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THE INFLUENCE OF ONTOGENY ON RESOURCE UTILIZATION AND
CONTAMINANT DYNAMICS IN THREE FISHES WITH DIFFERENT FORAGING
STRATEGIES

by

Cecilia E. Heuvel

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

Windsor, Ontario, Canada

2018

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by
Cecilia E. Heuvel

APPROVED BY:

J. Ciborowski
Department of Biological Sciences

S. Mundle
Great Lakes Institute for Environmental Research

Y. Zhao
OMNRF Aquatic Research and Monitoring Section

A. Fisk, Co-Advisor
Great Lakes Institute for Environmental Research

D. Haffner, Co-Advisor
Great Lakes Institute for Environmental Research

April 23, 2018

DECLARATION OF CO-AUTHORSHIP/PREVIOUS PUBLICATION

I. Co-Authorship Declaration

I hereby declare that this thesis incorporates material that is the result of joint research undertaken under the supervision of my supervisors Dr. Aaron Fisk (University of Windsor) and Dr. Douglas Haffner (University of Windsor) as follows: Chapter 2 of this thesis contains material from a manuscript titled “Ontogenetic variation in isotopic niche of large bodied freshwater fishes with different feeding strategies” that will be submitted to *Freshwater Biology*, and was co-authored with G.D. Haffner, Y-M Zhao, S.C. Colborne, A. Despenic and A.T. Fisk. Chapter 3 contains material from a manuscript titled “The relative importance of ontogeny on PCB concentrations in freshwater fish” that was co-authored by A.T. Fisk, Y-M Zhao, and G.D. Haffner. The key concepts, primary contributions, data collections, laboratory work, data analysis, interpretation, and writing within both chapters was performed by the author, and the contributions of co-authors was primarily through the provision of help with data collection, laboratory work, statistical procedures, idea refinement, and editing.

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II. Previous Publication

This thesis includes 2 original papers that have been previously published/submitted for publication in peer reviewed journals, as follows:

Thesis Chapter	Publication title/full citation	Publication status
Chapter 2	Ontogenetic variation in isotopic niche of large bodied freshwater fishes with different feeding strategies	To be submitted to <i>Freshwater Biology</i>
Chapter 3	The relative importance of ontogeny on PCB concentrations in freshwater fish	To be submitted

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ABSTRACT

Ontogeny has the potential to influence the resource utilisation and contaminant dynamics of freshwater fishes but this has rarely been compared among species with different foraging strategies. Here, stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$), and PCBs (IUPAC #: 153, 138, and 180) were used to investigate differences in resource utilisation and contaminant accumulation across ontogeny among three fishes with different foraging strategies (Benthivore: freshwater drum, *Aplodinotus grunniens*; Piscivore: walleye, *Sander vitreus*; and Omnivore: white perch, *Morone americana*) in Lake Erie's western basin. All three species had distinct patterns of resource utilisation and contaminant accumulation with size (ontogeny) as indicated by their PCB concentrations and stable isotope values. This suggests that ontogeny plays an important role in trophic dynamics of freshwater ecosystems, and that a species functional role should not be categorized by their adult life stage.

DEDICATION

To my family; for all the love and support you provide.

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TABLE OF CONTENTS

DECLARATION OF COAUTHORSHIP/PREVIOUS PUBLICATION.....	iii
ABSTRACT.....	v
DEDICATION.....	vi
ACKNOWLEDGEMENTS.....	vii
LIST OF TABLES.....	ix
LIST OF FIGURES.....	xi
CHAPTER	
I. GENERAL INTRODUCTION	
1.1 Introduction.....	1
1.2 References.....	9
II. ONTOGENETIC VARIATION IN ISOTOPIC NICHE OF LARGE-BODIED FRESHWATER FISHES WITH DIFFERENT FORAGING STRATEGIES	
2.1 Introduction.....	19
2.2 Methods.....	24
2.3 Results.....	28
2.4 Discussion.....	34
2.5 References.....	40
III. THE RELATIVE INFLUENCE OF ONTOGENY ON PCB CONCENTRATIONS IN FRESHWATER FISH SPECIES WITH DIFFERENT FEEDING STRATEGIES	
3.1 Introduction.....	56
3.2 Methods.....	61
3.3 Results.....	64
3.4 Discussion.....	65
3.5 References.....	70
IV. GENERAL DISCUSSION	
4.1 Summary.....	82
4.2 References.....	86
VITA AUCTORIS.....	88

LIST OF TABLES

Chapter 1

Table 1.1	Feeding guild, key life history traits (hatch length, total length at Age 1: TL_{Age1} , maximum total length: TL_{max}) and diet of three common species (freshwater drum, walleye, and white perch) within Lake Erie's western basin. References for each trait are indicated by letters in superscripts and listed below.	18
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Chapter 2

Table 2.1	Stable isotopes (mean \pm 1 SE, unless $n < 2$) for baseline species, freshwater drum (FD), walleye (WE), and white perch (WP) in the western basin of Lake Erie over two seasons. Ranges for size classes are defined in total length as < 200 mm for small, 200-400 mm for medium, and > 400 mm for large. Fish within large size classes showed no temporal differences in isotopic composition so all fish were averaged across the entire sampling year. All baseline samples are pooled samples of multiple individuals from various sample dates and sites.	48
Table 2.2	Standard ellipses areas (SEA_B , $\%o^2$) along the $\delta^{13}C$ - $\delta^{15}N$, $\delta^{13}C$ - $\delta^{34}S$, and $\delta^{34}S$ - $\delta^{15}N$ axes for freshwater drum, walleye, and white perch. Ranges in total length for size classes are as follow: small (< 200 mm), medium (200-400 mm), and large (> 400 mm). Large fish showed no temporal variance in isotopic composition, therefore their SEA_B are representative of the entire sample year. Groups with small sample sizes ($n < 3$) were omitted from analysis (see Table 2.1).	49
Table 2.3	Overlap of niche when modelled with (A & C) 2-isotopes (carbon and nitrogen) and (B & D) 3-isotopes (carbon, nitrogen, and sulphur) in nicheROVER for spring (A-B) and summer (C-D) caught individuals. All values are listed as percentages (%) and	50

should be read as the overlap of species a in species b's niche. Each overlap value is the average of 10,000 simulations. Highlighted cells indicate interspecific niche overlap between species within the small (green), medium (orange), and large (blue) size classes. Light grey cells represent intraspecific niche overlap between size classes within a species. Groups with small sample sizes ($n < 3$ for two isotopes, $n < 5$ for three isotopes) were excluded from the analysis.

Chapter 3

Table 3.1	Lipids content (% , mean \pm 1 SE), concentrations ($\mu\text{g}/\text{kg}$ w.w., mean \pm 1 SE) of PCB 153, 138 and 180, and stable isotope values of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ (‰, mean \pm SE) for small (< 200 mm), medium (200 – 400 mm) and large (> 400 mm) freshwater drum, walleye, and white perch in the western basin of Lake Erie.	79
Table 3.2	Slopes and intercepts of regressions for log concentrations ($\mu\text{g}/\text{kg}$ w.w.) of PCB 153, 138, and 180 with total length (mm) for freshwater drum, walleye, and white perch from western basin of Lake Erie.	80

LIST OF FIGURES

Chapter 2		
Figure 2.1	Sampling locations of baseline species (benthic invertebrates and seston) within the western basin of Lake Erie for the OMNRF lower trophic level monitoring program with coordinates and depth. The dashed line represents the Canada-US border.	52
Figure 2.2	Trends in $\delta^{13}\text{C}$ (top row), $\delta^{15}\text{N}$ (middle row), and $\delta^{34}\text{S}$ (bottom row) with total length for freshwater drum (a-c), walleye (d-f), and white perch (g-i) with total length. Dashed black lines and open circles are significant linear relationships within the spring, and solid black lines and filled in squares are significant relationships during the summer.	53
Figure 2.3	SIBER stable isotope ellipses (SEA_B) estimating the isotopic niche of freshwater drum (a-c), walleye (d-f), and white perch (g-i) for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (top), $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ (middle), and $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$ (bottom) across size classes (Small >200 mm: solid lines and triangles, Medium 200-400mm: dashed lines and squares, and Large >400mm: blue circles and blue dashed lines) and seasons (spring: green, summer: red, year round (large only): blue). No large white perch or small summer walleye were caught during the study period; thus, they were omitted from the analysis.	54
Figure 2.4	SIBER stable isotope ellipses estimating the variation in niche among species (freshwater drum: triangles and solid lines, walleye: squares and dashed lines, and white perch: circles and dot-dashed lines) and seasons (spring: green, summer: red, year-round: blue) at different size classes (Small <200mm [a-c], Medium 200-400mm [d-f], and Large >400mm [g-i]) for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (top), and $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ (bottom). Ellipses represent the standard ellipses area (SEA_C) of each niche. No large white perch or small summer walleye were caught during the study period; thus, they were omitted from the analysis.	55

Chapter 3

Figure 3.1 Relationships of PCB 153, 138 and 180 with total length based on 81 concentrations measured in freshwater drum (green triangles), walleye (red squares) and white perch (blue circles). Relationships that were marginally significant are dotted lines ($p < 0.1$), and significant relationships are solid lines ($p < 0.05$).

CHAPTER I: GENERAL INTRODUCTION

1.1 Introduction

1.1.1 Food Web Theory

Food webs are representations of our understanding of the trophic relationships between predators and prey in the natural world (Lindeman, 1942; Hutchinson, 1959; Hairston & Hairston, 1993; Pimm, 2002; McCann, 2007). They provide an indication of species interactions, as well as energy and nutrient flow throughout ecosystems (Hairston & Hairston, 1993; Moore *et al.*, 2004). As a result, our understanding of ecosystems depends on how we are able to identify and measure factors influencing food web structure (Gao, Barzel & Barabási, 2016; McMeans *et al.*, 2016). To this end, there are four main hypotheses that attempt to explain why food webs might be structured the way they are and why the number of trophic levels in any given food web is limited: 1) Hutchinson's energetic limitation hypothesis, 2) Pimm's dynamic stability hypothesis, 3) Pavar's dimensionality hypothesis, and 4) McCann's predator mobility hypothesis. It is important to note that while each hypothesis makes different arguments for food web structure, they are not mutually exclusive and each may be true to some extent.

Lindeman (1942) and Hutchinson (1959)'s energetic limitation hypothesis posits that the number of trophic levels within any given food web is limited due to the amount of energy within an ecosystem. Solar radiation is fixed by primary producers, creating a limited pool of energy for consumers to utilize and regulating the productivity of the system from the bottom up (Pimm, 2002). As energy is transferred (i.e. consumed) to higher trophic levels, energy is lost through respiration, waste production, growth, and

inefficient assimilation by consumers, so that there is less energy available at upper trophic levels than lower ones (Lindeman, 1942; Hutchinson, 1959; Pimm, 2002). Within this hypothesis, other basal energy sources (e.g. detritus) are created from dying or dead organisms that were not consumed by higher trophic levels and which can fuel microbial and detrital energy pathways (Lindeman, 1942; Wetzel, 1995; Vadeboncoeur et al., 2002; Moore et al., 2004). These additional energy pathways broaden the basal energy supply by allowing other consumers to exploit energy that would otherwise be lost from the ecosystem through the death of organisms and contribute to higher trophic levels through benthic pathways as detritus (Wetzel, 1995; Vadeboncoeur et al., 2002; Moore et al., 2004).

Alternatively, Stuart Pimm concludes that population dynamics govern food web structure (Pimm & Lawton, 1977). This hypothesis states that as the number of trophic levels increases, it will take longer for an ecosystem to return to its original state after a disturbance (i.e. its return time), and the less likely it is that the ecosystem will recover to its original state (Pimm & Lawton, 1977; Pimm, 2002). Population dynamics of species tend to be habitually variable due to stochastic environmental conditions, which require individuals to trade off reproductive effort, growth, and survival (Jørgensen & Holt, 2013). Environmental conditions may dictate that a given ecosystem is unable to support a third or fourth trophic level simply because there isn't enough solar energy fixed by primary producers to maintain a population of primary or secondary predators over time (Pimm, 2002). Additionally, while Pimm argues that it is advantageous for species to feed on lower trophic levels because more food is available there (Pimm & Lawton, 1977), at its core, this hypothesis seems to return to this idea of energy limitation, as a

greater availability of food translates into more energy for an individual to consume and subsist off of (Hutchinson, 1959; Wetzel, 1995; Moore et al., 2004; Vadeboncoeur et al., 2005).

Pawar's dimensionality hypothesis states that the length of chains in food webs could be longer in 3-D environments (e.g. the pelagic zone of a lake) than 2-D environments (e.g. the benthic zone of a lake) because it minimizes the energetic costs of foraging for organisms (Briand & Cohen, 1987; Cohen & Fenchel, 1994; Pawar, Dell & Savage, 2012). This hypothesis builds upon the empirical generalization of Briand and Cohen (1987) who suggested searching for prey in a 3-D environment maximized the probability of encountering prey. As well, predators foraging in a 3-D environment can search a larger area simultaneously because its range of detection (e.g. sight, sound, smell, etc.) has an extra axis (3 vs. 2) rather than a flattened circle as it would be in a 2-D search environment (Briand & Cohen, 1987; Pawar *et al.*, 2012).

Similarly, McCann's predator mobility hypothesis states that food web structure is limited by the mobility of the top predator linking resources and habitat across spatially expansive food webs (e.g. large lakes, oceans; McCann et al., 2005). Since large predators tend to have a low trophic efficiency as a result of the high cost of activity, greater mobility allows predators to switch prey and habitat to optimize energy flow (McCann *et al.*, 2005; Rooney, McCann & Moore, 2008; McMeans *et al.*, 2016). The central tenet of this hypothesis, as with the other three, seems to centre around the energy consumption and expenditure of an organism, suggesting that the flow of energy within ecosystems could be driving the structure of food webs (Hutchinson, 1959; Briand &

Cohen, 1987; Cohen & Fenchel, 1994; Moore *et al.*, 2004; McCann *et al.*, 2005; Vadeboncoeur *et al.*, 2005; Pawar *et al.*, 2012; McMeans *et al.*, 2016).

If energy flow and trophic links between different functional groups are driving the structure of food webs then understanding how energy is transferred through food webs is increasingly important to understanding ecosystem structure, and we must move away from a single species management to an ecosystem-based approach to fully comprehend a community's structure within a system (McMeans *et al.*, 2016). The identity of a species is not as important as its functional role within the ecosystem, since different species can functionally fill the same role, creating functional redundancy (Hilborn *et al.*, 2003; McCann, 2007; Gao *et al.*, 2016), and foraging strategies offer a method of differentiating a species' function within the ecosystem (McMeans *et al.*, 2016).

1.1.2 Quantifying Food Webs

Quantifying the strength of trophic links within ecosystems continues to be a major challenge for managing freshwater ecosystems and is dependent on the amount and types of resources available for species to utilize (Hairston & Hairston, 1993; Ney, 1993; Chipps & Wahl, 2008; McMeans *et al.*, 2016). Stable isotopes (e.g. carbon, $\delta^{13}\text{C}$; nitrogen, $\delta^{15}\text{N}$; and sulphur, $\delta^{34}\text{S}$) provide an indication of energy flow by acting as tracers of trophic position and resource use of a species (Vander Zanden, Casselman & Rasmussen, 1999; Vander Zanden & Vadeboncoeur, 2002; Rowland *et al.*, 2015; McMeans *et al.*, 2016). The value of $\delta^{15}\text{N}$ is indicative of trophic position, whereas $\delta^{13}\text{C}$ can be used to differentiate between benthic/littoral and pelagic primary production, which provides insight into which resources predators exploit (Post, 2002; Guzzo *et al.*, 2011). Additionally, recent research incorporating $\delta^{34}\text{S}$ as a third isotope has indicated

that sulphur can be used to trace benthic and water column (i.e. pelagic) habitat use (Colborne *et al.*, 2016). The three isotopes in conjunction can be used to understand niche, as a species' isotopic signature will be higher in $\delta^{15}\text{N}$ compared to its diet, whereas $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ will be a mixture of different prey source isotopes (Fry, 2007; Colborne *et al.*, 2016).

Recent developments in our knowledge of contaminant dynamics suggest that persistent organic compounds (POPs), such as polychlorinated biphenyls (PCBs), are also good tracers to quantify energy flow within aquatic ecosystems, due to their stability, ubiquity and hydrophobicity (Norstrom, McKinnon & DeFreitas, 1976; Hebert & Haffner, 1991; Fisk *et al.*, 2002; Paterson *et al.*, 2005; Burtnyk *et al.*, 2009; McLeod *et al.*, 2015). Elimination rates of PCBs with Log K_{ow} greater than 6.3 are negligible compared to the lifespan of most aquatic fish species, and these compounds are accumulated almost solely through an individual's diet (Fisk *et al.*, 1998; Russell, Gobas & Haffner, 1999; Paterson, Drouillard & Haffner, 2007a; Paterson *et al.*, 2007b), thus acting as a relatively accurate tracer of the energy consumed and assimilated by an individual within its lifetime (Paterson *et al.*, 2005).

1.1.3 Influencing Food Web Structure: Environmental Stressors

Aquatic ecosystems are changing due to anthropogenic climate change, overharvesting, invasive species, and other environmental stressors which are changing the structure, function, and energy movement within food webs (Hecky *et al.*, 2004; Paterson *et al.*, 2009; Steffen *et al.*, 2014). Many of these anthropogenic stressors are driven by increased aquaculture and urbanization, which often unintentionally change freshwater ecosystems with little understanding of the consequences to ecosystem health

and resilience (Paterson *et al.*, 2009). Our understanding of the impacts of anthropogenic stressors is further confounded by the complexity of processes governing freshwater ecosystems (McMeans *et al.*, 2016). Furthermore, research efforts often target large, commercially important top predators, or conversely focus on primary production within ecosystems, thus limiting the scope of focus to the narrowest or widest points of the food web and generally ignoring species located at intermediate trophic levels (e.g. detritivores, omnivores; Boecklen *et al.*, 2011). However, recent findings suggest that management efforts should protect ecosystem function and biological structure instead of species (McMeans *et al.*, 2016), since fishery production is dependent on species interactions responsible for energy and nutrient flow at an ecosystem level (Paterson *et al.*, 2005).

1.1.4 The Laurentian Great Lakes

The Laurentian Great Lakes, hereafter Great Lakes, are one of the largest freshwater systems in the world, accounting for 20% of its available freshwater resources (Steffen *et al.*, 2014). Anthropogenic stressors, such as those mentioned above, have driven many ecological (Smith, 1972; Mills *et al.*, 2003; Dobiesz *et al.*, 2005), chemical (Howell *et al.*, 1996; Dobiesz *et al.*, 2005), and physical changes (Smith, 1972; Lynch, Taylor & Smith, 2010) within the lake ecosystems, threatening their health and survival. The magnitude of each stressor's impact on each lake varies but there is little doubt that the Great Lakes of today are very different than those first encountered by European settlers in the 17th century (Smith, 1972; Mills *et al.*, 2003).

1.1.5 Lake Erie

Of the Laurentian Great Lakes, Lake Erie is likely the most threatened by anthropogenic stressors, of which cultural eutrophication is a particular concern (Richards, Calhoun & Matisoff, 2002; Bridgeman, Chaffin & Filbrun, 2013; Kane *et al.*, 2014; Steffen *et al.*, 2014). Lake Erie is one of the most densely populated lakes in the basin and as a result is heavily impacted by agriculture, industry, and urbanisation (Richards *et al.*, 2002; Steffen *et al.*, 2014). Located within a region of prime agricultural land, the lake is swathed by heavily farmed acreage which has resulted in cultural eutrophication of the lake and recurring, often toxic, cyanobacterial blooms within the lake's western basin (Bridgeman *et al.*, 2013; Steffen *et al.*, 2014).

Algal blooms became so severe in the 1960's and 70's that the lake was termed "dead" by the media, and major rehabilitation efforts (e.g. the Great Lakes Water Quality Agreement, 1972) were mounted to bring the lake back to health (Bridgeman *et al.*, 2013; Steffen *et al.*, 2014). Early efforts succeeded in lowering phosphorus loadings to the lake through improved sewage treatment and reduced the occurrence of harmful algae blooms. However, blooms have begun reoccurring since the mid-1990's (Kane *et al.*, 2014; Steffen *et al.*, 2014). Nutrient loadings (e.g. soluble reactive phosphorus) from tributaries (particularly the Maumee River) draining into the western basin have been correlated with increases in harmful algal biomass (Joosse & Baker, 2011; Kane *et al.*, 2014; Watson *et al.*, 2016).

Lake Erie supports the largest commercial freshwater fishery globally, of which a major constituent is Walleye (*Sander vitreus*; Vandergoot *et al.*, 2010; Stepien *et al.*, 2012). As a result, in addition to its value as a source of freshwater to residents of the

Great Lakes, Lake Erie also holds economic value for those involved in the fisheries (Vandergoot *et al.*, 2010; Stepien *et al.*, 2012). As such, not only is it critical for the lake to be clean but also able to support a sustainable commercial fishery (Hartman, 1972; Hartman & Margraf, 1992; Stepien *et al.*, 2012; Steffen *et al.*, 2014). Consequently, any knowledge pertaining to the trophic interactions of commercially important species within the lake is critical to maintaining and managing commercial fisheries and sustaining them into the future (Hartman, 1972; Hartman & Margraf, 1992; Sarvala, 1992; McMeans *et al.*, 2016). However, these commercially important species subsist upon other organisms within the lake, and thus, knowledge of the dynamics of other species is important to set sustainable catch limits (Hartman & Margraf, 1992; Sarvala, 1992; Hall, Alverson & Metzals, 2000).

1.1.6 Study Species

Freshwater drum (*Aplodinotus grunniens*), walleye, and white perch (*Morone americana*) are three common, similarly sized fish species within Lake Erie's western basin. All three fishes have distinct life history traits and utilize different feeding strategies, which make them good species to compare differences in resource utilisation and trophic position (Table 1). In brief, freshwater drum is a large benthivore that primarily preys on benthic invertebrates and Bivalvia mussels (Bur, 1982; French & Bur, 1996; Scott & Crossman, 1998; Corkum, 2010). Walleye is among the top predators of the western basin of Lake Erie and transitions to piscivory rapidly within its first year of life (Mittelbach & Persson, 1998; Scott & Crossman, 1998), and white perch is a generalist omnivore that feeds on a wide variety of prey (e.g. zooplankton, benthic invertebrate, fish, fish eggs) throughout the course of its life (Schaeffer & Margraf, 1987;

Parrish & Margraf, 1990; Mittelbach & Persson, 1998; Scott & Crossman, 1998; Guzzo *et al.*, 2013). Of the three species, walleye has the fastest growth, and white perch grows the slowest (Bur, 1984; Mittelbach & Persson, 1998; Scott & Crossman, 1998).

1.1.7 Objectives and Hypotheses:

A deeper understanding of how different feeding strategies affect trophic positions and resource use across a wide range of sizes. Lake Erie is a good system to conduct this sort study as it is home to a number of appropriate species, is an important fishery, and very little research has been conducted on the fish community, particularly in recent years. Additionally, few isotope or contaminant studies have been conducted on any of the species mentioned above, making them good species to target to learn more about their ecology. As such, the objective of my research will be divided into two research chapters with the ultimate goal to quantify the resource utilisation in each foraging strategy over a range of sizes:

- 1) To determine how habitat use and trophic position changes with size of fishes within three different foraging strategies in Lake Erie's western basin using stable isotope analysis (SIA, Chapter 2).
- 2) To determine the extent of resource partitioning between three common species with different feeding strategies in western Lake Erie (Chapter 2).
- 3) To investigate the relative role of ontogeny in quantifying the contaminant dynamics of PCBs within three Lake Erie fish species (Chapter 3).

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Table 1.1: Feeding guild, key life history traits (hatch length, total length at Age 1: TL_{Age1}, maximum total length: TL_{max}) and diet of three common species (freshwater drum, walleye, and white perch) within Lake Erie’s western basin. References for each trait are indicated by letters in superscripts and listed below.

Species	Feeding Guild	Hatch Length (mm)	TL _{Age1} (mm)	TL _{max} (mm)	Diet
Freshwater Drum	Benthivore ^{a,b}	3.2 – 4.4 ^c	157 ^{a,d}	750 ^d	Young of the year (YOY, < 100 mm): initially zooplankton (primarily cladoceran), with increasing dependence on benthic invertebrates (primarily chironomids), Age 1-5 (100 – 300 mm): benthic invertebrates (chironomids), zooplankton (cladoceran), eventually fish Age 6+ (> 300 mm): decapods, small Bivalvia, fish, dreissenid mussels <i>a,b,e,f</i>
Walleye	Piscivore ^{a,g,h}	6.0 – 8.6 ^{a,g}	206 ^{a,g}	790 ^{a,g}	YOY (< 200 mm): zooplankton, and benthic invertebrates, before transitioning to fish Age 1+ (>200 mm): Fish predominately, some benthic invertebrates <i>a,f,j</i>
White Perch	Omnivore ^{g,k,l,m}	1.7 – 3.0 ^{a,m}	87 ^{a,g}	495 ^{a,g,m}	YOY – Age 3 (< 200 mm): Zooplankton, benthic invertebrates, insect larvae Age 3+ (> 200 mm) Zooplankton, benthic invertebrates, fish eggs, fish, dreissenid mussels ^{a,f,k,l,n}

References: a) Scott & Crossman, 1998; b) Bur, 1982; c) Swedberg & Walburg, 1970; d) Bur, 1984; e) French & Bur, 1996; f) Corkum, 2010; g) Mittelbach & Persson, 1998; h) Overman & Parrish, 2001; i) Hartman & Margraf, 1992; j) Vander Zanden *et al.*, 1997; k) Guzzo *et al.*, 2013; l) Schaeffer & Margraf, 1987; m) Stanley & Danie, 1983; n) Parrish & Margraf, 1990

CHAPTER II:
ONTOGENETIC VARIATION IN ISOTOPIC NICHE OF LARGE-BODIED
FRESHWATER FISHES WITH DIFFERENT FORAGING STRATEGIES

2.1 Introduction

Ecological niche can be determined by numerous factors over the course of ontogeny. Two of the most common are diet and habitat use (Werner & Gilliam, 1984; Post, 2003), resulting from trade-offs between resource availability, interspecific competition, and predation risk (Werner & Hall, 1988). Diet in fish is often regulated by gape width, with a transition from smaller to larger prey as an individual grows. One example of this are juvenile piscivore fish, which typically feed on zooplankton/small invertebrates but switch to larger invertebrates and fish as they grow (Amundsen *et al.*, 2003; Post, 2003; Galarowicz, Adams & Wahl, 2006). Less is known about ontogenetic shifts in other feeding guilds (e.g. planktivores, benthivores), but there is evidence to suggest that piscivores are not the only group that undergo changes in niche due to ontogeny (Werner & Hall, 1988; Ng *et al.*, 2008).

Shifts in diet can also be associated with changes in habitat use and may indicate a trade-off between optimal foraging, environmental conditions, and survival (Werner & Gilliam, 1984; Byström *et al.*, 2004; Galarowicz *et al.*, 2006). Three main habitats exist in freshwater lakes for organisms to exploit: the littoral zone which generally has depths less than 5 m and is populated by emergent or submergent macrophytes; the benthic zone which is the part of the lake bed located at depths greater than 5 m; and, the pelagic zone, a region of the lake with depths greater than 5 m located in the open water (Wetzel, 2001). Smaller individuals are more vulnerable to predation and may use suboptimal

habitat (e.g., reduced food resources, suboptimal temperatures) to avoid predators, but this danger will decrease with increasing size allowing selection of better habitat with optimal resources and a lower risk of predation. Bluegill (*Lepomis macrochirus*) have been shown to shift from a predominately littoral (e.g. invertebrates) to a pelagic diet (e.g. zooplankton) at a discrete size threshold to maximize prey quality and minimize both predation risk and resource competition with the closely related pumpkinseed sunfish (*Lepomis gibbosus*; Werner & Hall, 1988). As well, under high predation pressure individuals cannot be as selective about prey items (i.e. more generalized diets) which would result in larger niche exploitation by the population (Eklöv & Svanbak, 2006).

Niche can also be influenced by resource partitioning, likely to reduce resource competition within communities (Schoener, 1974; Ross, 1986), or can be the result of past interactions. For example, Coregonids within the Laurentian Great Lakes (hereafter Great Lakes) partition habitat resources among species and morphs by depth while foraging for similar prey found across a depth gradient (Schmidt, Harvey & Vander Zanden, 2011). Resource partitioning among species may also change with ontogeny. A species that feeds littorally throughout its juvenile stage but switches to a pelagic diet when it matures will not only alter diet, but also the species it interacts with (Werner & Gilliam, 1984; Werner & Hall, 1988; Byström *et al.*, 2003).

Despite the possibility of changes in niche driven by ontogeny, a species ecological role is primarily defined by later or larger life stages. Moreover, most research conducted on ontogenetic variation of niche in piscivores focuses on the early life history or until the switch to piscivory has occurred (e.g. larval, fry and early juvenile stages) and often does

not look at further changes as the fish continues to grow (Mittelbach & Persson, 1998). Given that different life stages of species should be assessed in fisheries models and management, there is a need to understand how niche changes with ontogeny (Werner & Gilliam, 1984). Management decisions are frequently based on the early life stages of fishes (e.g. spawning habitat, larval requirements) and their role within the community as adults when they are likely to be harvested, but less consideration is given to intermediate life history stages when they may interact with species completely unrelated to their larval and adult life histories. As such, we may be missing information about the role of species at critical life stages during their development. For instance, Lake Erie is home to one of largest commercial freshwater fisheries in the world, focused largely on the piscivore walleye (*Sander vitreus*; Vandergoot *et al.*, 2010; Stepien *et al.*, 2012). Walleye undergo a series of ontogenetic diet shifts within their first year of life as they shift from consuming primarily zooplankton and benthic invertebrates to fish (Graeb *et al.*, 2005; Galarowicz *et al.*, 2006). As a result of this transition, young of the year (YOY) walleye may experience interspecific competition with different species than they do after their transition to a piscivorous diet (Werner & Gilliam, 1984; Byström *et al.*, 2003), and knowledge of the dynamics of other species within the system would potentially help explain changes in walleye population structure and size (Hartman & Margraf, 1992; Sarvala, 1992; Hall, Alverson & Metuzals, 2000). Thus, taking a broader ecosystem approach to fisheries management would allow managers to understand how the ecological niche of commercially important species within the lake contribute to the larger food web, and potentially help identify bottlenecks (Hartman, 1972; Hartman & Margraf, 1992; Sarvala, 1992; McMeans *et al.*, 2016).

Stable isotopes provide a metric to quantify ecological niche because the isotopic space (i.e. isotopic niche) reflects diet and habitat use (Fry, 2007; Layman *et al.*, 2007; Newsome *et al.*, 2007). Carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) stable isotopes have been used as indicators of habitat use and trophic position, respectively, in both aquatic and terrestrial ecosystems (Post, 2002; Boecklen *et al.*, 2011; Nawrocki *et al.*, 2016). Sulphur stable isotopes ($\delta^{34}\text{S}$) are used predominately to quantify marine versus freshwater habitat use, but recently they have been used to differentiate between open water and benthic habitats in freshwater ecosystems (Newsome *et al.*, 2007; Croisetière *et al.*, 2009; Colborne *et al.*, 2016). While two isotope niche analysis is most commonly used, recent research suggests that three isotopes can provide better resolution, especially when there is little difference in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ between sources (Phillips & Gregg, 2003; Swanson *et al.*, 2015; Colborne *et al.*, 2016).

Lake Erie provides a good freshwater ecosystem for investigating the role ontogeny plays in defining ecological niche and how this can vary across species with different feeding strategies. Lake Erie is large (25,700 km²) and home to over 130 fish species, a number of which reach similar adult sizes but have different feeding strategies (Hartman, 1972; International Joint Commission, 2014). A large number of forage species and young of the year (YOY) fish, including the freshwater drum (*Aplodinotus grunniens*), use open water habitat (Gopalan *et al.*, 1998). To this end, we quantified isotopic niche, using three isotopes, in three fish species that reach a similar maximum size but belong to different feeding guilds within the western basin of Lake Erie to assess the influence of ontogeny. The three species included: a benthivore, freshwater drum (max length: 750 mm; Bur, 1982, 1984); a piscivore, walleye (max length: 790 mm; Mittelbach & Persson,

1998; Scott & Crossman, 1998); and an omnivore, white perch (*Morone Americana*, max length: 495 mm; Stanley & Danie, 1983; Guzzo *et al.*, 2013). Freshwater drum in Lake Erie undergo two distinct transitions in diet, where individuals ≤ 150 mm are primarily benthic feeders, switch to a pelagic diet between 150-250 mm, and then revert back to mainly benthic at lengths ≥ 250 mm (Bur, 1982; French & Bur, 1996; Morrison, Lynch & Dabrowski, 1997). Walleye are specialist piscivores and are the most abundant predator in the lake's western basin (Hartman & Margraf, 1992; Vandergoot *et al.*, 2010; Stepien *et al.*, 2012). Large walleye (> 400 mm) are able to consume prey fish with a maximum total length of 300 mm, although the average is closer to 200 mm (Overman & Parrish, 2001). As a result, fish less than 200 mm in total length in western Lake Erie likely face high predation pressure, which lessens as they approach 300 mm.

The goal of this research is to investigate ontogenetic variation in isotopic niche in three freshwater fishes of similar adult size. We hypothesized that these species will partition resources within similar size classes among species and between size classes within species. Such strategies would be indicated by low degrees of overlap in isotopic niche. More specifically we addressed the following hypotheses: H₁) There will be a greater isotopic niche overlap in the smaller than larger size classes between species because smaller individuals cannot be as selective about prey; H₂) there will be a shift in resource use from benthic/littoral habitat containing refuge from predators to pelagic habitat with little refuge for walleye and white perch, indicated by a negative relationship for $\delta^{13}\text{C}$ and increasing total length, and a positive relationship for $\delta^{34}\text{S}$ and total length; and H₃) a shift toward more littoral/benthic resource use by freshwater drum from pelagic zooplankton through ontogeny, indicated by a positive relationship for $\delta^{13}\text{C}$ with total

length and a negative relationship for $\delta^{34}\text{S}$ with total length. Finally, we tested the hypothesis that three isotopes would decrease the degree of overlap between baseline resources and provide more resolution than two, based on previous work done on Great Lakes' fish (e.g. Colborne *et al.*, 2016).

2.2 Methods

2.2.1 Location and Sample Collection:

Walleye (n = 73), white perch (n = 64), and freshwater drum (n = 136) were collected from the western basin of Lake Erie during the annual fish community trawl surveys conducted by the Ohio Department of Natural Resources (ODNR), Ohio United States Geological Survey (Ohio USGS), and Ontario Ministry of Natural Resources and Forestry (OMNRF) during May, June, August, September, and November 2016. No white perch larger than 350 mm in total length were caught over the duration of the sampling period, and only walleye larger than 400 mm were caught during September and November. Seston, dreissenid mussels, and benthic invertebrates were also collected as resource baselines to compare the study species from four sites in the western basin on a bi-weekly basis from the OMNRF lower trophic level monitoring program (Figure 2.1). Samples were put on ice and transported to the Great Lakes Institute for Environmental Research (GLIER) at the University of Windsor and stored at -20 °C for later sample preparation. Upon dissection, the total length and weight of each fish was measured and a white muscle sample was taken between the pectoral and dorsal fins for stable isotope analysis.

2.2.3 Stable Isotope Analysis: Sulphur, Carbon, and Nitrogen

Muscle samples were lyophilized at $-48\text{ }^{\circ}\text{C}$ and $133 \times 10^3\text{ mbar}$ for 48 hours, and then homogenized into a fine powder by hand using a mortar and pestle or dissection scissors. For sulphur ($\delta^{34}\text{S}$), freeze dried samples were weighed into tin cups (sample mass 6000-6500 μg) without any further processing and analyzed on a Delta V Plus ThermoScientific Continuous Flow Mass Spectrometer (Thermo Scientific, Bremen, Germany) coupled to a 4010 Elemental Combustion System (Costech Instruments, Valencia, CA, USA) in the GLIER Chemical Tracers Laboratory. Instrument accuracy throughout the period of sample analysis, as measured by NIST standards ($n = 41$ for all), was 0.2‰ (NIST 8554), 0.3‰ (NIST 8555), and 0.1‰ (NIST 8529). Precision, as measured by five internal laboratory standards (NIST 1577c, NIST 8529, NIST 8555, tilapia muscle, and USGS 42; $n = 18$ for each) was $\leq 0.3\text{‰}$. Reproducibility of sample replicates (run in duplicate for every eighth sample) was $\pm 0.1\text{‰}$ ($n = 12$) and was within the generally accepted $\pm 0.3\text{‰}$ range.

Lipids have been shown to bias $\delta^{13}\text{C}$ in fish muscle compared to pure protein (Fry *et al.*, 2003; Boecklen *et al.*, 2011), thus lipids were extracted using a 2:1 chloroform:methanol mixture to remove this bias (Colborne *et al.*, 2016; Nawrocki *et al.*, 2016). Briefly, approximately 0.5 g of muscle tissue were subsampled and 1.9 mL of a 2:1 chloroform:methanol mixture added to each and vortexed. Samples were left in a water bath (30°C) for 24 hours and then centrifuged for 4-6 minutes to separate tissue from lipids in the supernatant. The 2:1 chloroform:methanol mixture was poured off, and the process was repeated a second time. Afterwards the samples were dried and re-ground into a fine powder.

Samples for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis were weighed into tin cups for a final mass of 400-600 μg . Carbon and nitrogen isotopic composition were determined using a Delta V Advantage ThermoScientific Continuous Flow Mass Spectrometer (Thermo Scientific, Bremen, Germany) coupled to a 4010 Elemental Combustion System (Costech Instruments, Valencia, CA, USA). NIST standards run during the analysis of samples during this study had values for $\delta^{15}\text{N}$ within 0.1‰ (NIST 8573 and NIST 8574), and 0.2‰ (NIST 8547), and for $\delta^{13}\text{C}$ within 0.1‰ (NIST 8573, 8542, and 8544) of certified values. Precision of four laboratory standards (NIST 1577c, tilapia muscle, USGS 40 and Urea (n = 104 for each)), run every 12 samples, were 0.2‰ for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Sample reproducibility of sample tissue replicates (measured in triplicate every 10 samples) was $\pm 0.1\%$ (n = 83) for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and was within the acceptable $\pm 0.2\%$ range.

2.2.4 Statistical Analysis

Non-parametric statistical tests (e.g. Kruskal-Wallis) were conducted as some data did not meet the assumptions of normal distributions [Shapiro-Wilks test; $\delta^{13}\text{C}$ for summer freshwater drum ($p \leq 0.003$), spring white perch ($p = 0.01$ for both), and small summer white perch; $\delta^{15}\text{N}$ for spring small freshwater drum ($p = 0.001$), medium spring walleye ($p = 0.001$) and medium summer white perch ($p = 0.04$), and $\delta^{34}\text{S}$ for large freshwater drum and walleye ($p \leq 0.002$)] or equal variances [Levene's test: $\delta^{13}\text{C}$ for the between spring and summer freshwater drum size classes and between summer white perch size classes models ($p \leq 0.03$ for all), and $\delta^{15}\text{N}$ for between spring and summer freshwater drum size classes, between species in the small size class, and between summer white perch size classes ($p \leq 0.04$ for all)].

Seasonal shifts in isotopic composition have been shown to be present in a previous study on fish in Lake Erie (e.g. Guzzo *et al.*, 2011). Kruskal-Wallis tests indicated that there were significant differences in isotope values for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ between individuals caught in the spring (May and June) and those caught in the summer (August, September, and November) in the small and medium size classes, so fish were grouped according to the season they were caught in. Only large walleye (> 400 mm total length) were caught during September and November, and because fish larger than 400 mm showed no significant temporal differences in isotope values, the large size class was treated as a single group in all further statistical analyses.

Length was used as a proxy of age because they are highly correlated in each of the species used here (Hile, 1954; Bur, 1984; Schaeffer & Margraf, 1986; Henderson & Morgan, 2002). Relationships between isotope values and total length for each species were assessed using linear regressions (dependent variable: $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, or $\delta^{34}\text{S}$; independent variable: total length).

Fish were grouped into three size classes (small: <200 mm, medium: 200-400 mm, and large: >400 mm) for further statistical analysis, according to the expected changes in resource use by freshwater drum and white perch (Bur, 1982; Stanley & Danie, 1983; Morrison *et al.*, 1997; Guzzo *et al.*, 2013), and the maximum prey size walleye are likely to consume (Hartman & Margraf, 1992). Kruskal-Wallis tests were performed to assess differences between size classes within species, and among species within size classes for each isotope and by season. Post hoc tests (Dunn's test) among species and seasons for each isotope were conducted if there were significant differences between size classes or among species.

2.2.5 Isotopic Niche Analysis

Despite the data following nonparametric distributions, Bayesian analyses methods were used to analyse isotopic niche because they have been shown to be robust to deviations from normality (Syväranta *et al.*, 2013). Standard ellipses area (SEA_B) was calculated in SIBER (Stable Isotope Bayesian Ellipses in R) to summarize niche size along the carbon-nitrogen ($\delta^{13}C$ - $\delta^{15}N$) axis, the carbon-sulphur ($\delta^{13}C$ - $\delta^{34}S$) axis, and the sulphur-nitrogen ($\delta^{34}S$ - $\delta^{15}N$) axis within species and among species (Jackson *et al.*, 2011). The nicheROVER (Niche Region and Niche Overlap Metrics for Multidimensional Ecological Niches) package was used to model the degree of niche overlap in two ways: 1) two isotopes using $\delta^{13}C$ and $\delta^{15}N$, the isotopes most frequently used in niche and foraging studies, and; 2) a three isotope model incorporating $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ (Swanson *et al.*, 2015). We considered niche overlap to be biologically significant if it was greater than 60% based on the criteria used for stomach contents (e.g. Schoener's diet overlap index; Gopalan *et al.*, 1998; Cabral, Lopes & Loeper, 2002). All statistical analysis was conducted in R version 3.4 (R Core Team, 2017).

2.3 Results

Carbon stable isotopes in baseline samples (e.g. benthic invertebrates and seston) ranged from -19.6 ‰ (n = 1) in amphipods to -29.8 ‰ (± 0.9 SE, n = 3) in Chironomidae, and most were lower than the three fish species (Table 2.1). Nitrogen stable isotopes in the baseline were around half (mean: 7.5 ‰) those measured in the fish species and ranged from 6.1 ‰ (± 0.5 SE, n = 7) in spring seston to 12.0 ‰ (n = 1) in Planariidae (Table 2.1). A wide range of sulphur stable isotopes (-1.4 ± 0.4 ‰ in Chironomidae to 6.0

± 0.6 ‰ in summer seston) were measured in the baseline, which were comparable to $\delta^{34}\text{S}$ in the fish species (0.4-3.5 ‰; Table 2.1).

2.3.1 Relationships between stable isotopes and length by season

Freshwater drum exhibited significant linear relationships between length and $\delta^{13}\text{C}$ for spring captured individuals ($R^2 = 0.09$, $F_{1,47} = 5.8$, $p = 0.02$) but not summer ($R^2 = -0.01$, $F_{1,47} = 0.2$, $p = 0.7$), both seasons were significant for $\delta^{15}\text{N}$ and length (spring: $R^2 = 0.45$, $F_{1,47} = 41.0$, $p < 0.001$; summer: $R^2 = 0.14$, $F_{1,85} = 5.8$, $p < 0.001$), but neither season had $\delta^{34}\text{S}$ values related to length (spring: $R^2 = 0.09$, $F_{1,24} = 3.4$, $p = 0.07$; summer: $R^2 = -0.04$, $F_{1,20} = 5.8$, $p = 0.7$; Figure 2.2a-c). Walleye had significant relationships with total length for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in the summer ($\delta^{13}\text{C}$: $R^2 = 0.15$, $F_{1,29} = 6.2$, $p = 0.02$; $\delta^{15}\text{N}$: $R^2 = 0.53$, $F_{1,29} = 35.3$, $p < 0.001$) but not the spring ($\delta^{13}\text{C}$: $R^2 = -0.02$, $F_{1,40} = 0.0$, $p = 1.0$; $\delta^{15}\text{N}$: $R^2 = 0.04$, $F_{1,40} = 2.8$, $p = 0.1$), nor $\delta^{34}\text{S}$ in either season (spring: $R^2 = -0.04$, $F_{1,20} = 0.2$, $p = 0.6$; summer: $R^2 = 0.10$, $F_{1,16} = 2.9$, $p = 0.1$; Figure 2.2d-f). White perch had no significant relationships with any isotope measured with total length during the spring ($\delta^{13}\text{C}$: $R^2 = -0.01$, $F_{1,49} = 0.5$, $p = 0.5$; $\delta^{15}\text{N}$: $R^2 = 0.02$, $F_{1,49} = 1.8$, $p = 0.2$; $\delta^{34}\text{S}$: $R^2 = -0.04$, $F_{1,21} = 0.1$, $p = 0.7$), nor for summer $\delta^{13}\text{C}$ ($R^2 = 0.07$, $F_{1,11} = 1.9$, $p = 0.2$) but did for $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ in the summer ($\delta^{15}\text{N}$: $R^2 = 0.42$, $F_{1,11} = 9.8$, $p = 0.01$; $\delta^{34}\text{S}$: $R^2 = 0.74$, $F_{1,6} = 20.4$, $p = 0.004$; Figure 2.2g-i).

2.3.2 Seasonal differences in stable isotopes by species

Significant differences in isotopes existed between seasons for $\delta^{13}\text{C}$ in white perch ($\chi^2 (1) = 7.2$, $p = 0.01$) but not for freshwater drum ($\chi^2 (2) = 1.8$, $p = 0.4$) or walleye ($\chi^2 (2) = 3.5$, $p = 0.2$). White perch had significantly higher $\delta^{13}\text{C}$ in spring than during the summer (Dunn's test, $p = 0.01$; Table 2.1). All species had significant differences in $\delta^{15}\text{N}$

between seasons (freshwater drum: $\chi^2 (2) = 56.5, p < 0.001$; walleye: $\chi^2 (2) = 37.9, p < 0.001$; white perch: $\chi^2 (1) = 27.5, p < 0.001$); $\delta^{15}\text{N}$ was significantly lower during the summer than the spring in all species ($p \leq 0.004$ for all). The large freshwater drum and walleye size classes, where fish caught throughout the entire year were pooled into a single group because they did not have significant seasonal differences, had significantly lower $\delta^{15}\text{N}$ than the spring caught fish ($p \leq 0.004$), and for walleye the pooled large size class also had higher $\delta^{15}\text{N}$ than summer caught fish (Table 2.1). Freshwater drum had significant differences between season for $\delta^{34}\text{S}$ ($\chi^2 (2) = 14.2, p = 0.001$) but walleye ($\chi^2 (2) = 1.7, p = 0.4$) and white perch ($\chi^2 (1) = 1.0, p = 0.3$) did not. Spring freshwater drum had lower $\delta^{34}\text{S}$ ($p < 0.001$ for both) than summer or the pooled large drum ($p = 0.5$; Table 2.1).

2.3.3 Ontogenetic stable isotope variation

Spring freshwater drum had significant differences between size classes for all isotopes (Kruskal-Wallis Test; $\delta^{13}\text{C}$: $\chi^2 (2) = 16.2, p < 0.001$; $\delta^{15}\text{N}$: $\chi^2 (2) = 43.4, p < 0.001$; and $\delta^{34}\text{S}$: $\chi^2 (2) = 14.1, p = 0.001$; Table 1, Figure 2.3a-c). Small freshwater drum had significantly lower $\delta^{13}\text{C}$ (Dunn's Test: $p < 0.001$ for both) than the medium and large size classes which had similar $\delta^{13}\text{C}$ ($p = 0.2$). Small and medium freshwater drum during the spring had similar $\delta^{15}\text{N}$ ($p = 0.1$), which was significantly higher than freshwater drum in the large size class ($p \leq 0.002$ for both). Medium freshwater drum in spring had significantly lower $\delta^{34}\text{S}$ than the large size class ($p < 0.001$). Large and medium freshwater drum had similar $\delta^{34}\text{S}$ to the small size class in spring ($p \geq 0.05$ for both). Spring walleye had no significant differences in $\delta^{13}\text{C}$ ($\chi^2 (2) = 3.7, p = 0.2$), or $\delta^{34}\text{S}$ ($\chi^2 (2) = 1.1, p = 0.6$) between size classes (Figure 2.3d-f). There were significant differences

between size classes for $\delta^{15}\text{N}$ in spring walleye ($\chi^2 (2) = 9.7, p = 0.01$). Walleye in the medium and small size class had similar $\delta^{15}\text{N}$ ($p = 0.3$), which was higher than the large size class ($p \leq 0.01$ for both). In spring, white perch had no significant differences in any of the isotopes measured between size classes ($\delta^{13}\text{C}$: $\chi^2 (1) = 1.2, p = 0.3$; $\delta^{15}\text{N}$: $\chi^2 (1) = 0.0, p = 0.8$; and $\delta^{34}\text{S}$: $\chi^2 (1) = 0.0, p = 0.9$; Table 2.1, Figure 2.3g-i).

Summer freshwater drum had significant differences between size classes in $\delta^{15}\text{N}$ ($\chi^2 (2) = 39.2, p < 0.001$) but not in $\delta^{13}\text{C}$ ($\chi^2 (2) = 0.5, p = 0.8$) or $\delta^{34}\text{S}$ ($\chi^2 (2) = 3.6, p = 0.4$; Table 1, Figure 2.3a-c). Medium freshwater drum had the highest $\delta^{15}\text{N}$, followed by the large size class, while the small size class had the lowest $\delta^{15}\text{N}$ ($p < 0.001$ for all). Walleye showed no significant difference in $\delta^{13}\text{C}$ ($\chi^2 (2) = 2.4, p = 0.3$) or $\delta^{34}\text{S}$ ($\chi^2 (2) = 4.4, p = 0.1$) between size classes, but did have significant differences in $\delta^{15}\text{N}$ ($\chi^2 (2) = 39.2, p < 0.001$; Figure 2.3d-f). Small and medium walleye had similar $\delta^{15}\text{N}$ ($p = 0.1$) which was significantly lower than the large walleye ($p < 0.001$ for both). White perch showed significant differences in $\delta^{13}\text{C}$ ($\chi^2 (1) = 6.4, p = 0.01$), $\delta^{15}\text{N}$ ($\chi^2 (1) = 4.1, p = 0.04$) and $\delta^{34}\text{S}$ ($\chi^2 (1) = 3.8, p = 0.05$) between size classes (Figure 2.3h-i). Small white perch had lower $\delta^{13}\text{C}$ ($p = 0.01$), $\delta^{15}\text{N}$ ($p = 0.04$) and $\delta^{34}\text{S}$ ($p = 0.05$) than medium white perch.

2.3.4 Stable isotope variation among species within size class and season

There were significant differences in $\delta^{13}\text{C}$ ($\chi^2 (2) = 21.1, p < 0.001$) and $\delta^{15}\text{N}$ ($\chi^2 (2) = 7.8, p = 0.02$) among species in the small size class during the spring (Figure 2.4a-c). Walleye had the highest $\delta^{13}\text{C}$, followed by white perch, with freshwater drum having the lowest (Dunn's test, $p \leq 0.003$ for all). Walleye had higher $\delta^{15}\text{N}$ ($p = 0.01$ for both) than freshwater drum and white perch ($p = 0.2$). Sulphur ($\delta^{34}\text{S}$) did not have significant

differences among species in the small size class ($\chi^2 (2) = 3.0, p = 0.3$). The medium size class fish differed for all isotope among species during the spring ($\delta^{13}\text{C}$: $\chi^2 (2) = 6.0, p = 0.04$; $\delta^{15}\text{N}$: $\chi^2 (2) = 13.8, p = 0.001$; $\delta^{34}\text{S}$: $\chi^2 (2) = 15.5, p < 0.001$; Figure 2.4d-f). White perch had significantly lower $\delta^{13}\text{C}$ ($p \leq 0.02$) and $\delta^{15}\text{N}$ ($p \leq 0.01$) than freshwater drum and walleye, but freshwater drum and walleye did not differ ($p \geq 0.04$). Freshwater drum had significantly lower $\delta^{34}\text{S}$ (both $p = 0.001$) than either white perch or walleye, which did not differ ($p = 0.2$).

During the summer, there were significant differences in $\delta^{13}\text{C}$ ($\chi^2 (2) = 19.5, p < 0.001$) and $\delta^{34}\text{S}$ ($\chi^2 (2) = 8.2, p = 0.02$) between species within the small size class (Figure 2.4a-c). Walleye had similar $\delta^{13}\text{C}$ to both white perch and freshwater drum ($p \geq 0.1$), and white perch had significantly lower $\delta^{13}\text{C}$ than freshwater drum ($p < 0.001$). Walleye had significantly higher $\delta^{34}\text{S}$ than white perch ($p = 0.003$), and freshwater drum had similar $\delta^{34}\text{S}$ to both ($p \geq 0.03$). All three species had similar $\delta^{15}\text{N}$ within the small size class ($\chi^2 (2) = 3.0, p = 0.2$). Medium fish had similar $\delta^{13}\text{C}$ ($\chi^2 (2) = 0.3, p = 0.9$) and $\delta^{15}\text{N}$ ($\chi^2 (2) = 3.1, p = 0.2$) during the summer, but there were significant differences in $\delta^{34}\text{S}$ ($\chi^2 (2) = 9.5, p = 0.01$) between species (Figure 2.4d-f). Freshwater drum had lower $\delta^{34}\text{S}$ ($p \leq 0.02$ for both) than walleye and white perch ($p = 0.4$).

Large freshwater drum and walleye had similar $\delta^{13}\text{C}$ ($\chi^2 (1) = 2.3, p = 0.1$) but large walleye had significantly higher $\delta^{15}\text{N}$ ($\chi^2 (1) = 29.5, p < 0.001$) and $\delta^{34}\text{S}$ ($\chi^2 (2) = 14.4, p < 0.001$) than large freshwater drum (Table 1, Figure 2.4g-i). Note that there were no white perch caught in the large size class.

2.3.5 Isotopic niche area and overlap

The standard ellipses areas (SEA_B) of the isotopic niche of spring caught fish were larger than those caught in summer along all pairwise isotope configurations ($\delta^{13}C$ - $\delta^{15}N$, $\delta^{13}C$ - $\delta^{34}S$, and $\delta^{34}S$ - $\delta^{15}N$), with the exception of medium freshwater drum which had similar SEA_B in both seasons. In spring, small freshwater drum (4.8-13.3 ‰², across the different isotope combinations) and small white perch (3.8-6.8 ‰²) had the largest SEA_B across all combinations, while the smallest SEA_B belonged to small walleye (0.6-0.7 ‰²) and medium white perch (0.5-0.7 ‰²). During the summer, all species and size classes had similar niche area along the $\delta^{13}C$ - $\delta^{15}N$ axis (0.7-1.9 ‰²). Small freshwater drum (0.4 ‰²) had the smallest and medium freshwater drum (3.7 ‰²) the largest niche area along the $\delta^{13}C$ - $\delta^{34}S$ axis, whereas medium white perch (0.4 ‰²) had the smallest and small white perch (3.9 ‰²) the largest niches along the $\delta^{34}S$ - $\delta^{15}N$ axis during the summer (Table 2.2).

In general, overlap between niches was much higher when modelled using 2 isotopes ($\delta^{13}C$ and $\delta^{15}N$) versus three isotopes ($\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$), the exceptions being the overlap between spring medium-sized freshwater drum and the small freshwater drum which had a slightly higher degree of overlap in the three-isotope model (25.7 %) than the two-isotope model (19.9 %, Table 2.3). This was especially true in the medium size classes which had large overlaps (mean; spring: 70.7%, summer: 44.9%) between all species in both seasons when only $\delta^{13}C$ and $\delta^{15}N$ were used to model niche and little overlap when all three isotopes were used to model niche (mean; spring: 8.8%, summer: 4.1%). Additionally, there was less overlap between isotopic niche of different species and size classes in the summer (average; two isotopes: 41.1%, three-isotopes:

15.4%) than the spring (two-isotopes: 48.6%, three-isotopes: 24.4%; Table 2.3, Figure 2.4).

2.4 Discussion

These three species of large bodied freshwater fish of Lake Erie had distinct resource utilization strategies across ontogeny based on isotopic niche analyses using three stable isotopes, demonstrating resource partitioning through both habitat use and trophic position. However, some size and species combinations had significant niche overlap in the spring, suggesting that there could be competition for resources at various life stages and seasons, and/or they are keyed into abundant prey types that could support multiple consumers without resource partitioning. In the summer, there was minimal isotopic niche overlap, indicating species had specific resource use strategies.

While past research on white perch in western Lake Erie showed that temporal shifts in isotopic composition occur (Guzzo *et al.*, 2011, 2013), only $\delta^{15}\text{N}$ had significant temporal differences for the three species in the present study. Higher $\delta^{15}\text{N}$ during the spring than the summer across all species and size classes, despite little change in baseline $\delta^{15}\text{N}$, could be a result of periods of low feeding/starvation/food scarcity during the winter, which is known to increase $\delta^{15}\text{N}$ (Colborne & Robinson, 2013; Stockwell *et al.*, 2014), and not a change in trophic position. Sources of carbon were consistent across season and fish species with a few minor exceptions (e.g. small freshwater drum) based on $\delta^{13}\text{C}$, and indicates they were feeding on prey that had a similar carbon source.

Values of $\delta^{34}\text{S}$ did not follow the same trends as $\delta^{13}\text{C}$, which suggests these fish species fed in different habitats and/or different prey species. Unfortunately, our

understanding of $\delta^{34}\text{S}$ dynamics in freshwater is limited, which constrains our ability to assign ecological significance to the patterns observed. Croisetière *et al.*, (2009) found that organisms feeding pelagically had higher $\delta^{34}\text{S}$ values than those feeding benthically, consistent with what we observed in invertebrates in this study. However, Colborne *et al.*, (2016) did not observe this pattern in pelagic and benthic forage fish of Lake Ontario. In a review of isotopic niches, higher $\delta^{34}\text{S}$ was associated with benthic feeding (Newsome *et al.*, 2007), which was opposite to the trends found here and by Croisetière *et al.*, (2009).

Clearly, there is a need to better understand the dynamics of $\delta^{34}\text{S}$ in freshwater systems but this does not preclude us comparing isotopic trends between our study species. Indeed, including a third isotope ($\delta^{34}\text{S}$) into the analysis provided greater resolution of species niche and trophic relationships in Lake Erie fish, consistent with other recent papers (Solomon *et al.*, 2011; Ofukany *et al.*, 2014; Colborne *et al.*, 2016). Incorporating $\delta^{34}\text{S}$ into the niche analysis reduced the degree of overlap observed among species and within species compared with only $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. For example, fishes belonging to the medium size class experienced approximately 50-70% niche overlap depending on the season, with several niches overlapping almost completely (> 90%), but less than 30% overlap when $\delta^{34}\text{S}$ was included. Thus, if $\delta^{34}\text{S}$ had not been included, the degree of overlap would have been overestimated, potentially leading to erroneous conclusions on the relative importance of interspecific competition, or non-limiting resources in the Lake Erie food web. Since niches are multi-dimensional by nature, if significant overlap occurs on two axes it is possible that they diverge on another (Hutchinson, 1959; Ross, 1986), as Colborne *et al.* (2016) demonstrated with lake trout (*Salvelinus namaycush*) in Lake Ontario. Croisetière *et al.*, (2009) also better

differentiated between benthic and pelagic algae in freshwater boreal lakes when using $\delta^{34}\text{S}$ in addition to $\delta^{13}\text{C}$. For this reason, discussion will focus primarily on the results from the three-isotope niche model.

Differences in niche overlap between seasons demonstrates the importance of resource availability for fish species in Lake Erie and likely other freshwater ecosystems. In spring, niche overlap declined among species with increasing size and could be explained by small fish foraging opportunistically while using similar habitat to avoid predation (Werner & Gilliam, 1984). Medium and large fish will have mostly escaped predation risk, and as a result are freed to use their preferred habitats and prey, allowing them to partition resources more effectively (Schael, Rudstam & Post, 1991; Morrison *et al.*, 1997; Overman & Parrish, 2001). Increasing overlap among species with increasing size in the summer, could partially be due to the exclusion of the small walleye size class from analysis as a result of small sample sizes. However, previous research in Lake Erie suggests that prey such as zooplankton is most abundant during spring and early summer months as a result of the spring phytoplankton bloom, indicating resources may be less limiting during this time, allowing for species diets and resource use to overlap more without encountering interspecific competition (Wu & Culver, 1992; Pothoven *et al.*, 2009).

While fishes partitioned resources in Lake Erie, the axis on which this occurred changed depending on size class and season, highlighting the importance of ontogeny. As expected based on their described feeding ecology, large fish partitioned resources through both trophic position and habitat ($\delta^{15}\text{N}$, $\delta^{34}\text{S}$), with freshwater drum occupying a lower trophic position and using more benthic resources than walleye, lending further

support of the accuracy of the inferences made about the less commonly studied small and medium-sized groups for these same species (Bur, 1982; Hartman & Margraf, 1992). Small fish also partitioned resources across both habitat and trophic position, but unlike their larger conspecifics, spring small freshwater drum appeared to be using more pelagic resources than white perch and walleye compared to baseline $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$, although this trend reversed during the summer. These changes in niche from spring to summer are consistent with diet studies on young-of-the year (YOY) white perch and freshwater drum in Lake Erie which indicated that, while both species undergo an ontogenetic shift from zooplankton to benthic invertebrates, these shifts occur at different times in the year so there is minimal overlap within their niches (Gopalan *et al.*, 1998). Medium fishes in our study partitioned resources predominantly through habitat use ($\delta^{13}\text{C}$, $\delta^{34}\text{S}$), with little differentiation between niche through trophic position, unlike the other two size classes. Medium freshwater drum had a $\delta^{34}\text{S}$ value close to benthic invertebrates (Chironimidae, *Hexagenia* spp., and Dreissenidae) and white perch had the most pelagic $\delta^{13}\text{C}$ value compared to seston, which agrees with what is known about the feeding ecology of both freshwater drum and white perch (Bur, 1982; Parrish & Margraf, 1990). In many cases, the differences in resource use would have gone unnoticed if $\delta^{34}\text{S}$ had been omitted from analysis because the three species had similar $\delta^{13}\text{C}$ (e.g. medium and large size classes).

The specialization of a species' diet by season could play an important role in determining intraspecies resource use in fish. Walleye and white perch only had significant relationships for changing resource use with total length during the summer months, suggesting that the influx of prey caused by the spring bloom could mask intraspecific resource use by allowing all conspecifics to target abundant prey (Wu &

Culver, 1992; Pothoven *et al.*, 2009). Furthermore, the appearance of new age classes and a reduction in prey abundance during the summer might emphasize differences in resource use across size classes through ontogeny (Wu & Culver, 1992; Gopalan *et al.*, 1998). Only white perch exhibited a shift toward pelagic habitat use (higher $\delta^{34}\text{S}$) with increasing size, and, contrary to our predictions, walleye actually had a slight increase in $\delta^{13}\text{C}$ with length indicating a move toward more littoral habitat. This could mean that predation pressure is greater on the slower growing white perch than walleye which switches to a piscivorous diet early in its life history (~20-80 mm; Graeb *et al.*, 2005; Galarowicz *et al.*, 2006). These patterns could be explained by the specialization of the two species, as walleye showed smaller isotopic niche areas and could be coupling littoral and pelagic habitat as body size increases to maximize foraging efficiency (McCann, Rasmussen & Umbanhowar, 2005), and white perch has a more generalized resource use with large niche areas, particularly in its small size classes. This agrees with what is known about the resource use and diet of the two species (Hartman & Margraf, 1992; Scott & Crossman, 1998).

The pattern of feeding ecology across ontogeny in freshwater drum demonstrated how generalization can hide important changes in the trophic role of a species. As expected, spring freshwater drum used more littoral/benthic habitat ($\delta^{13}\text{C}$) with increasing size, however this trend disappeared during the summer. Freshwater drum are considered a primarily benthic species (Bur, 1982; Scott & Crossman, 1998), and yet isotopes in this study suggest they use a significant amount of pelagic habitat within Lake Erie. This could be partially due to shallow depth of Lake Erie's western basin (< 10 m) which could mean that pelagic habitat is more accessible from benthic and littoral zones than in

lakes with greater depths and more separation between habitats (Schindler & Scheuerell, 2002). Additionally, past research found that large freshwater drum fed heavily on dreissenid mussels after their invasion into Lake Erie in 1987 which have a higher $\delta^{34}\text{S}$ (i.e. more pelagic) compared to other benthic species (e.g. Chironomidae, *Hexagenia* spp.), which could mean that freshwater drum are feeding predominately within benthic habitat, but their isotopic signature is reflecting the higher $\delta^{34}\text{S}$ of dreissenid mussels (French & Bur, 1996; Morrison *et al.*, 1997). Freshwater drum trophic position ($\delta^{15}\text{N}$) declined with increasing size during the spring, which could be the result of large freshwater drum consuming low trophic level organisms such as dreissenid mussels as shown by baseline $\delta^{34}\text{S}$ within this study and previous research within Lake Erie (French & Bur, 1996; Morrison *et al.*, 1997). Conversely, summer freshwater drum experienced a slight increase in trophic position with increasing size, although this trend was weak and better described by a curvilinear relationship where freshwater drum occupied a low trophic position at small sizes, which increased until they were ~250-300 mm in length, and then declined again at larger sizes. Bur (1982) suggested that small fish were an important component of the diet of 250-400 mm freshwater drum, which could explain the high trophic position of the medium size class in this study.

In this study, we found that species with distinct resource use strategies partitioned resources both temporally and across ontogeny. Decreases in niche overlap in summer, when food resources were more limiting suggests that resource availability is an important factor in among species resource partitioning. Additionally, ontogenetic variation in niche can influence the axis upon which resources are partitioned among species. Within species resource utilisation demonstrated that seasonal specialisation of a

species diet and ontogeny is important to understanding the role a species plays within the larger ecosystem, and generalisation of this can hide important changes. Finally, as is consistent with other recent studies (e.g. Solomon *et al.*, 2011; Ofukany *et al.*, 2014; Colborne *et al.*, 2016), the addition of a third isotope to our analysis improved the resolution of trophic and species relationships observed.

2.5 References

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Table 2.1: Stable isotopes (mean \pm 1 SE, unless $n < 2$) for baseline species, freshwater drum (FD), walleye (WE), and white perch (WP) in the western basin of Lake Erie over two seasons. Ranges for size classes are defined in total length as < 200 mm for small, 200-400 mm for medium, and > 400 mm for large. Fish within large size classes showed no temporal differences in isotopic composition so all fish were averaged across the entire sampling year. All baseline samples are pooled samples of multiple individuals from various sample dates and sites.

Species	Size Class	Season	n	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	n	$\delta^{34}\text{S}$ (‰)
Baseline	<i>Amphipoda</i>	Summer	1	-19.6	6.7	-	-
	<i>Chironomidae</i>	Summer	3	-29.8 ± 0.9	7.2 ± 0.5	3	-1.4 ± 0.4
	<i>Dreissenidae</i>	Summer	14	-24.2 ± 0.3	7.6 ± 0.2	6	3.0 ± 0.1
	<i>Hexagenia</i>	Summer	5	-25.2 ± 0.4	9.0 ± 0.3	5	2.0 ± 0.3
	<i>Oligochaeta</i>	Summer	1	-24.6	8.7	-	-
	<i>Planariidae</i>	Summer	1	-23.0	12.0	-	-
	<i>Seston</i>	Spring	8	-28.0 ± 0.5	6.1 ± 0.2	6	4.7 ± 0.2
		Summer	35	-25.0 ± 0.2	7.5 ± 0.2	7	6.0 ± 0.6
FD	<i>Small</i>	Spring	7	-24.4 ± 0.2	16.9 ± 0.5	6	1.6 ± 0.9
		Summer	34	-21.7 ± 0.1	13.7 ± 0.2	9	2.6 ± 0.2
	<i>Medium</i>	Spring	22	-21.5 ± 0.2	17.2 ± 0.1	9	0.4 ± 0.4
		Summer	23	-21.6 ± 0.2	15.9 ± 0.1	6	1.7 ± 0.5
	<i>Large</i>	-	50	-21.7 ± 0.1	14.8 ± 0.2	18	2.5 ± 0.2
	Total	-	136	-21.8 ± 0.1	15.2 ± 0.1	48	1.9 ± 0.2
WE	<i>Small</i>	Spring	16	-21.2 ± 0.1	17.5 ± 0.1	8	3.3 ± 0.1
		Summer	2	-21.8 ± 0.2	15.1 ± 0.2	2	4.1 ± 0.3
	<i>Medium</i>	Spring	20	-21.6 ± 0.1	17.3 ± 0.1	8	3.4 ± 0.4
		Summer	15	-21.3 ± 0.1	15.8 ± 0.1	6	3.5 ± 0.2
	<i>Large</i>	-	20	-21.3 ± 0.2	16.9 ± 0.2	16	3.5 ± 0.1
	Total	-	73	-21.5 ± 0.1	16.9 ± 0.1	39	3.4 ± 0.1
WP	<i>Small</i>	Spring	31	-22.1 ± 0.2	16.8 ± 0.2	14	2.7 ± 0.5
		Summer	10	-22.8 ± 0.2	14.0 ± 0.2	5	1.2 ± 0.6
	<i>Medium</i>	Spring	20	-22.1 ± 0.1	16.9 ± 0.1	9	2.9 ± 0.3
		Summer	3	-21.8 ± 0.2	15.1 ± 0.4	3	3.3 ± 0.3
	Total	-	64	-22.2 ± 0.1	16.3 ± 0.2	31	2.5 ± 0.3

Table 2.2: Standard ellipses areas (SEA_B , $\%o^2$) along the $\delta^{13}C$ - $\delta^{15}N$, $\delta^{13}C$ - $\delta^{34}S$, and $\delta^{34}S$ - $\delta^{15}N$ axes for freshwater drum, walleye, and white perch. Ranges in total length for size classes are as follow: small (< 200 mm), medium (200-400 mm), and large (> 400 mm). Large fish showed no temporal variance in isotopic composition, therefore their SEA_B are representative of the entire sample year. Groups with small sample sizes ($n < 3$) were omitted from analysis (see Table 2.1).

Species	Size Class	Season	$\delta^{13}C$ - $\delta^{15}N$	$\delta^{13}C$ - $\delta^{34}S$	$\delta^{34}S$ - $\delta^{15}N$
Freshwater Drum	<i>Small</i>	Spring	4.8	13.3	7.7
		Summer	1.9	0.4	2.2
	<i>Medium</i>	Spring	1.9	3.8	1.8
		Summer	1.8	3.7	1.4
	<i>Large</i>	-	3.1	1.6	2.8
Walleye	<i>Small</i>	Spring	0.6	0.7	0.6
	<i>Medium</i>	Spring	1.0	2.1	2.3
		Summer	0.7	1.1	0.6
	<i>Large</i>	-	1.9	1.4	1.6
White Perch	<i>Small</i>	Spring	3.8	6.8	6.0
		Summer	1.1	1.0	3.9
	<i>Medium</i>	Spring	0.5	0.6	0.7
		Summer	0.4	0.1	0.4

Table 2.3: Overlap of niche when modelled with (A & C) 2-isotopes (carbon and nitrogen) and (B & D) 3-isotopes (carbon, nitrogen, and sulphur) in nicheROVER for spring (A-B) and summer (C-D) caught individuals. All values are listed as percentages (%) and should be read as the overlap of species a in species b's niche. Each overlap value is the average of 10,000 simulations. Highlighted cells indicate interspecific niche overlap between species within the small (green), medium (orange), and large (blue) size classes. Light grey cells represent intraspecific niche overlap between size classes within a species. Groups with small sample sizes ($n < 3$ for two isotopes, $n < 5$ for three isotopes) were excluded from the analysis.

A – Spring: Two Isotopes (Carbon and Nitrogen)									
a ↓	b → Size Class	Freshwater Drum			Walleye			White Perch	
		Small	Medium	Large	Small	Medium	Large	Small	Medium
FD	Small		14.4	18.9	0.2	1.7	6.5	47.3	3.6
	Medium	19.9		47.2	42.4	68.4	81.2	89.4	40.5
	Large	36.7	13.9		4.0	8.1	33.1	64.5	4.51
WE	Small	2.9	93.9	44.4		91.1	97.7	98.0	23.8
	Medium	10.1	94.4	45.7	61.5		95.5	98.6	46.2
	Large	15.1	78.0	66.3	41.9	65.6		95.2	35.3
WP	Small	40.0	57.2	51.3	15.5	38.0	61.7		28.5
	Medium	35.7	97.9	59.2	19.5	76.7	93.8	100.0	

B – Spring: Three Isotopes (Carbon, Nitrogen, and Sulphur)									
a ↓	b → Size Class	Freshwater Drum			Walleye			White Perch	
		Small	Medium	Large	Small	Medium	Large	Small	Medium
FD	Small		4.8	10.7	0.0	0.1	2.0	39.6	0.5
	Medium	25.7		10.8	1.0	6.4	4.5	74.4	1.3
	Large	29.6	1.7		0.7	2.8	10.2	48.0	1.4
WE	Small	0.1	8.3	13.6		36.8	94.0	84.6	3.5
	Medium	0.9	9.8	26.1	22.4		76.6	96.9	10.3
	Large	5.0	5.2	26.8	27.7	46.9		89.7	7.5
WP	Small	21.1	10.9	26.0	4.27	18.3	32.0		7.3
	Medium	14.2	6.8	54.0	6.8	27.0	71.1	99.8	

C – Summer: Two Isotopes (Carbon and Nitrogen)									
a ↓	b → Size Class	Freshwater Drum			Walleye			White Perch	
		Small	Medium	Large	Small	Medium	Large	Small	Medium
FD	Small		25.8	80.5	-	12.7	7.4	29.4	6.9
	Medium	44.4		90.3	-	59.3	69.2	5.3	8.5
	Large	59.3	55.0		-	28.1	33.1	29.4	8.6
WE	Small	-	-	-		-	-	-	-
	Medium	65.2	99.2	98.7	-		78.6	3.4	15.3
	Large	9.8	63.5	66.3	-	26.4		0.3	4.0
WP	Small	49.7	9.8	94.5	-	1.6	0.5		4.4
	Medium	83.0	76.1	98.3	-	56.0	39.6	27.1	

D – Summer: Three Isotopes (Carbon, Nitrogen, and Sulphur)									
a ↓	b → Size Class	Freshwater Drum			Walleye			White Perch	
		Small	Medium	Large	Small	Medium	Large	Small	Medium
FD	Small		3.9	69.4	-	0.1	0.5	0.4	-
	Medium	4.1		53.2	-	1.7	9.1	0.8	-
	Large	18.1	17.0		-	3.5	10.2	7.0	-
WE	Small	-	-	-		-	-	-	-
	Medium	0.5	10.7	66.3	-		88.6	0.8	-
	Large	0.1	3.7	26.8	-	12.2		0.3	-
WP	Small	0.8	1.6	49.0	-	0.3	1.0		-
	Medium	-	-	-	-	-	-	-	-

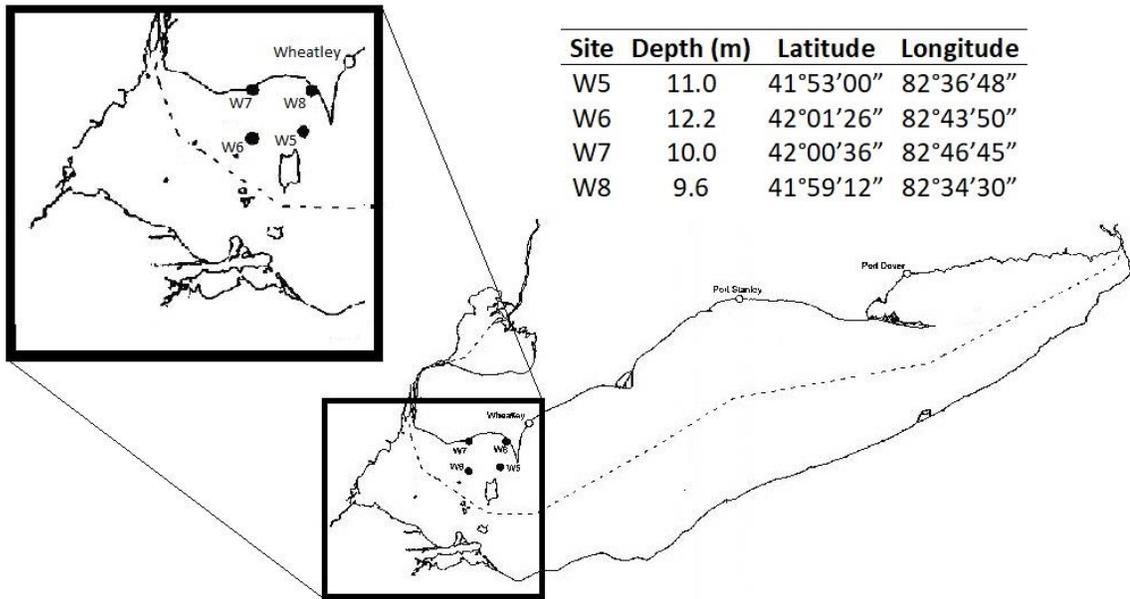


Figure 2.1: Sampling locations of baseline species (benthic invertebrates and seston) within the western basin of Lake Erie for the OMNRF lower trophic level monitoring program with coordinates and depth. The dashed line represents the Canada-US border.

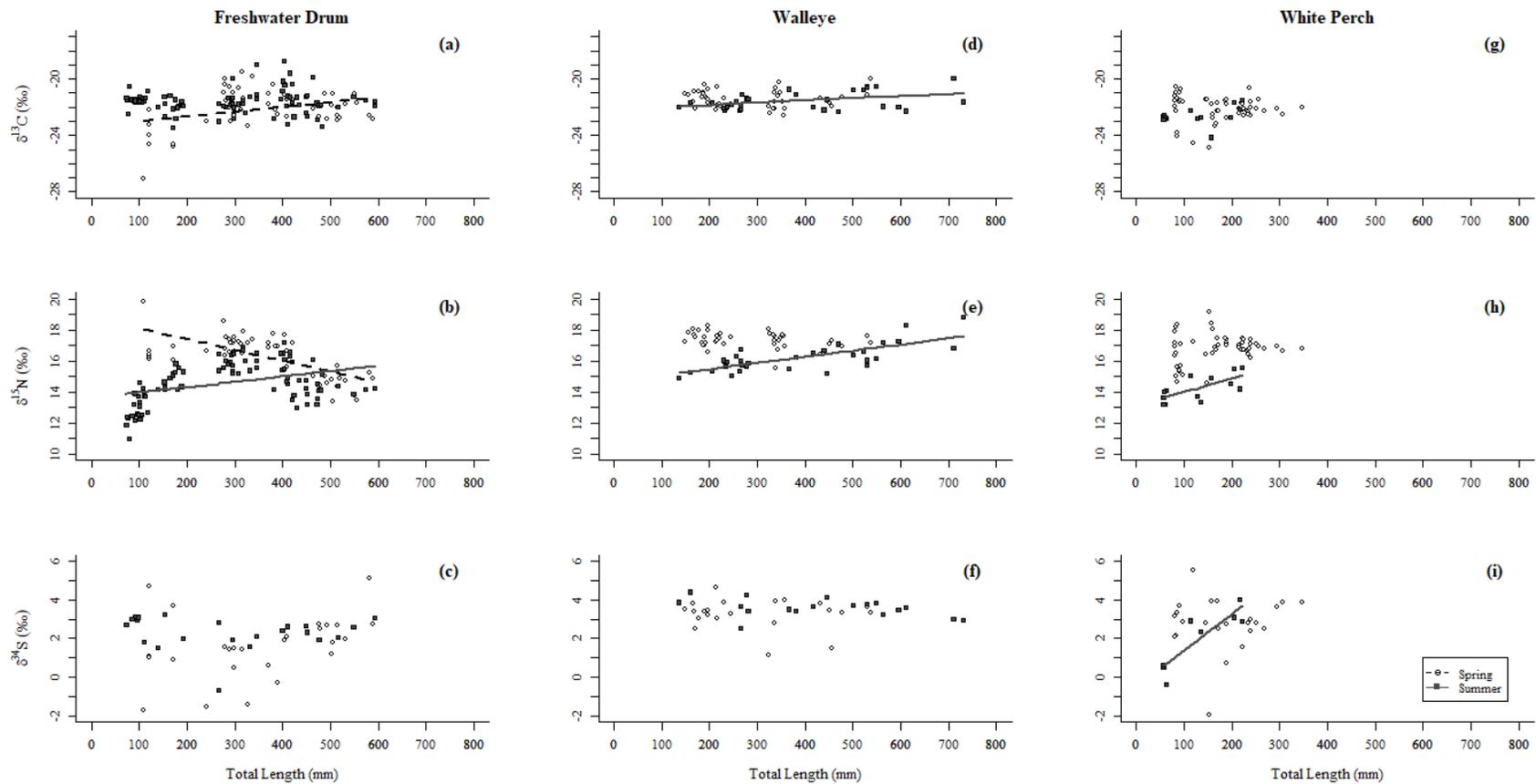


Figure 2.2: Trends in $\delta^{13}\text{C}$ (top row), $\delta^{15}\text{N}$ (middle row), and $\delta^{34}\text{S}$ (bottom row) with total length for freshwater drum (a-c), walleye (d-f), and white perch (g-i) with total length. Dashed black lines and open circles are significant linear relationships within the spring, and solid black lines and filled in squares are significant relationships during the summer.

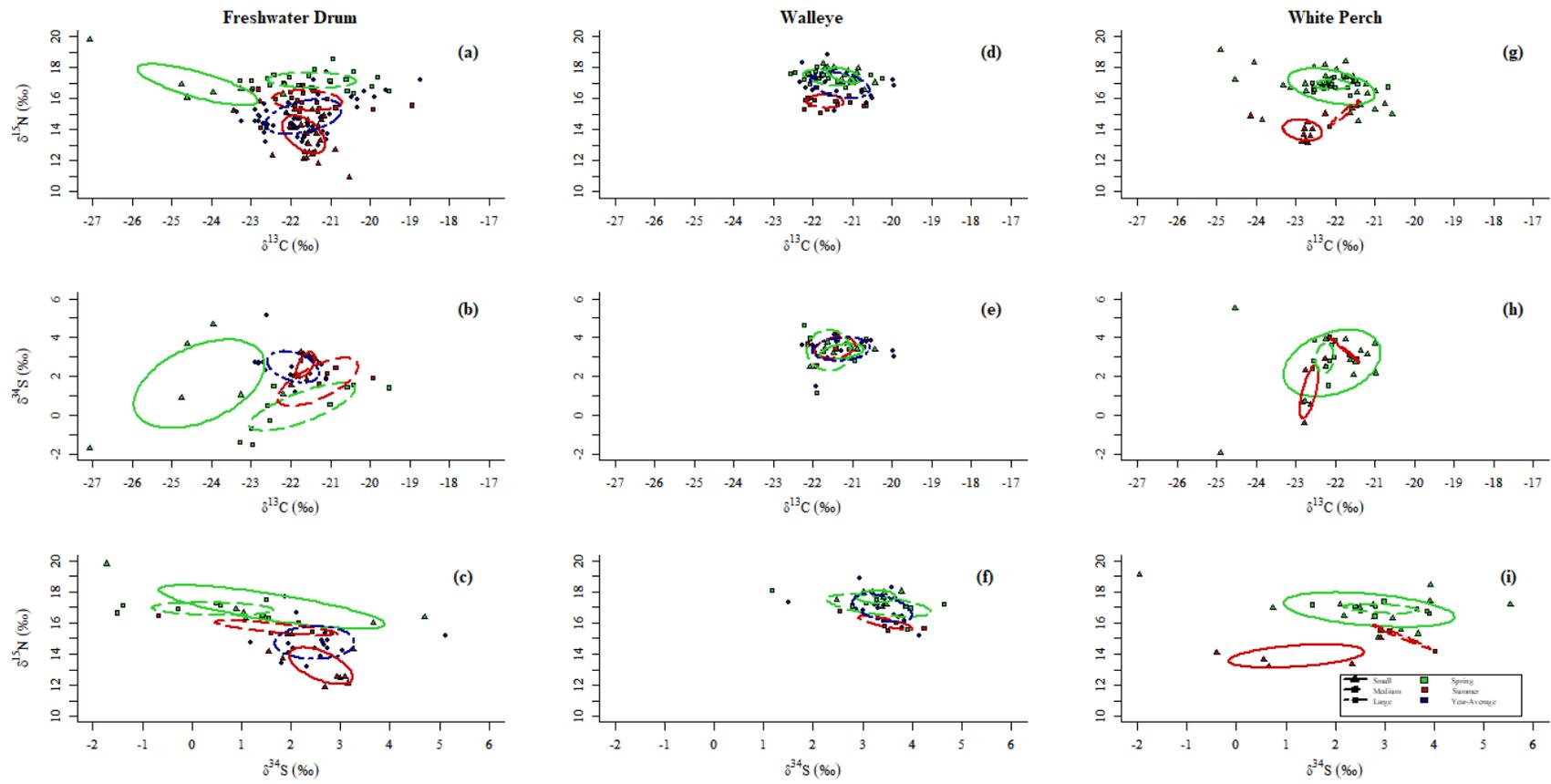


Figure 2.3: SIBER stable isotope ellipses (SEA_B) estimating the isotopic niche of freshwater drum (a-c), walleye (d-f), and white perch (g-i) for $\delta^{13}C$ and $\delta^{15}N$ (top), $\delta^{13}C$ and $\delta^{34}S$ (middle), and $\delta^{34}S$ and $\delta^{15}N$ (bottom) across size classes (Small >200 mm: solid lines and triangles, Medium 200-400mm: dashed lines and squares, and Large >400mm: blue circles and blue dashed lines) and seasons (spring: green, summer: red, year round (large only): blue). No large white perch or small summer walleye were caught during the study period; thus, they were omitted from the analysis.

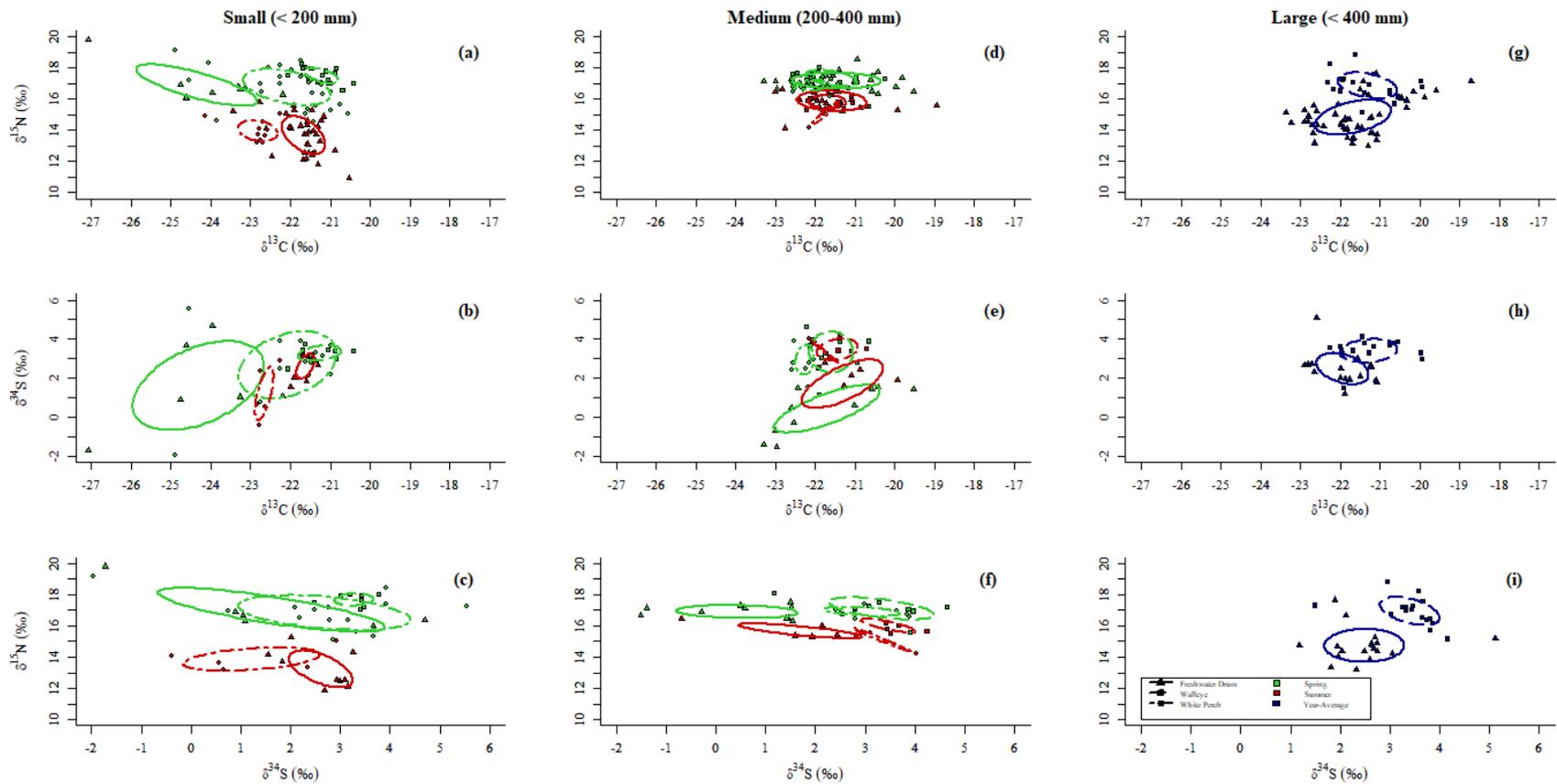


Figure 2.4: SIBER stable isotope ellipses estimating the variation in niche among species (freshwater drum: triangles and solid lines, walleye: squares and dashed lines, and white perch: circles and dot-dashed lines) and seasons (spring: green, summer: red, year-round: blue) at different size classes (Small <200mm [a-c], Medium 200-400mm [d-f], and Large >400mm [g-i]) for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (top), and $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ (bottom). Ellipses represent the standard ellipse area (SEAC) of each niche. No large white perch or small summer walleye were caught during the study period; thus, they were omitted from the analysis.

CHAPTER III:

THE RELATIVE INFLUENCE OF ONTOGENY ON PCB CONCENTRATIONS IN FRESHWATER FISH SPECIES WITH DIFFERENT FEEDING STRATEGIES

3.1 Introduction

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), are a source of concern in aquatic systems due to their toxicity and propensity to bioaccumulate and biomagnify within food webs (Debruyne & Gobas, 2006).

Bioaccumulation is the uptake of a chemical from an organism's environment into its tissues, leading to higher concentrations of POPs in biota than the environment (Mackay & Hughes, 1984; Gobas, Muir & Mackay, 1988), and is governed by a number of processes including physicochemical (Mackay & Hughes, 1984), biological (Borgå *et al.*, 2004), and environmental processes (Rasmussen *et al.*, 1990; Paterson *et al.*, 2016).

Biomagnification is said to occur when the concentrations of a chemical are elevated above those expected from bioaccumulation and can be explained by the amplification of concentrations with increasing trophic position (Kiriluk *et al.*, 1995; Leblanc, 1995; Kidd *et al.*, 1998). Thermodynamic models of bioaccumulation and biomagnification typically assume that concentrations of a chemical in lipid-normalized tissue will achieve a steady-state with environmental and dietary concentrations (i.e. fugacity; Mackay & Hughes, 1984; Gobas *et al.*, 1988; Debruyne & Gobas, 2006). How a chemical partitions within the aquatic environment can be described by its octanol-water coefficient ($\log K_{ow}$), often logged, which characterizes the hydrophobicity of the chemical (Fisk *et al.*, 1998). For PCB congeners that have low $\log K_{ow}$ (≤ 6.5) accumulation is predominantly from water sources, whereas highly hydrophobic PCBs (> 6.5) will be derived almost entirely from an organism's diet (Thomann & Connolly, 1984; Arnot & Gobas, 2004; Paterson,

Drouillard & Haffner, 2006). These physicochemical properties, along with biological processes such as metabolism, and growth, foraging, and gill ventilation rates, determine the concentrations of PCBs in an organism (Fisk *et al.*, 1998). Freshwater fish have minimal to no capacity to eliminate PCBs with $\log K_{ow} > 6.5$ via biotransformation (Fisk *et al.*, 1998; Paterson, Drouillard & Haffner, 2007a; Paterson *et al.*, 2007b) and given this extreme hydrophobicity, it is unlikely that they will ever reach a steady-state concentration under ambient environmental conditions (Liu, Haffner & Drouillard, 2010).

Species-specific concentrations of PCBs are often the result of dissimilar ecology (e.g. trophic position, feeding ecology, habitat use, etc.; Borgå *et al.*, 2004; Lopes *et al.*, 2011; Baptista *et al.*, 2013; Paterson *et al.*, 2016), and physiology (e.g. lipid content, metabolism; Pastor *et al.*, 1996; Borgå *et al.*, 2004). Many studies have found trophic position to be a predictor of PCB concentrations, with concentrations of PCBs increasing with trophic position (Rasmussen *et al.*, 1990; Kiriluk *et al.*, 1995; Kidd *et al.*, 2001; Paterson *et al.*, 2006; Kelly *et al.*, 2007; McIntyre & Beauchamp, 2007). Fish species occupying similar trophic positions but utilizing different habitats or foraging strategies, may also have different PCB concentrations. For example, species that utilize benthic resources tend to have higher concentrations than species using pelagic resources (Hebert & Haffner, 1991; Borgå *et al.*, 2004). Both trophic position and resource use (e.g. habitat, diet) can be quantified through stable isotopes of nitrogen ($\delta^{15}\text{N}$) and carbon ($\delta^{13}\text{C}$; Newsome *et al.*, 2007; Croisetière *et al.*, 2009; Colborne *et al.*, 2016), and used to quantify how PCB concentrations vary with changes in both variables within/between species (Kiriluk *et al.*, 1995; Fisk *et al.*, 2002; Paterson *et al.*, 2016).

PCB's are lipophilic compounds, which makes them sensitive to variations in lipid content between species and individuals, which needs to be accounted for when quantify and studying bioaccumulation (Hebert & Keenleyside, 1995; Kainz & Fisk, 2009). As a result, fish species with higher lipid content are likely to have higher PCB concentrations than those with less lipids (Kainz & Fisk, 2009). For this reason, PCB concentrations are often lipid-corrected to make comparisons between species and individuals possible without being biased by varying lipid content (Hebert & Keenleyside, 1995).

Body size is also an important factor that can influence PCB concentrations in fish (Borgå *et al.*, 2004). Elimination of PCBs is diminished in larger bodied fish because their surface area to volume ratio and metabolism are reduced (Thomann, 1989). Since fish are gape limited predators, larger fish generally have a greater capacity to eat at higher trophic positions than smaller fish, which may confound/exacerbate the impact of body size on PCB concentrations through the process of biomagnification (Borgå *et al.*, 2004; Paterson *et al.*, 2007b).

Fish increase in size across several orders of magnitude from eggs/larvae to adults, often resulting in ontogenetic changes in foraging habits (Amundsen *et al.*, 2003; Post, 2003; Galarowicz, Adams & Wahl, 2006), trophic position (Mittelbach & Persson, 1998; Post, 2003), and habitat use (Werner & Hall, 1988), but little research has been conducted to look at species differences in PCB concentrations at different sizes as a result of ontogeny. Additionally, growth rates provide an elimination pathway through the dilution of PCBs into new tissue (Paterson *et al.*, 2007b), potentially confounding the effect ontogeny may have on contaminant loads. As a result, body size, growth, and its implications on the ontogeny and ecology of a species is important for understanding

PCB concentrations within a species. PCB congeners with $\log K_{ow} > 6.5$ (e.g. IUPAC #: 153, 138, 180) are almost entirely accumulated from dietary sources in fish, meaning that any differences in concentrations between individuals or species would be the result of differing feeding ecology (e.g. trophic position, resource use; McLeod *et al.*, 2015; Paterson *et al.*, 2016).

To understand the relative role of trophic position versus habitat use and fish size on PCB concentrations, a direct comparison of species with different feeding ecologies in the same system is needed. The Laurentian Great Lakes (hereafter Great Lakes), and particularly Lake Erie, provide a good system for this type of study, due to the diversity of species and habitats within them. PCBs and other POPs (e.g. DDT, dioxins) have been of concern in the Great Lakes ecosystems since the 1960s and 70s (Baumann & Whittle, 1988; Morrison, Whittle & Haffner, 2002). Programs to monitor concentrations of these contaminants within various compartments (e.g. sediment, biota) have been in place since the mid-1960s (Baumann & Whittle, 1988; Marvin *et al.*, 2004), and while concentrations have declined over the past fifty years, these contaminants persist within the environment and result in fish consumption advisories for humans (Sadraddini *et al.*, 2011; Kashian *et al.*, 2014).

Lake Erie is of particular concern because it has been subject to some of the most intense anthropogenic stressors within the Great Lakes. In particular, eutrophication (Steffen *et al.*, 2014) and contamination from anthropogenic chemicals (Morrison *et al.*, 2002) have been major concerns both to human and ecosystem health as the lake is a source of drinking water and home to a major fishery (Stepien *et al.*, 2012). The Detroit River, draining into the lake's western basin, is the source of most PCBs (Oliver &

Bourbonniere, 1985), which are mostly retained by the lake's shallow western basin creating a gradient of increasing contamination from east to west (Oliver & Bourbonniere, 1985; Marvin *et al.*, 2004). Additionally, food has been identified as the most important exposure route to PCBs for organisms in the western basin (Koslowski *et al.*, 1994).

We used three species of fish that achieve a similar adult size but with different feeding strategies within the western basin of Lake Erie to quantify the relative importance of ontogeny on concentrations of PCB 153, 138, and 180 in fish. Trophic position and habitat use were traced using $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$, respectively, to inform on potential changes in resource use over ontogeny. The three species included: a benthivore, freshwater drum (*Aplodinotus grunniens*, max length: 750 mm; Bur, 1982, 1984); a piscivore, walleye (*Sander vitreus*, max length: 790 mm; Mittelbach & Persson, 1998; Scott & Crossman, 1998); and an omnivore, white perch (*Morone Americana*, max length: 495 mm; Stanley & Danie, 1983; Guzzo *et al.*, 2013). We chose these three PCBs because they are highly hydrophobic ($\log K_{\text{OW}} > 6.5$), recalcitrant (i.e., not biotransformed), primarily accumulate through diet, and are present in Lake Erie in high enough concentrations to be quantifiable. Assessment of the contaminant dynamics of these species is lacking, particularly for freshwater drum and white perch, and no research has ever been conducted to look specifically at how PCB concentrations varies with ontogeny of these species. We hypothesized that: 1) PCB concentrations would increase with total length for all three species; and 2) the slope of this relationship would be greatest for walleye, because they are predators, second highest for white perch,

because they make a jump to piscivory as they grow, and lowest for freshwater drum, because they are slow growing and benthic.

3.2 Methods

3.2.1 Location and Sample Collection

Freshwater Drum, walleye, and white perch across a range of sizes were collected from the Western Basin of Lake Erie during interagency trawls conducted by the Ohio Department of Natural Resources (ODNR), Ohio United States Geological Survey (Ohio USGS), and Ontario Ministry of Natural Resources and Forestry (OMNRF) in 2016 (Table 3.1). Samples were put on ice and transported back to the Great Lakes Institute for Environmental Research (GLIER) at the University of Windsor and stored -20°C until processed for isotopes (muscle only) and PCBs. The total length and weight of each fish was measured, a 0.5 g sample of muscle tissue taken from below the dorsal fin for stable isotope analysis, and the entire fish homogenized for analysis of PCB concentrations.

3.2.2 PCB Extraction and Quantification

Samples were analyzed to determine concentrations of PCB congeners using the micro-extraction and Florisil clean-up process as described in Daley, et al. (2009). Approximately 1g of homogenized sample was ground in ~10g of anhydrous sodium sulphate in a glass mortar and pestle to dehydrate the tissue, and wet packed into a mini-column pre-packed with glass wool, ~2cm anhydrous Na₂SO₄, and 15mL of a 1:1 Hexane(Hex)-Dichloromethane(DCM) (v/v) extraction mixture. Mortar and pestle were rinsed with 10mL of Hex:DCM that was added to the mini-columns, and spiked with extraction performance recovery standards, 35ng of a PCB 34 and 50ng of a BDE-71 (2,3',4',6-Tetrabromodiphenyl ether). The mini-columns were drained after 2 h, and the

eluate transferred to 125mL flat bottom flasks. Approximately 5 mL of isooctane was added to the eluate and evaporated under vacuum to approximately 5 mL. Samples were diluted to 10mL with hexane, and 1mL was used to determine lipid content gravimetrically. Samples were transferred back into flat-bottom flasks and evaporated under vacuum to ~2mL.

For clean-up and fractionation, samples were transferred to glass columns packed with 6g of activated Florisil and 2cm of Na₂SO₄. The first fraction was collected using 50mL of hexane. Samples were evaporated under vacuum to < 1 mL and diluted to a final volume of 1mL with isooctane. All samples were analyzed on an Agilent 6890 series gas chromatography system (Santa Clara, California, USA) equipped with a gas chromatography-electron capture detector (GC-ECD) at the GLIER Organic Analytical Laboratory (University of Windsor, Windsor, ON). PCB congeners (IUPAC #) 153, 138, and 180 were quantified using the suite of PCBs in the Quebec Certified PCBs standard solution from AccuStandard (New Haven, Connecticut, USA).

Every set of 6 samples was randomly selected to prevent drift in values and was extracted simultaneously with a method blank and in-house reference tissue homogenate of Detroit River carp for quality assurance. All PCB concentrations quantified in the reference tissue within this study were in compliance with GLIER's organic analytical laboratory quality assurance guidelines (mean \pm 2 standard deviation (SD)). Recoveries of the internal standards was $91 \pm 1\%$ (standard error, n = 86) for PCB 34 and $95 \pm 1\%$ for BDE-71, and samples were not recovery corrected.

3.2.3 Stable Isotope Analysis: Sulphur, Carbon, and Nitrogen

Lyophilized (-48°C and $133 \times 10^3\text{mbar}$ for 48 hours) muscle samples were powdered by hand using a mortar and pestle or dissection scissors. Lipids were extracted prior to $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis, using a 2:1 chloroform:methanol mixture (as described by Nawrocki *et al.*, 2016) to remove the bias they can create in $\delta^{13}\text{C}$ (Fry *et al.*, 2003; Boecklen *et al.*, 2011). Briefly, 1.9 mL of a 2:1 chloroform:methanol mixture was added to a $\sim 0.5\text{g}$ subsample of muscle tissue, and placed in a 30°C water bath for 24 hours. Samples were then centrifuged for 4-6 minutes before the 2:1 chloroform:methanol mixture was poured off, and another 1.9 mL of the mixture added. Finally samples were vortexed for 10 sec, and centrifuged for 4-6 minutes before the chloroform:methanol mixture was removed and air-dried and re-homogenized.

Final samples for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis were weighed into tin cups at a mass between 400 and 600 μg . Carbon and nitrogen isotopic composition were determined by a Delta V Advantage ThermoScientific Continuous Flow Mass Spectrometer (Thermo Scientific, Bremen, Germany) coupled to a 4010 Elemental Combustion System (Costech Instruments, Valencia, CA, USA) in the Chemical Tracer Lab at GLIER (University of Windsor, Windsor, ON). Instrument accuracy, as measured by NIST standards run during the analysis of samples during this study had values for $\delta^{15}\text{N}$ within 0.1‰ (NIST 8573 and NIST 8574), and 0.2‰ (NIST 8547), and for $\delta^{13}\text{C}$ within 0.1‰ (NIST 8573, 8542, and 8544) of certified values. Four laboratory standards (NIST 1577c, tilapia muscle, USGS 40 and Urea ($n = 104$ for each)), run every 12 samples, had a precision of 0.2‰ for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Sample reproducibility of sample tissue replicates (measured in triplicate every 10 samples) was $\pm 0.1\%$ ($n = 83$) for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, and was within the acceptable $\pm 0.2\%$ range.

3.2.4 Statistical Analysis

Kruskal-Wallis tests were used to assess differences in resource use ($\delta^{13}\text{C}$) and trophic position ($\delta^{15}\text{N}$) among species because some groups did not meet the assumptions of normality (Shapiro-Wilks Test, $p < 0.01$ for walleye and white perch $\delta^{13}\text{C}$). If significant differences in $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ were detected, post hoc tests (Dunn's Test) were performed.

PCB's were natural log transformed to meet the assumptions of parametric tests (Shapiro-Wilks Test, $p > 0.05$; Levene's Test, $p > 0.7$ for all groups). A GLM was performed in JMP version 13.1.0 (SAS Insititute Inc, 2014) to determine if there were significant differences among species for the accumulation of each PCB congener with total length. If species was a significant variable, post hoc tests (Tukey's HSD) were conducted. Linear regressions for each species and PCB congener with total length were then run, and the slopes compared using a repeated measures ANCOVA. All statistical tests were conducted in JMP version 13.1.0 (SAS Insititute Inc, 2014).

3.3 Results

PCB concentrations increased with size for all species and congeners (Table 3.1). PCB 153 had the highest concentrations in all species ($12.5 \pm 1.7 \mu\text{g}/\text{kg}$ w.w., mean ± 1 SE), followed by PCB 138 ($10.5 \pm 1.5 \mu\text{g}/\text{kg}$ w.w.), and 180 ($9.1 \pm 1.3 \mu\text{g}/\text{kg}$ w.w., Table 3.1). Overall, PCB concentrations were similar between species, although there were some differences in specific size classes (Table 3.1). Habitat use, based on $\delta^{13}\text{C}$, was similar in all species and across size classes with slight differences among species (Kruskal-Wallis Test; $\chi(2) = 9.1$, $p = 0.01$). White perch ($-22.3 \pm 0.2\%$) had slightly higher $\delta^{13}\text{C}$ than walleye ($-21.5 \pm 0.1\%$; Dunn's Test, $p < 0.01$), and freshwater drum

was similar to both species ($p > 0.2$). Trophic position, based on $\delta^{15}\text{N}$, differed among species ($\chi(2) = 19.6$, $p < 0.001$), and was highest in walleye (17.0 ± 0.2 ‰) and lowest in freshwater drum (15.0 ± 0.3 ‰; $p < 0.001$), while white perch $\delta^{15}\text{N}$ was statistically similar to both species ($p > 0.1$; Table 3.1).

When total length was accounted for using GLM, walleye had lower PCB 153 and 138 concentrations than white perch (Tukey's HSD, $p \leq 0.02$ for both), while freshwater drum had similar concentrations to both species for both congeners ($p \geq 0.1$ for all). For PCB 180, walleye had lower concentrations than both white perch and freshwater drum ($p \leq 0.04$), which had similar concentrations to each other ($p = 0.8$).

Relationships between PCB 153 concentrations and total length were significant for freshwater drum ($R^2 = 0.39$, $F_{1,18} = 15.1$, $p < 0.001$) and white perch ($R^2 = 0.58$, $F_{1,11} = 19.2$, $p < 0.001$), but only marginally for walleye ($R^2 = 0.11$, $F_{1,22} = 4.1$, $p < 0.1$; Figure 1, Table 3.2). The slopes of these relationships were the same or similar with PCB 138 and 180 (Repeated Measures ANCOVA, $F_{2,56} = 1.9$, $p = 0.2$; Figure 1, Table 3.2) but differed between species ($F_{4,112} = 8.4$, $p < 0.001$). White perch had the steepest slopes for PCB concentration with total length (slope $\approx 7.7 \times 10^3$ for all congeners) compared to walleye which had the lowest slopes (Tukey's HSD, $p \leq 0.03$, slope $\approx 2.0 \times 10^3$ for all; Table 3.2). Freshwater drum had similar slopes to both white perch and walleye for PCB 153 and 138 ($p \geq 0.1$, slope $\approx 2.9 \times 10^3$), but had a different slope from walleye for PCB 180 ($p < 0.05$, slope $\approx 3.4 \times 10^3$)

3.4 Discussion

The patterns of PCB concentrations across ontogeny in fish with different feeding ecology demonstrate the complexity of contaminant dynamics in freshwater food webs. In all species PCB concentrations increased with size, although this was only marginally significant ($p < 0.1$) in walleye. The slope of this relationship (i.e. the increase in PCB concentration with size) was highest in white perch, intermediate in freshwater drum, and lowest in walleye. Differences in slope between these species are related to trophic shifts and growth rates, highlighting that ontogenetic changes in PCB concentrations vary across species with varying trophic ecology.

PCB concentrations were similar to those previously reported in the western basin of Lake Erie for the three species studied. For example, Morrison et al., (2002) found similar lipid corrected PCB 138 concentrations in walleye collected in 1994 and 1995 to those measured here when concentration was lipid normalized. As well, lipid corrected PCB concentrations in white perch and freshwater drum from the Detroit River in the 1980s were similar to those in our study (Russell, Gobas & Haffner, 1999). Finally, Morrison et al., (1998) predicted that concentrations of PCBs in Lake Erie would decline in many prey fish (including white perch) due to the introduction of zebra mussels (*Dreissena polymorpha*) but that large bodied fishes (e.g. freshwater drum) and predators (e.g. walleye) would experience no changes or slight increases in concentration, consistent with the results in this study. These results suggest that PCB concentrations in the western basin of Lake Erie have remained relatively constant since the 1990s, which has been noted in other studies (Sadraddini *et al.*, 2011).

The consistent values of $\delta^{13}\text{C}$ across the three species and size classes, suggest they are feeding within the same general food web. Guzzo *et al.* (2011, 2013) and Campbell *et al.* (2009) found similar $\delta^{13}\text{C}$ for all three species in Lake Erie to the present study. This is somewhat unexpected, especially for the benthic freshwater drum, but could be due to the shallow and productive nature of the western basin of Lake Erie that likely blurs habitat boundaries and allows fish to couple resources from different habitats more easily (Dolson *et al.*, 2009). Seasonal large-scale movements by fish could also obscure $\delta^{13}\text{C}$, and likely $\delta^{15}\text{N}$. Walleye in Lake Erie are known to undergo annual migrations out of the western basin to the central and eastern basin, leaving in early summer and returning in the autumn (Raby *et al.*, 2018). Information on drum and white perch movements have not been directly studied, but survey work suggests they move out of the western basin around the same time as walleye (Ontario Ministry of Natural Resources and Forestry, 2016). White perch populations in their native ranges, as they are non-native to Lake Erie, have been found to have partial migrations (Kerr & Secor, 2012).

Trophic position based on $\delta^{15}\text{N}$ varied among species and between size classes, and indicate that the species were feeding at different trophic levels. White perch had higher $\delta^{15}\text{N}$ than previously reported in Lake Erie, as did walleye, but freshwater drum had lower $\delta^{15}\text{N}$ (Campbell *et al.*, 2009; Guzzo *et al.*, 2011, 2013). Walleye had the highest $\delta^{15}\text{N}$ overall, freshwater drum had the lowest, and white perch had intermediate values to both species. While walleye showed no changes in trophic position across different sizes, white perch showed an increase in $\delta^{15}\text{N}$ with total length, and freshwater drum had a period of high $\delta^{15}\text{N}$ when they were between 200-400mm in total length. White perch are a late piscivore so this increase in $\delta^{15}\text{N}$ with size is not unexpected (Schaeffer & Margraf,

1986; Mittelbach & Persson, 1998), and freshwater drum are known to feed on small fish between 250-400mm which would increase their trophic position for those lengths (Bur, 1982).

Lipids generally increased with total length for all species and may play an important role in PCB concentrations of these species at larger sizes. Lake Erie freshwater drum had similar lipid content to those in Alabama lakes and rivers (Rypel, Bayne & Mitchell, 2006). Additionally, freshwater drum and white perch had similar lipid content to those reported for the Detroit River (Russell *et al.*, 1999). Walleye had lower lipid content than previously reported in Lake Erie (De Vault *et al.*, 1996).

PCBs increased with total length in all three species, consistent with many studies in fish (Gewurtz, Bhavsar & Fletcher, 2011). This relationship was strong in white perch and freshwater drum, explaining over 57 and 39% of the variation, respectively, but only marginally significant in walleye, explaining < 12% variability in their PCB concentrations. Strong size – PCB concentration relationships have been found in a wide range of walleye populations in the Great Lakes (Johnston *et al.*, 2002). The weak relationship for this walleye population is driven by similar concentrations in small and medium size classes and variable PCB concentrations, and could be due to the consistent trophic position, based on $\delta^{15}\text{N}$, across size. As well, walleye lipid content was similar in medium and large size classes, whereas the freshwater drum and white perch had higher lipid contents in the largest size classes.

The rate of increase in PCB concentration with size or ontogeny, quantified by the slope of this relationship, was twice as high in white perch than freshwater drum or walleye, although freshwater drum slopes were not statistically different from the other

species. Walleye have the faster growth rate, with the capacity to grow to 200mm in total length in their first year of life compared with 87 and 157mm in white perch and freshwater drum, respectively (Bur, 1984; Mittelbach & Persson, 1998; Scott & Crossman, 1998). Growth decreases PCB concentrations through the dilution of body burden as new tissue is added, particularly in highly hydrophobic PCB congeners ($\log K_{ow} > 6.5$; Connolly & Pederson, 1988; Paterson *et al.*, 2007b). These results suggest that growth rates strongly influence the rate at which PCBs increase in size in freshwater fish.

Most commonly, increases in PCB concentrations with size in fish is associated with increases in trophic position, linked to increasing mouth gap, and decreases in elimination rate with size (Olsson, Valters & Burreau, 2000; Paterson *et al.*, 2007b). White perch $\delta^{15}\text{N}$ increased with size, explaining the steep slope of PCB accumulation. However, this trend was not observed for freshwater drum, and size likely played a more important role in PCB uptake for this species.

PCB concentrations in medium and large fish diverged among species, likely as a result of differing ecology. Medium white perch and large walleye both had high concentrations of PCBs and $\delta^{15}\text{N}$ compared to smaller individuals and freshwater drum. Growth rates slow as individuals approach their asymptotic length, reducing an organism's ability to reduce PCB concentrations through growth dilution (Paterson *et al.*, 2006), and larger fish have a reduced capacity to eliminate contaminants, increasing concentrations further (Kiriluk *et al.*, 1995; Sijm & Van Der Linde, 1995; Paterson *et al.*, 2007b). Additionally, differences in prey contamination levels will begin to dominate

differences among species PCB concentrations because fish will be large enough to have switched to their preferred foraging strategy (Paterson *et al.*, 2006).

Relationships between PCB concentration and total length for congeners 153, 138, and 180 were identical, confirming our assumption that uptake of these three congeners follow the same pathways. The slope of PCB accumulation with length was the same or very similar for all three congeners within a species. All three congeners have large log K_{OW} values (> 6.5) and as a result are likely accumulated only through diet (Fisk *et al.*, 1998). As a result, any differences in slope observed between the three species is partially due to diet.

3.5 References

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Table 3.1: Lipids content (% , mean \pm 1 SE), concentrations ($\mu\text{g}/\text{kg}$ w.w., mean \pm 1 SE) of PCB 153, 138 and 180, and stable isotope values of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{34}\text{S}$ (‰, mean \pm SE) for small (< 200 mm), medium (200 – 400 mm) and large (> 400 mm) freshwater drum, walleye, and white perch in the western basin of Lake Erie.

Species	Size Class	n	Lipid Content	Concentration ($\mu\text{g}/\text{kg}$ w.w.)			Stable Isotopes (‰)	
				PCB 153	PCB 138	PCB 180	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
Freshwater Drum	<i>Small</i>	7	1.8 \pm 1.0	4.6 \pm 0.3	3.5 \pm 0.1	3.1 \pm 0.2	-22.0 \pm 0.4	13.7 \pm 0.6
	<i>Medium</i>	7	1.2 \pm 0.3	13.5 \pm 4.0	10.5 \pm 3.2	10.1 \pm 3.1	-21.5 \pm 0.4	16.2 \pm 0.3
	<i>Large</i>	8	4.0 \pm 0.8	16.9 \pm 2.3	13.0 \pm 1.6	15.9 \pm 3.2	-22.0 \pm 0.2	14.8 \pm 0.5
	Total	23	2.4 \pm 0.5	12.0 \pm 1.9	9.3 \pm 1.5	10.0 \pm 1.8	-21.8 \pm 0.2	15.0 \pm 0.3
Walleye	<i>Small</i>	4	0.8 \pm 0.3	6.8 \pm 1.8	5.9 \pm 1.6	4.7 \pm 1.1	-21.8 \pm 0.1	17.1 \pm 0.7
	<i>Medium</i>	8	1.5 \pm 0.6	6.2 \pm 1.0	5.3 \pm 0.9	3.9 \pm 0.6	-21.6 \pm 0.2	16.9 \pm 0.3
	<i>Large</i>	14	1.5 \pm 0.2	18.0 \pm 6.1	16.3 \pm 5.7	13.1 \pm 4.5	-21.3 \pm 0.2	17.0 \pm 0.2
	Total	26	1.4 \pm 0.2	12.6 \pm 3.4	11.3 \pm 3.2	9.0 \pm 2.5	-21.5 \pm 0.1	17.0 \pm 0.2
White Perch	<i>Small</i>	8	1.9 \pm 0.4	8.6 \pm 2.6	7.2 \pm 2.2	5.2 \pm 1.7	-22.4 \pm 0.4	15.8 \pm 0.7
	<i>Medium</i>	6	4.2 \pm 0.7	19.1 \pm 5.1	16.2 \pm 3.9	12.0 \pm 3.6	-22.2 \pm 0.1	16.7 \pm 0.2
	Total	14	2.9 \pm 0.5	13.1 \pm 2.9	11.1 \pm 2.3	8.1 \pm 2.0	-22.3 \pm 0.2	16.2 \pm 0.4

Table 3.2: Slopes and intercepts of regressions for log concentrations ($\mu\text{g/kg w.w.}$) of PCB 153, 138, and 180 with total length (mm) for freshwater drum, walleye, and white perch from western basin of Lake Erie.

PCB Congener	Dependent Variable	Intercept	Slope	Adj. R²	p-value
PCB 153	Freshwater Drum	1.3	2.8×10^{-3}	0.39	< 0.001
	Walleye	1.3	2.0×10^{-3}	0.11	0.05
	White Perch	0.8	7.7×10^{-3}	0.58	< 0.001
PCB 138	Freshwater Drum	1.0	2.9×10^{-3}	0.39	< 0.001
	Walleye	1.1	2.0×10^{-3}	0.10	0.07
	White Perch	0.7	7.7×10^{-3}	0.61	< 0.001
PCB 180	Freshwater Drum	0.9	3.4×10^{-3}	0.41	< 0.001
	Walleye	0.8	2.2×10^{-3}	0.11	0.05
	White Perch	0.3	7.9×10^{-3}	0.57	< 0.001

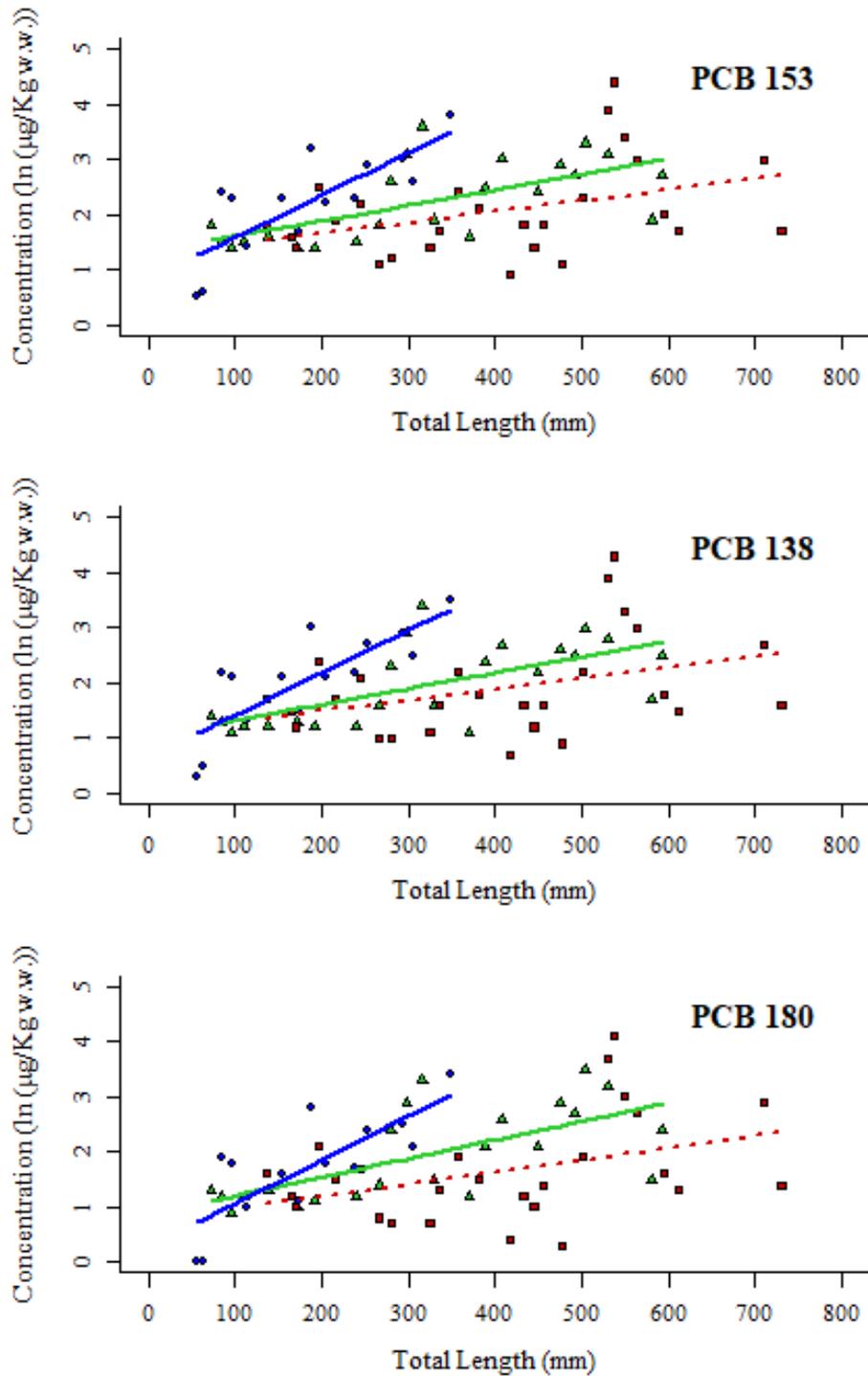


Figure 3.1: Relationships of PCB 153, 138 and 180 with total length based on concentrations measured in freshwater drum (green triangles), walleye (red squares) and white perch (blue circles). Relationships that were marginally significant are dotted lines ($p < 0.1$), and significant relationships are solid lines ($p < 0.05$).

CHAPTER IV: GENERAL DISCUSSION

4.1 Summary

Food webs represent our understanding of the trophic interactions and energy flow between species within ecosystems. A number of different hypotheses attempt to explain why food webs are structured the way they are using different mechanisms to rationalise the patterns observed within natural ecosystems (see Chapter 1 for a detailed description). However, each hypothesis seems to centre around the energy consumption and expenditure of organisms, which changes with resource use (Hutchinson, 1959), trophic position (Hutchinson, 1959; Pimm & Lawton, 1977; Pimm, 2002), predator mobility (McCann, Rasmussen & Umbanhowar, 2005), and foraging patterns (e.g. 2-D vs. 3-D; Pawar, Dell & Savage, 2012).

Energy appears to be an important driver of food web dynamics within Lake Erie's western basin, which is consistent with the central tenets of all four hypotheses posed in Chapter 1. All three species showed support for Hutchinson's energy limitation hypothesis by showing seasonal shifts in resource use and trophic position, which indicated they were probably exploiting seasonally abundant prey resources. It is not possible to comment on whether the data presented in this thesis supported Pimm's dynamic stability hypothesis or Pawar's dimensionality hypothesis because I did not have the relevant population statistics or movement data necessary to do so. The patterns in isotopic niche and rate of PCB accumulation with size in walleye partially supported McCann's predator mobility hypothesis (McCann *et al.*, 2005), with individuals having a greater variability in PCB concentration with increasing size, possibly due to habitat

coupling and some individuals preferring more contaminated habitat or food. Freshwater drum also partially supported this hypothesis but also supported Hutchinson's energy limitation hypothesis as their resource use and trophic position changed with size, perhaps reflecting a trade-off between energy use and resource consumption.

As a result, understanding energy flow and trophic links between species or functional groups is important to explaining ecosystem structure, and single-species approaches to ecosystem management are no longer a viable option. To this end, the objective of the research conducted here was to quantify the resource use of three species (freshwater drum, walleye, and white perch) using different feeding strategies across a range of sizes to assess (a) ontogenetic differences in habitat use and trophic position [Chapter 2], (b) how ontogeny affected resource partitioning of long-lived, large-bodied freshwater fishes [Chapter 2], and (c) how ontogeny impacted the PCB concentrations in fish with different feeding strategies [Chapter 3].

Chapter 2 used stable isotopes of carbon ($\delta^{13}\text{C}$), nitrogen ($\delta^{15}\text{N}$), and sulphur ($\delta^{34}\text{S}$) to determine how the habitat use and trophic position of three common Lake Erie fishes changed with size (ontogeny), and how the species partitioned resources. Stable isotopes analysis showed that ontogeny played an important role in determining the isotopic niche of freshwater drum, walleye and white perch within Lake Erie, indicating that the three species fulfill different functional roles within the ecosystem both at a species level and within species ontogenetically. Freshwater drum in particular had a very distinct pattern of resource use and trophic position at different sizes.

There was less overlap between the isotopic niches of species when comparing resource use and trophic position within a size class than between size classes indicating

that species partitioned resources differently at different size intervals. Species that had larger niche areas (e.g. small white perch) tended to experience greater overlap than species that had smaller niches (e.g. walleye). Additionally, using three isotopes in analysis decreased the amount of overlap observed between groups significantly consistent with the Hutchinson (1959)'s prediction that niches will show greater divergence when more variables are measured and assessed.

Chapter 3 looked at the role of ontogeny on PCB concentrations of congeners (IUPAC #) 153, 138, and 180 in three Lake Erie fishes. Stable isotopes of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) were used to determine the resource use and trophic position of each species. PCB accumulation for all three species with size (i.e. ontogeny) was distinctly different for each of the three species. Growth dilution due to fast growth rates appeared to play a significant role in the contaminant dynamics of walleye, but trophic position and size was more important in white perch and freshwater drum respectfully. Total length was used as a proxy for age, but aging fish using otoliths or scales would have provided a means to determine growth rate and its importance to governing contaminant dynamics for each species (Hile, 1954; Bur, 1984; Schaeffer & Margraf, 1986; Henderson & Morgan, 2002). If age had been determined for each individual, I expect we would have seen similar slopes and PCB concentrations as age is highly correlated with length in all three species studied. Overall, the study highlighted the complexity of contaminant dynamics in freshwater systems, and that different factors are important to regulating contaminants in different species.

Overall, the research here shows that ontogeny plays an important part in both the resource utilisation and contaminant dynamics of species with different feeding

strategies. Each species had distinct resource utilisation and PCB accumulation patterns at different sizes, indicating that they filled different functional roles within the ecosystem. Additionally, these roles changed with size/age suggesting that they may fill different functions at different periods in their lives. Thus, the functional role of a species cannot be determined solely by the adult or most common life stage or size of a species because ecological niche will vary depending on life stage.

The use of a third isotope ($\delta^{34}\text{S}$) to study trophic interactions and isotopic niche highlighted differences in species ecology that otherwise would have been overlooked, consistent with other recent papers (Croisetière *et al.*, 2009; Solomon *et al.*, 2011; Ofukany *et al.*, 2014; Colborne *et al.*, 2016). In productive systems, such as Lake Erie, there may not be enough variability in $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ to identify individual sources (i.e. pelagic vs. littoral primary production) from stable isotopes, but the addition of a third isotope such as $\delta^{34}\text{S}$ may provide enough variability to separate different sources (Phillips & Gregg, 2003). As a result, future papers may benefit from incorporating a third isotope into stable isotope studies, but more research must be conducted to determine the ecological significance of differences in those isotopes within ecosystems.

The research presented here found that species belonging to different feeding guilds had different patterns of resource use and contaminant accumulation through ontogeny, however we do not know whether these patterns are consistent within feeding guilds. Contaminant accumulation was assessed with only three PCB congeners, and organic contaminants with different hydrophobicity ($\log K_{ow}$) are known to accumulate differently. As such, it would be useful to investigate how organic contaminants with different $\log K_{ow}$ accumulate through ontogeny. Finally, PCBs and other organic

compounds have been shown to be good tracers of energy within ecosystems (Paterson, Drouillard & Haffner, 2006; McLeod *et al.*, 2015), so future research should consider quantifying the energy consumption of these three species using PCBs and stable isotopes.

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VITA AUCTORIS

Name: Cecilia E. Heuvel

Place of Birth: Belleville, Ontario

Year of Birth: 1994

Education: Kenner Collegiate Vocational Institute, Peterborough Ontario
2008-2012

Trent University, Peterborough Ontario
2012-2015 B.Sc. Honours

Great Lakes Institute for Environmental Research
University of Windsor, Windsor Ontario
2016-2018 M.Sc.