56) | .12 |
| | Round goby* | 4.01(.18) | .00 |
| | Rainbow smelt* | 2.50(0.16) | .00 |
| | Bloater chub* | 2.78(.20) | .00 |

Table C.6: Mean difference δ^{15} N for species within the Main Basin.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples, *Dreissenid* mussels were excluded.

| Species | Relationship | Mean difference (SE) | p value |
|---------------------------|---------------------|-----------------------------|---------|
| Dreissenid mussels | Zooplankton | 2.07(0.83) | .11 |
| Round goby | Zooplankton* | 6.67(.65) | .00 |
| | Dreissenid mussels* | 4.60(0.77) | .00 |
| | Rainbow smelt* | 1.99(.50) | .00 |
| | Bloater chub* | 2.08(.46) | .00 |
| Rainbow smelt | Zooplankton* | 4.68(.59) | .00 |
| | Dreissenid mussels* | 2.61(.72) | .01 |
| | Bloater chub | .10(.36) | 1.00 |
| Bloater chub | Zooplankton* | 4.58(.55) | .00 |
| | Dreissenid mussels* | 2.51(.69) | .01 |

Table C.7: Mean difference δ^{13} C for species within Georgian Bay.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. *Mysis* were excluded due to lack of samples.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. *Mysis* were excluded due to lack of samples.

| Species | Relationship | Mean difference (SE) | p value |
|----------------------|----------------|-----------------------------|---------|
| Round goby | M vsis $*$ | 9.29(.96) | .00 |
| | Rainbow smelt* | 3.47(.85) | .00 |
| | Bloater chub* | 4.66(.83) | .00 |
| Rainbow smelt | M vsis $*$ | 5.82(.65) | .00 |
| | Bloater chub | 1.18(.44) | .05 |
| Bloater chub | Mysis* | 4.63(.62) | .00 |

Table C.10: Mean difference δ^{13} C for species within the North Channel.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples, Zooplankton and *Dreissenid* mussels were excluded.

APPENDIX D

Table D.1: Mean dry weight energy density values (kJ/g) for species amongst Lake Huron's 3 basins.

| Species | Main Basin | Georgian Bay | North Channel |
|----------------------|-------------------|---------------------|----------------------|
| Zooplankton | 18.34 (.59) | 18.13(.53) | 18.11 (1.02) |
| Dreissenid mussels | 18.61 (.21) | 18.47(01) | 18.44 |
| Mysis | 18.70 (.56) | 19.14 | 18.98 (.79) |
| Round goby | 16.69(.83) | 15.91(.61) | 16.40(0.48) |
| Rainbow smelt | 18.23 (1.29) | 16.07(0.73) | 18.40 (.65) |
| Bloater chub | 18.32 (1.50) | 20.00 (2.46) | 21.86 (.96) |
| Deepwater sculpin | 17.18 (.98) | n/a | n/a |

Note. The bracketed values indicate 1 standard deviation. The denotation 'n/a' indicates that samples were not collected for corresponding the species.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples the following species were excluded: North Channel *Dreissenid* mussels and Georgian Bay *Mysis*.

| Species | Relationship | Mean difference (SE) | p value |
|----------------------|---------------------|-----------------------------|---------|
| Zooplankton | Rainbow smelt | .10(.32) | 1.00 |
| | Bloater chub | .01(0.48) | 1.00 |
| | Round goby | 1.65(.51) | .26 |
| | Deepwater sculpin* | 1.16(0.25) | .00 |
| Mysis | Zooplankton | .36(.33) | .90 |
| | Dreissenid mussels | .08(.30) | 1.00 |
| | Rainbow smelt | .46(.39) | .89 |
| | Bloater chub | .37(.53) | .99 |
| | Round goby | 2.01(.56) | .16 |
| | Deepwater sculpin* | 1.52(.33) | .03 |
| Dreissenid mussels | Zooplankton | .28(.20) | .79 |
| | Rainbow smelt | .38(.30) | .85 |
| | Bloater chub | .29(0.46) | .99 |
| | Round goby | 1.93(0.49) | .20 |
| | Deepwater sculpin* | 1.43(0.21) | .00 |
| Rainbow smelt | Round goby | 1.55(.55) | .29 |
| | Deepwater sculpin* | 1.06(0.33) | .04 |
| Bloater chub | Rainbow smelt | .09(0.53) | 1.00 |
| | Round goby | 1.63(0.66) | .30 |
| | Deepwater sculpin | 1.15(0.49) | .29 |
| Deepwater sculpin | Round goby | .49(.52) | .94 |

Table D.3: Mean difference of energy density for species within the Main Basin.

Note. * indicates statistical significance at *p*< .05; the values within the brackets indicate 1 standard error.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. *Mysis* were excluded due to lack of samples.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples, *Dreissenid* mussels were excluded.

APPENDIX E

Table E.1: Mean lipid content (%) for species amongst Lake Huron's 3 basins.

Note. The bracketed values indicate 1 standard deviation. The denotation 'n/a' indicates that samples were not collected for corresponding the species.

Table E.2: Mean difference in lipid content (%) for study species across Lake Huron's three basins.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples the following species were excluded: North Channel *Dreissenid* mussels and Georgian Bay *Mysis*.

| Species | Relationship | Mean difference (SE) | p value |
|---------------------------|---------------------|-----------------------------|-----------|
| Mysis | Zooplankton | 1.82(.97) | .58 |
| | Dreissenid mussels | .01(1.14) | 1.00 |
| | Rainbow smelt | .24(.99) | 1.00 |
| | Bloater chub | .17(1.07) | 1.00 |
| Dreissenid mussels | Zooplankton | 1.81(.69) | .31 |
| | Rainbow smelt | .23(.72) | 1.00 |
| | Bloater chub | .16(.83) | 1.00 |
| Rainbow smelt | Zooplankton* | 1.58(0.41) | .01 |
| Bloater chub | Zooplankton | 1.66(.58) | .13 |
| | Rainbow smelt | .08(.62) | 1.00 |
| Round goby | Zooplankton* | 6.17(0.46) | .00. |
| | Mysis | 4.35(1.01) | .08 |
| | Dreissenid mussels* | 4.36(0.76) | .02 |
| | Rainbow smelt* | 4.59(.51) | .00. |
| | Bloater chub* | 4.52(.65) | .00. |
| Deepwater sculpin | Zooplankton* | 11.95 (.79) | .00 |
| | Mysis* | 10.12 (1.20) | .00. |
| | Dreissenid mussels* | 10.14 (.99) | .00. |
| | Rainbow smelt* | 10.37(.81) | .00 |
| | Bloater chub* | 10.29 (.91) | .00 |
| | Round goby* | 5.77(.84) | .00 |

Table E.3: Mean difference in lipid content (%) for species within the Main Basin.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error.

| Species | Relationship | Mean difference (SE) | p value |
|---------------------------|--------------------|-----------------------------|---------|
| Zooplankton | Dreissenid mussels | .75(2.40) | 1.00 |
| | Rainbow smelt | 2.34(2.27) | .83 |
| | Round goby | .06(2.31) | 1.00 |
| Dreissenid mussels | Rainbow smelt | 1.60(0.79) | .46 |
| Bloater chub | Zooplankton | 1.60(2.34) | .95 |
| | Dreissenid mussels | 2.36(.96) | .25 |
| | Rainbow smelt* | 3.94(0.59) | .00 |
| | Round goby | 1.66(0.73) | .19 |
| Round goby | Dreissenid mussels | .68(.90) | .93 |
| | Rainbow smelt* | 2.28(.48) | .02 |

Table E.4: Mean difference in lipid content (%) for species within Georgian Bay.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. *Mysis* were excluded due to lack of samples.

Table E.5: Mean difference in lipid content (%) for species within the North Channel.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples, *Dreissenid* mussels were excluded.

APPENDIX F

| Species | Main Basin | Georgian Bay | North Channel |
|---------------------------|-------------------|---------------------|----------------------|
| Zooplankton | 9.23(7.10) | 16.80 (12.10) | 4.42 |
| Dreissenid mussels | 15.21 (5.42) | 19.23 (2.40) | 13.92 |
| Mysis | 15.45 (8.59) | 45.90 | 13.78 (9.06) |
| Round goby | 19.98 (9.20) | 16.84(6.15) | 13.31 (3.83) |
| Rainbow smelt | 36.75 (22.91) | 17.22 (8.74) | 31.06 (9.62) |
| Bloater chub | 36.72 (11.56) | 80.21 (24.38) | 56.13 (29.81) |
| Deepwater sculpin | 47.91 (15.15) | n/a | n/a |

Table F.1: Mean mercury concentration (ng/g) for species amongst Lake Huron's 3 basins.

Note. The bracketed values indicate 1 standard deviation. The denotation 'n/a' indicatesthat samples were not collected for corresponding the species.

Table F.2: Mean difference in mercury concentration (ng/g) for study species acrossLake Huron's three basins.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples the following species were excluded: NorthChannel *Dreissenid* mussels and Georgian Bay *Mysis*.

| Species | Relationship | Mean difference (SE) | p value |
|---------------------------|---------------------|-----------------------------|---------|
| Mysis | Zooplankton | 6.21(4.28) | .76 |
| | Dreissenid mussels | .24(4.95) | 1.00 |
| Dreissenid mussels | Zooplankton | 5.98(3.66) | .68 |
| Rainbow smelt | Zooplankton* | 27.52 (4.59) | .00 |
| | Mysis* | 21.30 (5.68) | .02 |
| | Dreissenid mussels | 21.54 (5.22) | .02 |
| | Bloater chub | .02(5.44) | 1.00 |
| | Round goby* | 16.77 (5.10) | .03 |
| Bloater chub | Zooplankton* | 27.49 (3.97) | .00 |
| | Mysis* | 21.28 (5.19) | .02 |
| | Dreissenid mussels* | 21.51 (4.68) | .02 |
| | Round goby* | 16.75 (4.54) | .02 |
| Round goby | Zooplankton | 10.74 (3.47) | .08 |
| | Mysis | 4.53(4.82) | .96 |
| | Dreissenid mussels | 4.76(4.27) | .90 |
| Deepwater sculpin | Zooplankton* | 38.68 (4.77) | .00. |
| | Mysis* | 32.46 (5.82) | .00 |
| | Dreissenid mussels* | 32.70 (5.38) | .00 |
| | Rainbow smelt | 11.16 (6.05) | .53 |
| | Bloater chub | 11.18 (5.59) | .44 |
| | Round goby* | 27.93 (5.25) | .00 |

Table F.3: Mean difference in mercury concentration (ng/g) for species within the MainBasin.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate1 standard error.

Table F.4: Mean difference in mercury concentration (ng/g) for species within Georgian Bay.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate1 standard error. *Mysis* were excluded due to lack ofsamples.

Table F.5: Mean difference in mercury concentration (ng/g) for species within the North Channel.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate1 standard error. Due to lack of samples, zooplankton and *Dreissenid* mussels wereexcluded.
APPENDIX G

Table G.1: Mean lipid corrected PCB 180 content (ng/g) for species amongst Lake Huron's 3 basins.

| Species | Main Basin | Georgian Bay | North Channel |
|---------------------------|-------------------|---------------------|----------------------|
| Zooplankton | 10.06 (8.66) | 8.79 (8.58) | 8.43(6.53) |
| Dreissenid mussels | 9.70(2.80) | 5.14(0.42) | 15.81 |
| Mysis | 35.70 (12.67) | 17.44 | 29.51 (8.08) |
| Round goby | 37.29 (22.31) | 47.26 (48.20) | 19.32 (8.52) |
| Rainbow smelt | 38.54 (26.79) | 31.50 (20.66) | 13.73 (4.18) |
| Bloater chub | 90.30 (48.23) | 73.56 (82.69) | 13.30 (4.35) |
| Deepwater sculpin | 67.93 (34.48) | n/a | n/a |

Note. The bracketed values indicate 1 standard deviation. The denotation 'n/a' indicates that samples were not collected for corresponding the species.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples the following species were excluded: North Channel *Dreissenid* mussels and Georgian Bay *Mysis*.

Table G.3: Mean difference in lipid corrected PCB 180 concentration (ng/g) for species within the Main Basin.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. *Mysis* were excluded due to lack of samples.

Note. * indicates statistical significance at p< .05; the values within the brackets indicate 1 standard error. Due to lack of samples, *Dreissenid* mussels were excluded.

VITA AUCTORIS

