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# Identifying the role of non-native species in the enhanced trophic transfer of mercury in the food web of Lake Erie, a North American Great Lake

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A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in Biology

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IDENTIFYING THE ROLE OF NON-NATIVE SPECIES IN THE ENHANCED  
TROPHIC TRANSFER OF MERCURY IN THE FOOD WEB OF LAKE ERIE, A  
NORTH AMERICAN GREAT LAKE

Thesis format: Integrated Article

by

Kaylin Liznick

Graduate Program in Biology

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science

The School of Graduate and Postdoctoral Studies  
The University of Western Ontario  
London, Ontario, Canada

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## Abstract

Increasing mercury (Hg) concentrations in top predatory fish is concerning for human and wildlife health. This study examined the amount of Hg available to the food web of Lake Erie, and explored the role that two recently established non-native species, dreissenid mussels and round goby, have played in the trophic transfer of Hg to sport fish. A comprehensive sampling of total Hg (THg) and methylmercury (MeHg) within Lake Erie water, sediment and seston with high temporal and spatial resolution describes environmental concentrations. In addition, biotic THg and MeHg are quantified in benthic invertebrates and three fish species. A steep spatial gradient in aqueous and sediment Hg concentrations, decreasing from West to East, was not reflected in Hg concentrations in seston and benthic invertebrates. Mean seasonal THg concentrations in dreissenids ( $53.38 \pm 3.99$  ng/g) were consistently lowest amongst all invertebrates sampled, which ranged in mean THg concentrations from  $102.56 \pm 9.12$  ng/g to  $203.65 \pm 19.02$  ng/g. Fish THg concentrations showed little difference among basins, further reflecting biotic disconnect from the spatial gradient in abiotic THg and MeHg concentrations, and indicating similar food web biomagnification among basins. Low THg concentrations in both of the non-native species, relative to other invertebrates and fish, suggest they play a minor role in the bulk transfer of THg to top predatory fish.

## Keywords

Mercury, Methylmercury, Bioaccumulation, Biomagnification, Bioconcentration, Lake Erie, Laurentian Great Lakes, Food Web, Trophodynamics, Non-Native Species, Biomonitoring

## Co-Authorship Statement

I hereby declare that I am the sole author of this thesis, except where noted (below). I understand that my thesis may be made electronically available to the public.

Exceptions to sole authorship:

For all chapters, Dr. Brian Branfireun acted as an advisor, reviser, editor, and offered suggestions on scientific content, and the treatment and presentation of data in this thesis. He will be listed as a co-author on any subsequent publication stemming from this work.

## Acknowledgments

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## Dedication

This thesis is dedicated to Melissa, who has the unique ability to get me laughing to the point of tears. This has been so important to me.

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# 1 Literature Review and Introduction

## 1.1 Laurentian Great Lakes

North America is fortunate to have access to the world's largest reserve of freshwater, overwhelmingly dominated by the Laurentian Great Lakes. These Lakes comprise about 18% of the world's water supply, and are the world's largest system of fresh, surface water lakes (Waples *et al.*, 2008). As indicated by the high population density of the Laurentian Great Lakes region, humans depend on the Great Lakes ecosystems for a number of services and amenities. The over 40 million people who reside in the Laurentian Great Lakes basin receive innumerable benefits from the five lakes (International Joint Commission, 2004). The Great Lakes influence regional climate, and stabilize the climate particularly in the summer (Notaro *et al.*, 2013). Many migratory species of birds and bats use geographic features of the Great Lakes as landmarks to guide their migrations (Bonter *et al.*, 2009; Peterson, 2012). In terms of human benefit, many of the residents of the Great Lakes basin use the fresh water for drinking and sustenance. The lakes provide fish and other aquatic biota for occasional consumption or subsistence, and water for irrigation of regional agriculture (Imm *et al.*, 2005; OMAFRA, 2014). Further, recreation, transportation, hydropower and employment through tourism contribute to the long list of services and benefits gained from close proximity to these integral bodies of water (International Joint Commission, 1985; Fuller *et al.*, 1995).

Lake Erie is the southernmost and shallowest of the Laurentian Great Lakes. It is among the largest of freshwater lakes in the world, ranking 9<sup>th</sup> by area and 15<sup>th</sup> by volume (Herdendorf, 1990). Its shoreline has the highest population density, and historically was the first of the Great Lakes to respond to environmental stress, and well as efforts to remediate their negative consequences (Matisoff & Ciborowski, 2005). The economic value of its fishery is substantial; Lake Erie is the most productive of the Great Lakes, contributing about 80% of the value of the Great Lakes commercial fishery (Regier & Hartman, 1973; OMNR, 2012). The lake has been known to French Canadian settlers since 1669, and has played a key role in the livelihood of the inhabitants of its watershed, especially after the establishment of its commercial fishery in 1820. Management of this

valued resource, along with the other trans-boundary Great Lakes, has resulted in the cooperation of Canada and the United States through various programs such as the Great Lakes Fisheries Commission and the International Joint Commission, as well as the signing of inter-governmental Acts such as the Great Lakes Water Quality Act of 1972 (Regier & Hartman, 1973). Lake Erie has a long history of physical and ecological changes due to anthropogenic stress (Mortimer, 1987), with the most recent notable stress being the invasion of several non-native species and the ensuing changes to the lake food web (Jude *et al.*, 1992; Johannsson *et al.*, 2000). Due to the public's reliance on Lake Erie's fishery, monitoring fish for contaminants of concern, which includes the element mercury (Hg), has also been a feature of the lake's management (Schmitt & Brumbaugh, 1990; Gewurtz *et al.*, 2011).

A geographically comprehensive and sample-intensive study has shown that 100% of fish from 500 freshwater lakes in the United States of America have traces of Hg, from 5 to 6605 ppb depending on trophic position in the food web (Stahl *et al.*, 2009). Mercury is a recognized environmental contaminant, contributing with other pollutants to the issuing of fish consumption advisories, which provide guidelines and recommendations on intake quantities for species of fish in a given region (OMOE, 2014). Exposure to Hg through consumption of fish can lead to adverse health effects in human nervous and cardiovascular systems, as well as in reproduction and fetal development (Mergler *et al.*, 2007). Increases in or high levels of Hg in consumable fish are considered a public health concern (Health Canada, 2004; World Health Organization, 2007).

## 1.2 The Global Mercury Pool – Past and Present

Mercury is regarded as a global environmental pollutant (Lindqvist, 1991; Watras & Huckabee, 1994). Its ability to be globally dispersed in the atmosphere as a gas results in its deposition to terrestrial and aquatic ecosystems, even in remote parts of the world (Fitzgerald *et al.*, 1998). The main natural sources of Hg include volcanoes, forests, soils, and open oceans, which account for 20% of the total Hg pool of around 2000 tonnes per year (Mason *et al.*, 1994). In 1994, Mason *et al.* estimated that anthropogenic sources of Hg accounted for 70-80% of all emissions to the atmosphere. Mercury exists in the environment in a number of chemical forms, which correspond to its valence states. The



atmosphere is an important reservoir for gaseous Hg, and many complex reactions with particulate chemicals and water vapor occur here, often influencing Hg valence states or converting elemental Hg into other compounds (Lin & Pehkonen, 1999). Gaseous elemental Hg(0) comprises >90% of the atmospheric Hg, while divalent Hg(II) and methylmercury (MeHg) make up 3% each (Slemr *et al.*, 1985; Lindberg & Stratton, 1998). Monovalent Hg(I) is unstable in environmental conditions and is rarely observed. Elemental Hg(0) has the longest atmospheric residence time of approximately 9 months, during which it can travel vast distances around the globe in the troposphere, and it returns back to Earth's surface primarily through dry deposition (Slemr *et al.*, 1885; Lindberg *et al.*, 2007). Divalent Hg(II) has a shorter atmospheric residence time of days to weeks, and it undergoes both dry and wet deposition. Compared to Hg(0) it is a highly surface-reactive species, and it is also highly water-soluble (Lindberg & Stratton, 1998).

A significant historical source of gaseous Hg to the atmosphere was gold and silver amalgamation processes in the Americas from 1550 to 1900 (Nriagu, 1994). Observations of total gaseous Hg in the Northern and Southern hemispheres indicate historical trends of increasing concentrations from the early 1920s to the 1970s, to a maximum in the late 80s, after which a decreasing trend was seen from 1990-1996, which has since remained constant (Slemr *et al.*, 2003). Emissions in the mid-1970s were estimated to be 11000 tonnes per year, which then fell to 4500 tonnes per year in the 1980s (Pirrone *et al.*, 1996). Atmospheric Hg has increased two- to three-fold over the past two centuries, and this can be attributed to the anthropogenic use of Hg and industrialization (Driscoll *et al.*, 2007).

Current assessments estimate that natural sources emit 5207 Mg of Hg per year, whereas anthropogenic sources emit 2320 Mg annually. It is important to note that, in these estimates, natural sources account for re-emission of previously deposited Hg through evasion at water-air interfaces and the combustion of biomass, as well as the conventional natural sources of volcanoes and geothermal sources (Pirrone *et al.*, 2010). Major current natural and anthropogenic sources of Hg tend to differ from historical ones, as efforts were put forth by the United Nations Environment Programme (UNEP) and North American governments to reduce the use of Hg and its emissions as byproducts (Canada-

U.S. Air Quality Agreement, 1978; AMAP/UNEP, 2008). Hg remains a by-product of many industrial processes occurring around the world to this day. The two significant current anthropogenic sources are the extraction and burning of fossil fuels, and artisanal, small-scale gold mining. Other recent major anthropogenic sources of Hg emissions are metal production, cement production, and waste incineration (AMAP/UNEP, 2008). Combustion of fuels accounts for 880 tonnes of Hg emissions globally, and Asian countries contribute 622 tonnes of this amount annually. Artisanal and small-scale gold mining occurs mainly in Africa, Asia and South America, and emits 350 tonnes of Hg into the atmosphere. Asian countries contributed 67% of total global anthropogenic Hg emissions, followed by North America and Europe (Pacyna *et al.*, 2010). Pirrone *et al.* (2010) also found that Hg emissions from Asia are increasing annually, mainly driven by energy demand, whereas both Europe and North America are reducing their Hg emission contributions.

In addition to global studies examining atmospheric Hg spanning many continents, there is a repository of information on regional Hg emissions and deposition to important ecological and economical areas. Certain areas of North America are of particular focus, due to the abundance of lakes and other aquatic ecosystems that can be particularly sensitive to Hg deposition (Driscoll *et al.*, 2007). Although these areas are still affected by the global pool of Hg, there is also a strong effect of regionally produced atmospheric Hg, with gradients caused by regional atmospheric emission and deposition of particulate Hg (Nater & Grigal, 1992). When considering regional sources, particulate Hg is important as it has a shorter atmospheric lifetime, deposits more locally than does gaseous Hg, and is more reflective of proximal sources. Pirrone *et al.* (1996) were able to attribute local emission increases and decreases in Detroit, Michigan, to openings and closures of Hg-emitting industrial sources. Studies in the Laurentian Great Lakes region have reported an overall decline in local Hg emissions and reduced inputs from observed peaks in the 1960s and 1970s (Painter *et al.*, 2001; Engstrom *et al.*, 2007). Sediment cores were used to assess long-term Hg deposition, and although studies agree that global Hg emissions have not abated, regional reductions in Hg emissions and deposition since the 1970s were likely due to pollution control technology, the reduction in coal energy

use, and possibly increased stack heights contributing to a longer range of deposition (Engstrom & Swain, 1997).

Mercury was released in the form of liquid waste by a number of chemical and pesticide companies near Lake Erie's shores prior to 1970. The BSAF Wyandotte and Dow Chemical Corporations, which produced chlorine gas and caustic soda using Hg amalgam, were major contributors in the Western basin of the lake. Estimated accidental Hg discharges were 4.5-9.1 kg per day from 1939 to 1970 and 22.7 kg per day from 1950-1970 for each respective company (Federal Water Quality Administration, 1970). In addition to the chemical production industry, the use of organic-mercurial fungicides in the lake's surrounding agriculture was prevalent prior to 1970, and the metropolitan areas of Detroit-Windsor, Monroe and Toledo were significant centres of coal burning, which contributed to regional atmospheric deposition of Hg (Walters *et al.*, 1974). Walters *et al.* (1974) characterized sections of Lake Erie's sediment, particularly in the Western basin, as polluted, defining pollution as 1 standard deviation above the natural background level, which they determined to be 0.02 - 0.07 ppm.

### 1.3 Methylation of Mercury

Mercury takes on many chemical forms. Divalent inorganic Hg (Hg(II)) is the most common form that enters and exists in aquatic ecosystems. Mercury also exists in an organic form, methylmercury (MeHg). The conversion of inorganic Hg(II) to MeHg occurs mainly through the processes carried out by sulphate-reducing bacteria (SRB) in enzyme-mediated reactions (Morel *et al.*, 1998). Some of the physical characteristics of certain aquatic ecosystems play an important role in the transformation of Hg(II) to MeHg, including temperature, oxygen concentration, pH, and substrate availability (Ullrich *et al.*, 2001). The conversion of Hg to MeHg is mediated by factors that fall into two general categories: those that affect the abundance and activity of methylating bacteria, and factors that influence the bioavailability of Hg to be methylated, the latter through speciation and delivery of solid or dissolved phase Hg to aquatic ecosystems (Heyes *et al.*, 2006).

Aquatic ecosystems play an important role in the cycling of Hg. Aquatic systems, such as lakes, receive Hg directly through surface atmospheric deposition, and also between 5 and 85% of total Hg (THg) loading from watershed runoff from their surrounding terrestrial basins (Grigal, 2002). Wetlands are key mediators of Hg transport from terrestrial to aquatic systems. While once believed to be pools or sinks for THg (Grigal, 2003), wetlands are more likely a short- and long-term source of THg because of fluxes associated with the watershed connectivity of wetland soils. Wetlands are also an important source of MeHg, and net production and short residence time of MeHg make wetlands a key transporter of this compound to aquatic systems (Selvendiran *et al.*, 2008). Wetlands and peatlands actively produce MeHg, and are sources of MeHg for freshwater systems (Brianfireun *et al.*, 1998). Some typical characteristics of wetlands, including anoxic conditions and high nutrient availability, enhance *in situ* MeHg production through stimulation of SRBs. Others, such as high dissolved organic carbon, transport Hg species to aquatic systems (Gilmour *et al.*, 1992; Driscoll *et al.*, 1995).

Methylation of inorganic Hg occurs mainly in littoral sediment, near the sediment-water interface. Methylation may also occur in the water column, although absolute methylation rates appear highest in sediment (Gilmour & Henry, 1991). Net increases in methylation (i.e. production of MeHg is higher than demethylation) were observed with increasing sulphate-reduction rates associated with higher sulphate concentrations (Gilmour *et al.*, 1992). The chemical form of Hg and presence of MeHg are also highly influenced by redox conditions and pH in aquatic systems (Ullrich *et al.*, 2001).

Temperature also plays a role in MeHg production, as higher temperatures stimulate microbial activity, and they also depress demethylation processes so that net methylation rates increase (Korthals & Winfrey, 1987; Bodaly *et al.*, 1993). These conditions correspond to an overall increase in methylation rates in aquatic systems in summer months. The array of factors that control the net production of MeHg and influence methylation rates can vary among lakes, and even within areas of large lakes (Rolfhus *et al.*, 2011; Kidd *et al.*, 2012).

## 1.4 Biomagnification of Methylmercury

Methylmercury has a much longer residence time in organisms than its inorganic counterpart, which contributes to its slow elimination (Mathers & Johansen, 1985). This is one of the qualities that make it a bioaccumulating compound. Another quality is its propensity to bind to muscle tissue, unlike other organic pollutants that tend to bind to fat, and muscle tissue has a longer turnover time (Mergler *et al.*, 2007). Because of the tendency to bioaccumulate relative to inorganic Hg, upwards of 95% of the total Hg in fish is in the methylated form (Bloom, 1992). A small portion of Hg burden in fish, up to 15%, may be from environmental sources such as water; however, the primary source of MeHg in fish is through ingestion (Hall *et al.*, 1997).

In aquatic food webs Hg enters at the point of primary producers, such as phytoplankton, periphyton, and algae (Watras & Bloom, 1992; Hill *et al.*, 1996). Not only does total Hg increase in organisms as it moves up a simple food chain of phytoplankton, zooplankton, to fish, but the proportion of total Hg that is MeHg increases with this trophic progression as well (Watras & Bloom, 1992). The total Hg in freshwater periphyton and zooplankton was comprised of 13-18% and 29-57% MeHg, respectively (Watras & Bloom, 1992; Watras *et al.*, 1998). Studies on freshwater benthic invertebrates reveal up to 50% of THg is in the methylated form (Hill *et al.*, 1996). Methylmercury enrichment at each trophic level, resulting in higher total Hg in organisms in upper trophic levels, illustrates the role of lower components of the food web in the delivery of Hg to top predatory species.

The biomagnification of Hg in aquatic ecosystems is affected by the food chain structure and the amount of trophic levels in the food web (Rasmussen *et al.*, 1990). Whole-lake experiments revealed that the addition of a key prey species, such as the crustacean *Mysis relicta* and forage fish such as smelt, representing a previously non-existent trophic level in Ontario lakes results in higher biomagnification of Hg at the top of the lake's food web (Cabana *et al.*, 1994). The use of stable nitrogen isotopes led to the measurement of continuous trophic position over the discrete trophic level model in fish, which better accounts for the complexity of aquatic food webs. This furthered the understanding that concentrations of contaminants such as polychlorinated biphenyls (PCBs) and Hg

become elevated in top predators as food webs become more complex following the insertions of new species (Vander Zanden & Rasmussen, 1996).

## 1.5 Lake Erie Food Web

The major species assemblages of Lake Erie prior to the 1990s are known, as the lake has been well studied since the 1960s. Reports on species surveys conducted by private and public research organizations provide a picture of the most common types of fish in each of the three basins of Lake Erie. They also often describe the dietary make-up of fish species that were deemed important to study. In the three lake basins, forage fish studied due to their abundance and importance in the diets of piscivorous predatory fish included emerald shiner (*Notropis atherinoides*), spottail shiner (*Notropis hudsonius*), trout-perch (*Percopsis omiscomaycus*), gizzard shad (*Dorosoma cepedianum*), alewife (*Alosa pseudoharengus*), white bass (*Morone chrysops*) and freshwater drum (*Aplodinotus grunniens*) (Muth & Busch, 1989). By the late 1990s, species assemblages changed and forage fish density narrowed down to the clupeids (alewife and gizzard shad) and rainbow smelt (*Osmerus mordax*), which was particularly abundant in the Eastern basin of Lake Erie (Forage Task Group, 2001). The diets of such forage fish are made up mostly of planktonic crustaceans such as cladocera, copepoda, and ostracoda, while being supplemented by amphipods and algae (Muth & Busch, 1989). Common sediment-dwelling benthic invertebrate orders and families of the time period included Oligochaeta (worms), Hirudinea (leeches), Gastropoda (molluscs), Amphipoda (including *Gammaridae*), Isopoda, and the insects Ephemeroptera (including *Hexagenia*, mayfly larvae), Trichoptera (caddisfly larvae) and Diptera (including *Chironomidae*, midge larvae) (Barton *et al.*, 1988).

Over time, walleye (*Sander vitreus*) and yellow perch (*Perca flavescens*) remained abundant piscivorous predators in all three basins of Lake Erie (Muth, 1985), with smallmouth bass (*Micropterus dolomieu*), lake trout (*Salvelinus namaycush*), and burbot (*Lota lota*) included in the rank of predators (Forage Task Group, 2001).

## 1.6 Non-Native Species

Non-native dreissenid (zebra and quagga) mussels arrived in Lake Erie through Lake St. Clair, and were established in the Western basin in 1986 (Hebert *et al.*, 1989). Dreissenid mussels originate from the Black, Azov and Caspian Seas, and are believed to have entered the Great Lakes waterways through ballast of cargo ships (Griffiths *et al.*, 1990). These bivalves were known to have impacts on the bodies of water they invaded, and Lake Erie was no exception. Dreissenid mussels ingest phytoplankton through filtration, which can alter lake-wide plankton biomass, and they also excrete feces and pseudofeces, which deposit on the lake floor and can affect the local fauna (Griffiths *et al.*, 1990). The mussels established quickly, due to high fecundity and an ample amount of their preferable hard and rocky substrate, and abundant food sources. In 1988, a small survey indicated densities of up to 200 individual mussels per m<sup>2</sup> (Hebert *et al.*, 1989), whereas just a few years later in some areas density was found as high as 300 000 mussels per m<sup>2</sup> (Leach, 1993). The fast and aggressive establishment primed the lake for a second non-native species, the demersal fish round goby (*Neogobius melanostomus*), which too thrived in Lake Erie (Johnson *et al.*, 2005b).

The round goby is an obligate benthivore that is also native to the Black, Azov and Caspian Seas (Jude *et al.*, 1992). As dreissenid bivalves were one of the goby's primary food sources in its native range, the fish had ample food supply from the time it arrived in the Great Lakes in 1990 (Crossman *et al.* 1992). Gobies quickly made their way to Lake Erie, and in 1994 the species was found in the Central basin in numbers indicating strong establishment (Forage Task Group, 2001). Many researchers have attributed this to a preference for rocky substrate, such as the bedrock outcrops that comprise many areas of the lake's bed, and the abundance of prey such as mussels and other benthic species *Hexagenia*, *Chironomidae* and crayfish (Ray & Corkum, 1997). Like the dreissenid mussel, the round goby had a highly concentrated population density in some areas. This peaked in in the early 2000s, with a maximum lake-wide population consisting of  $4.2 \pm 1.5$  billion individuals in 1999 (Johnson *et al.* 2005b) and a population estimate of 9.9 billion in the Western basin alone in 2002 (Johnson *et al.*, 2005a). All Lake Erie agencies reported high numbers of the goby in bottom trawls at the peak of their abundance,

despite their preferential habitat being difficult to sample, resulting the likelihood of under-sampling. Although abundance was highest in the Central basin due to a greater expanse of rocky substrate, lake-wide trawls indicated densities of up to 8000 individuals per hectare (Forage Task Group, 2001). The quick and aggressive establishment of the zebra and quagga mussels, coupled with the strong establishment of their main predator, the round goby, resulted in vast changes to the lake's food web structure by the 2000s.

## 1.7 Rationale, Aims and Objectives

Concerted efforts by multiple levels of international governments and stakeholders have resulted in remarkable progress in the remediation of some of Lake Erie's largest problems, that frequently centre around the management of environmental contaminants (Richards & Baker, 1993). Contamination by environmental pollutants has been a key topic of interest for decades, and the most restrictive contaminant in Great Lakes consumption advisories was historically PCBs (Bhavsar *et al.*, 2011). At points in time, concentrations of Hg in fish have been prohibitively high for consumption, resulting in the temporary closure of a portion of Lake Erie's fishery (U.S. National Resource Council Panel on Mercury, 1978). Mercury concentrations in sediments of some areas of Lake Erie vastly exceeded the Canadian Sediment Quality threshold and probable effect levels, values which represent concentrations below which adverse biological effects are expected to occur rarely, and above which adverse biological effects are expected to occur frequently, respectively (Painter *et al.*, 2001; Canadian Council of Ministers of the Environment, 2001). In addition, aqueous THg concentrations were highest in Lake Erie relative to other Great Lakes (Dove *et al.*, 2012). A reduction in the quality of Lake Erie's fish due to contaminants, including Hg, would have a great impact on the dependents of this resource, which would span consumers, commercial fishery employees and government's economies (Evers *et al.*, 2011; OMNR, 2012).

Analyses of a long-term (35 year), large (5807 sample) fish tissue Hg concentration dataset collected by the Ontario Ministry of the Environment revealed a recent increase in concentrations, becoming especially evident after the mid 1990s. This reversal of the declining fish Hg concentration trend was seen only in Lake Erie, while the other Great Lakes continued to experience decreases in fish tissue THg concentrations over time



(Bhavsar *et al.*, 2010; Azim *et al.*, 2011). This observed trend was independently validated through U.S.EPA Great Lakes Fish Monitoring Program dataset, where Lake Erie stood out as the only Great Lake undergoing trends of increasing Hg fish tissue in walleye and lake trout (Zananski *et al.*, 2011). Although Lake Erie walleye and trout tissue Hg concentrations remain among the lowest of all the Great Lakes (Bhavsar *et al.*, 2011), an unexplained and unchecked increasing trend in fish Hg concentrations requires attention, especially considering that Lake Erie walleye are experiencing a higher rate of increase than other fish such as smallmouth bass and white bass (Azim *et al.*, 2011).

The observed reversal in declining Hg concentrations coincides with the arrival of the two non-native species, dreissenid mussels and round goby, in Lake Erie (Hebert *et al.*, 1989; Crossman *et al.*, 1992). Considering that insertion of prey items into aquatic food webs, as well as increasing complexity of food webs, results in the enhanced bioaccumulation of contaminants including Hg in top predatory species (Cabana *et al.*, 1994; Vander Zanden & Rasmussen, 1996), the relationship between these specific invaders and the trophic transfer of Hg requires investigation. Yet the correlation between Lake Erie invaders and their effect on biotic Hg levels remains largely unexplored (Hogan *et al.*, 2007). This thesis explores the relationship between the introduction of non-native species and the cycling and trophic transfer of Hg in an important international freshwater resource, Lake Erie. It also provides a comprehensive, multi-compartmental empirical analysis of Hg concentrations in Lake Erie.

Despite the regional and national importance of Lake Erie, there are gaps in our knowledge and understanding of the cycling of Hg in this critical freshwater resource. With Hg concentrations in Lake Erie fish increasing, it is clear our knowledge of Hg cycling in the Lake Erie environment and biota must improve beyond routine sport fish monitoring, which consists of quantifying Hg in sport fish species of varying lengths. Total Hg and MeHg concentrations in abiotic and biotic compartments of lake are required over the summer sampling period in order to identify short-term temporal trends, and also from all three basins of the lake to clarify the influence of spatial patterns on biota.

The overall objective of this thesis is, therefore, to provide information on concentrations of Hg and MeHg in the Lake Erie environment, as well as the amount of Hg at the base of the Lake Erie food web, in order to further our understanding of recently observed trends in Lake Erie top predatory fish. This new information will help address my general working hypothesis that non-native zebra and quagga mussels, as well as round goby, have played a role in enhancing the trophic transfer for Hg through the Lake Erie food web to top predatory fish. To accomplish this, empirical evidence of Hg and the bioaccumulating form MeHg will be gathered from the abiotic environment, as well as in benthic invertebrate and fish species of the lake, which include the non-native species of interest.

A specific objective of this research is to quantify Hg and MeHg in the water, sediment and seston of Lake Erie at frequent, regular intervals over the sampling season. This is addressed in Chapter 2 with the aim of determining the amount of THg and MeHg that is available to aquatic biota of this lake system. The changes in the quantity of Hg and MeHg in these compartments over time is also described, and this information enhances our knowledge of the changes in MeHg over the summer sampling period, and the importance of continuous sampling. A second objective is to collect evidence to determine if the introduction of non-native dreissenid mussels and round goby may be wholly or in part responsible for the recent increases in Lake Erie sport fish mercury concentrations. This is addressed in Chapter 3, where the survey of Hg and MeHg available to aquatic biota is supplemented by quantifying Hg in sampled benthic invertebrates and fish of Lake Erie. This chapter also explores the concentrations of Hg and MeHg in the non-native species dreissenid mussels and round goby. This information is placed into broader context to deduce what role, if any, recent non-native invaders play in the lake-wide cycling of Hg.

## 1.8 References

- AMAP/UNEP, 2008. Technical Background Report to the Global Atmospheric Mercury Assessment. Arctic Monitoring and Assessment Programme / UNEP Chemicals Branch. 159 pp.
- Azim, M.E., Kumarappah, A., Bhavsar, S.P., Backus, S.M., Arhonditsis, G., 2011. Detection of the spatiotemporal trends of mercury in Lake Erie fish communities: a Bayesian approach. *Environ. Sci. Technol.* 45, 2217-2226.
- Barton, D.R., 1988. Distribution of some common benthic invertebrates in nearshore Lake Erie, with emphasis on depth and type of substratum. *J. Great Lakes Res.* 14, 34-43.
- Bhavsar, S.P., Gewurtz, S.B., McGoldrick, D.J., Keir, M.J., Backus, S.M., 2010. Changes in mercury levels in Great Lakes fish between 1970s and 2007. *Environ. Sci. Technol.* 44, 3273-3279.
- Bhavsar, S.P., Awad, E., Mahon, C.G., Petro, S., 2011. Great Lakes fish consumption advisories: is mercury a concern? *Ecotoxicology* 20, 1588-1598.
- Bloom, N.S., 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49, 1010-1017.
- Bodaly, R., Rudd, J., Fudge, R., Kelly, C., 1993. Mercury concentrations in fish related to size of remote Canadian Shield lakes. *Can. J. Fish. Aquat. Sci.* 50, 980-987.
- Bonter, D.N., Gauthreaux JR, S.A., Donovan, T.M., 2009. Characteristics of important stopover locations for migrating birds: Remote sensing with radar in the Great Lakes basin. *Conserv. Biol.* 23, 440-448.
- Branfireun, B., Hilbert, D., Roulet, N., 1998. Sinks and sources of methylmercury in a boreal catchment. *Biogeochemistry* 41, 277-291.

- Cabana, G., Tremblay, A., Kalff, J., Rasmussen, J.B., 1994. Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (*Salvelinus namaycush*). *Can. J. Fish. Aquat. Sci.* 51, 381-389.
- Canada-U.S. Air Quality Agreement. 1978. Agreement Between the Government of Canada and the Government of the United States of America on Air Quality. International Joint Commission: Ottawa, Ontario, & Washington, D.C.
- Canadian Council of Ministers of the Environment. 2001. Canadian sediment quality guidelines for the protection of aquatic life: Introduction, in: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment: Winnipeg, Manitoba.
- Crossman, E., Holm, E., Cholmondeley, R., Tuininga, K., 1992. First record for Canada of the rudd, *Scardinius erythrophthalmus*, and notes on the introduced round goby, *Neogobius melanostomus*. *Can. Field Nat.* 106, 206-206.
- Dove, A., Hill, B., Klawunn, P., Waltho, J., Backus, S., McCrea, R., 2012. Spatial distribution and trends of total mercury in waters of the Great Lakes and connecting channels using an improved sampling technique. *Environ. Pollut.* 161, 328-334.
- Driscoll, C., Blette, V., Yan, C., Schofield, C., Munson, R., Holsapple, J., 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. *Water Air Soil Pollut.* 80, 499-508.
- Driscoll, C.T., Han, Y., Chen, C.Y., Evers, D.C., Lambert, K.F., Holsen, T.M., Kamman, N.C., Munson, R.K., 2007. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *Bioscience* 57, 17-28.
- Engstrom, D.R., Swain, E.B., 1997. Recent declines in atmospheric mercury deposition in the upper Midwest. *Environ. Sci. Technol.* 31, 960-967.

- Engstrom, D.R., Balogh, S.J., Swain, E.B., 2007. History of mercury inputs to Minnesota lakes: Influences of watershed disturbance and localized atmospheric deposition. *Limnol. Oceanogr.* 52, 2467-2483.
- Evers, D.C., Wiener, J.G., Basu, N., Bodaly, R., Morrison, H.A., Williams, K.A., 2011. Mercury in the Great Lakes region: bioaccumulation, spatiotemporal patterns, ecological risks, and policy. *Ecotoxicology* 20, 1487-1499.
- Federal Water Quality Administration. 1970. Investigation of Mercury in the Lake St. Clair River – Lake Erie Systems. U.S. Department of Health, Education and Welfare: Washington, D.C.
- Fitzgerald, W.F., Engstrom, D.R., Mason, R.P., Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* 32, 1-7.
- Forage Task Group. 2001. Report of the Forage Task Group, March 2001. Lake Erie Committee, Great Lakes Fishery Commission: Windsor, Ontario.
- Fuller, K., Shear, H., Wittig, J., 1995. The Great Lakes: an environmental atlas and resource book, third ed. United States Environmental Protection Agency Great Lakes National Program Office: Chicago, IL.
- Gewurtz, S.B., Bhavsar, S.P., Fletcher, R., 2011. Influence of fish size and sex on mercury/PCB concentration: Importance for fish consumption advisories. *Environment International* 37, 425-434.
- Gilmour, C.C., Henry, E.A., 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.* 71, 131-169.
- Gilmour, C.C., Henry, E.A., Mitchell, R., 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* 26, 2281-2287.

- Griffiths, R.W., Schloesser, D.W., Leach, J.H., Kovalak, W.P., 1991. Distribution and dispersal of the zebra mussel (*Dreissena polymorpha*) in the Great Lakes region. *Can. J. Fish. Aquat. Sci.* 48, 1381-1388.
- Grigal, D., 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. *Env. Rev.* 10, 1-39.
- Hall, B., Bodaly, R., Fudge, R., Rudd, J., Rosenberg, D., 1997. Food as the dominant pathway of methylmercury uptake by fish. *Water Air Soil Pollut.* 100, 13-24.
- Health Canada. 2004. Mercury and Human Health. Her Majesty the Queen in Right of Canada, represented by the Minister of Health.
- Hebert, P.D., Muncaster, B., Mackie, G., 1989. Ecological and genetic studies on *Dreissena polymorpha* (Pallas): a new mollusc in the Great Lakes. *Can. J. Fish. Aquat. Sci.* 46, 1587-1591.
- Herdendorf, C.E., 1990. *Distribution of the World's Large Lakes*. Springer: Berlin Heidelberg.
- Heyes, A., Mason, R.P., Kim, E., Sunderland, E., 2006. Mercury methylation in estuaries: Insights from using measuring rates using stable mercury isotopes. *Mar. Chem.* 102, 134-147.
- Hill, W.R., Stewart, A.J., Napolitano, G.E., 1996. Mercury speciation and bioaccumulation in lotic primary producers and primary consumers. *Can. J. Fish. Aquat. Sci.* 53, 812-819.
- Hogan, L.S., Marschall, E., Folt, C., Stein, R.A., 2007. How non-native species in Lake Erie influence trophic transfer of mercury and lead to top predators. *J. Great Lakes Res.* 33, 46-61.
- Imm, P., Knobeloch, L., Anderson, H.A., The Great Lakes Sport Fish Consortium, 2005. Fish consumption and advisory awareness in the Great Lakes basin. *Environ. Health Persp.* 113, 1325-1329.

- International Joint Commission, 1985. Great Lakes Diversions and Consumptive Uses: A Report to the Governments of the United States and Canada Under the 1977 Reference. International Joint Commission: Ottawa, Ontario & Washington, D.C.
- International Joint Commission. 2004. Protection of the waters of the Great Lakes. International Joint Commission: Ottawa, Ontario & Washington, D.C.
- Johannsson, O.E., Dermott, R., Graham, D.M., Dahl, J.A., Scott Millard, E., Myles, D.D., LeBlanc, J., 2000. Benthic and pelagic secondary production in Lake Erie after the invasion of *Dreissena* spp. with implications for fish production. *J. Great Lakes Res.* 26, 31-54.
- Johnson, T.B., Allen, M., Corkum, L.D., Lee, V.A., 2005a. Comparison of methods needed to estimate population size of round gobies (*Neogobius melanostomus*) in Western Lake Erie. *J. Great Lakes Res.* 31, 78-86.
- Johnson, T.B., Bunnell, D.B., Knight, C.T., 2005b. A potential new energy pathway in central Lake Erie: the round goby connection. *J. Great Lakes Res.* 31, 238-251.
- Jude, D.J., Reider, R.H., Smith, G.R., 1992. Establishment of gobiidae in the Great Lakes basin. *Can. J. Fish. Aquat. Sci.* 49, 416-421.
- Kidd, K.A., Muir, D.C.G., Evans, M.S., Wang, X., Whittle, M., Swanson, H.K., Johnston, T., Guildford, S., 2012. Biomagnification of mercury through lake trout (*Salvelinus namaycush*) food webs of lakes with different physical, chemical and biological characteristics. *Sci. Total Environ.* 438, 135-143.
- Korthals, E.T., Winfrey, M.R., 1987. Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. *Appl. Environ. Microbiol.* 53, 2397-2404.
- Leach, J., 1993. Impacts of the zebra mussel (*Dreissena polymorpha*) on water quality and fish spawning reefs in Western Lake Erie, in: *Zebra Mussels: Biology, Impacts, and Control*. Lewis Publishers: Boca Raton, FL.

- Lin, C., Pehkonen, S.O., 1999. The chemistry of atmospheric mercury: a review. *Atmos. Environ.* 33, 2067-2079.
- Lindberg, S.A., Stratton, W., 1998. Atmospheric mercury speciation: Concentrations and behavior of reactive gaseous mercury in ambient air. *Environ. Sci. Technol.* 32, 49-57.
- Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, E., Seigneur, C., 2007. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *AMBIO* 36, 19-33.
- Lindqvist, O., Johansson, K., Bringmark, L., Timm, B., Aastrup, M., Andersson, A., Hovsenius, G., Håkanson, L., Iverfeldt, Å., Meili, M., 1991. Mercury in the Swedish environment — Recent research on causes, consequences and corrective methods. *Water Air Soil Pollut.* 55, xi-261.
- Mason, R.P., Fitzgerald, W.F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta.* 58, 3191-3198.
- Mathers, R.A., Johansen, P.H., 1985. The effects of feeding ecology on mercury accumulation in walleye (*Stizostedion vitreum*) and pike (*Esox lucius*) in Lake Simcoe. *Can. J. Zool.* 63, 2006-2012.
- Matisoff, G., Ciborowski, J.H., 2005. Lake Erie trophic status collaborative study. *Journal of Great Lakes Research* 31, 1-10.
- Mergler, D., Anderson, H.A., Chan, L.H.M., Mahaffey, K.R., Murray, M., Sakamoto, M., Stern, A.H., 2007. Methylmercury exposure and health effects in humans: a worldwide concern. *AMBIO* 36, 3-11.
- Morel, F.M., Kraepiel, A.M., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 29, 543-566.



- Mortimer, C.H., 1987. Fifty years of physical investigations and related limnological studies on Lake Erie, 1928–1977. *J. Great Lakes Res.* 13, 407-435.
- Muth, K.M., 1985. Changes in prey fish abundance in western Lake Erie during periods of high and low predator abundance. Presented papers from the Council of Lake Committees plenary session on Great Lakes predator–prey issues, 85-83.
- Muth, K.M., Busch, W.N., 1989. Food of forage fishes in western Lake Erie, 1975–76. *J. Great Lakes Res.* 15, 217-222.
- Nater, E.A., Grigal, D.F., 1992. Regional trends in mercury distribution across the Great Lakes states, north central USA. *Nature* 358, 139-141.
- Notaro, M., Holman, K., Zarrin, A., Fluck, E., Vavrus, S., Bennington, V., 2013. Influence of the Laurentian Great Lakes on Regional Climate. *J. Clim.* 26, 789-804.
- Nriagu, J.O., 1994. Mercury pollution from the past mining of gold and silver in the Americas. *Sci. Total Environ.* 149, 167-181.
- OMAFRA. Jan. 22 2014. Agriculture in the Great Lakes Basin. Ministry of Agriculture and Food. Queen’s Printer for Ontario. Retrieved on Mar. 3, 2014 from [http://www.omafra.gov.on.ca/english/environment/facts/gl\\_basin.htm](http://www.omafra.gov.on.ca/english/environment/facts/gl_basin.htm)
- OMNR. Jun. 8 2012. Great Lakes Fisheries. Ontario Ministry of Natural Resources. Queen’s Printer for Ontario. Retrieved Mar. 6, 2014 from [http://www.mnr.gov.on.ca/en/Business/GreatLakes/2ColumnSubPage/STEL02\\_173913.html](http://www.mnr.gov.on.ca/en/Business/GreatLakes/2ColumnSubPage/STEL02_173913.html)
- OMOE. January 2014. 2013-2014 Guide to Eating Ontario Sport Fish. Ontario Ministry of the Environment. Queen’s Printer for Ontario 2012-2013.

- Pacyna, E.G., Pacyna, J., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., Steenhuisen, F., Maxson, P., 2010. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmos. Environ.* 44, 2487-2499.
- Peterson, A. 2012. Bird and bat migration along Great Lakes coastlines: Progress report, March 2012. Wisconsin Stopover Initiative. 1-4.
- Painter, S., Marvin, C., Rosa, F., Reynoldson, T.B., Charlton, M.N., Fox, M., Lina Thiessen, P.A., Estenik, J.F., 2001. Sediment contamination in Lake Erie: a 25-Year retrospective analysis. *J. Great Lakes Res.* 27, 434-448.
- Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R., Friedli, H., Leaner, J., Mason, R., Mukherjee, A., Stracher, G., Streets, D., 2010. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* 10, 5951-5964.
- Pirrone, N., Keeler, G.J., Nriagu, J.O., 1996. Regional differences in worldwide emissions of mercury to the atmosphere. *Atmos. Environ.* 30, 2981-2987.
- Rasmussen, J., Rowan, D., Lean, D., Carey, J., 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. *Can. J. Fish. Aquat. Sci.* 47, 2030-2038.
- Ray, W.J., Corkum, L.D., 1997. Predation of zebra mussels by round gobies, *Neogobius melanostomus*. *Environ. Biol. Fishes* 50, 267-273.
- Regier, H.A., Hartman, W.L., 1973. Lake Erie's fish community: 150 years of cultural stresses. *Science* 180, 1248-1255.
- Richards, R.P., Baker, D.B., 1993. Trends in nutrient and suspended sediment concentrations in Lake Erie tributaries, 1975–1990. *J. Great Lakes Res.* 19, 200-211.

- Schmitt, C., Brumbaugh, W., 1990. National contaminant biomonitoring program: Concentrations of arsenic, cadmium, copper, lead, mercury, selenium, and zinc in U.S. Freshwater Fish, 1976–1984. *Arch. Environ. Contam. Toxicol.* 19, 731-747.
- Selvendiran, P., Driscoll, C.T., Montesdeoca, M.R., Bushey, J.T., 2008. Inputs, storage, and transport of total and methyl mercury in two temperate forest wetlands. *J. Geophys. Res-Biogeophys.* 113, G00C01 1-15.
- Slemr, F., Schuster, G., Seiler, W., 1985. Distribution, speciation, and budget of atmospheric mercury. *J. Atmos. Chem.* 3, 407-434.
- Slemr, F., Brunke, E., Ebinghaus, R., Temme, C., Munthe, J., Wängberg, I., Schroeder, W., Steffen, A., Berg, T., 2003. Worldwide trend of atmospheric mercury since 1977. *Geophys. Res. Lett.* 30, 23 1-4.
- Stahl, L., Snyder, B., Olsen, A., Pitt, J., 2009. Contaminants in fish tissue from US lakes and reservoirs: a national probabilistic study. *Environ. Monit. Assess.* 150, 3-19.
- Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. *Crit. Rev. Environ. Sci. Technol.* 31, 241-293.
- U.S. National Research Council Panel on Mercury 1978. An assessment of mercury in the environment. National Academy of Sciences, Washington, D.C.
- Vander Zanden, M.J., Rasmussen, J.B., 1996. A trophic position model of pelagic food webs: impact on contaminant bioaccumulation in lake trout. *Ecol. Monogr.* , 451-477.
- Walters Jr, L.J., Kovacik, T.L., Herdendorf, C.E., 1974. Mercury occurrence in sediment cores from Western Lake Erie. *Ohio J. Sci.* 74, 1-19.
- Waples, J.T., Squires, M., Eadie, B., Cotner, J., Val Klump, J., & McKinley, G. 2008. The Laurentian Great Lakes. *North American Continental Margins.* 73-81.

- Watras, C.J., Bloom, N., 1992. Mercury and methylmercury in individual zooplankton: implications for bioaccumulation. *Limnol. Oceanogr.* 37, 1313-1318.
- Watras, C.J., Huckabee, J.W., 1994. *Mercury Pollution Integration and Synthesis*. CRC Press: Boca Raton, FL.
- Watras, C., Back, R., Halvorsen, S., Hudson, R., Morrison, K., Wentz, S., 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219, 183-208.
- World Health Organization. 2007. *Exposure to Mercury: A Major Public Health Concern*. Public Health and Environment – World Health Organization.
- Zananski, T.J., Holsen, T.M., Hopke, P.K., Crimmins, B.S., 2011. Mercury temporal trends in top predator fish of the Laurentian Great Lakes. *Ecotoxicology* 20, 1568-1576.

## 2 Total and Methyl Mercury in Lake Erie Water, Sediment and Seston: Toward Identifying the Cause of Recent Increases in Fish Mercury

### 2.1 Introduction

#### 2.1.1 Mercury in Sport and Commercial Fish

Piscivorous fish in the Laurentian Great Lakes are commonly harvested for sport, sale, and consumption. These larger predatory fish are naturally at risk of accumulating the highest levels of mercury (Hg) in the food web of aquatic ecosystems (Rasmussen *et al.*, 1990). The fisheries of the Laurentian Great Lakes and many other smaller inland lakes are important economically and culturally (Evers *et al.*, 2011); however, elevated fish Hg levels can present a health risk to consumers. Consumption of fish and shellfish is the principal route of dietary methylmercury (MeHg) in both humans and wildlife (Cole *et al.* 2004; Mergler *et al.*, 2007). The hallmark health effects associated with elevated MeHg exposure in humans include diminished neurological functioning, tremor, ataxia, dysarthria, and sensory disturbances including visual and auditory (Harada, 1995). In wildlife such as fish and piscivorous mammals and birds, common exposure effects include reproductive and behavioral disturbances (Scheuhammer *et al.*, 2007; Burgess & Meyer, 2008; Sandheinrich *et al.*, 2011).

#### 2.1.2 Methylmercury in Fish

Upwards of 95% of the total Hg (THg) in fish is in the methylated form, as a result of the greater propensity for MeHg to bioaccumulate relative to inorganic Hg in the higher organisms of food webs (Bloom, 1992). Almost all MeHg in fish is accumulated through ingestion, with at most 15% contributed by water through gill uptake (Hall *et al.*, 1997). Whole-lake food manipulation and observational experiments show that dietary MeHg is also a concern for fish that graze on zooplankton or consume benthic invertebrates (Hall *et al.*, 1997; Bodaly & Fudge, 1999). Food chain length is a determinant of Hg concentrations in top predatory fish, as the addition of trophic levels in an aquatic food web increases the amount of Hg bioaccumulation in the highest organisms (Cabana *et al.*, 1994). Variations in food chain length and therefore bioaccumulation “steps” as they

relate to Hg are well described in the literature (Atwell *et al.*, 1998; Campbell *et al.*, 2003). The addition of organisms such as zooplankton or forage fish to aquatic food webs results in elevated Hg levels in higher fish (Futter, 1994; Cabana *et al.*, 1994). From the base of the food web upwards to the highest fish, these studies affirm that prey species play a very important role in the delivery of Hg in consumable fish, and that piscivorous animals become exposed to through consumption.

### 2.1.3 Methylmercury Availability to Aquatic Food Webs

Inorganic Hg(II) is converted to MeHg mainly through sulphate-reducing bacteria (SRB) in an enzymatically mediated reaction that is believed to be a by-product of normal bacteria functioning (Morel *et al.*, 1998). Methylmercury enters the base of the food web through passive uptake and active transport mechanisms into primary producers, such as algae, periphyton, and phytoplankton (Mason *et al.* 1996, Moyer *et al.* 2002).

Methylmercury associates with the soluble fraction of the cell, and when predators consume unicellular organisms this fraction of the cell is assimilated by the consumer, resulting in the persistence of MeHg. Conversely, inorganic Hg binds with particulate material, such as membranes; material that is more often excreted by the consumer (Morel *et al.*, 1998). This partially accounts for why MeHg bioaccumulates, whereas most forms of metals, including inorganic Hg(II), are not retained by the base of the food web.

Temperature, oxygen concentration, pH, and substrate availability are important physical characteristics that can directly and indirectly control the amount of inorganic Hg(II) that is converted to MeHg (Ullrich, 2001). Some of these factors, such as temperature, pH, and the presence of electron acceptors and donors, can affect the amount of Hg methylating bacteria that are present, which influences the net conversion of inorganic Hg(II) to MeHg (Marvin-DiPasquale *et al.*, 2009). These parameters vary among lakes, as well as within lakes, and can be directly related to MeHg abundance (Kidd *et al.*, 2012). The effects of localized MeHg production and uptake into the base of the food web are propagated upwards through the food web and can be seen at the level of piscivorous fish (Weiner *et al.*, 2006). As MeHg is the more bioavailable form of THg to

the food web, and the net amount of MeHg can vary by location, it is important to quantify MeHg in the abiotic environment, water and sediment.

A bioconcentration factor, also termed bioaccumulation factor, is the ratio of the contaminant concentration of a food web component to that of the environmental component, such water (Hill *et al.*, 1996; Rolfhus *et al.*, 2011). Higher bioconcentration factors for MeHg than inorganic Hg(II) indicate that the methylated form is more readily taken up by the base of the aquatic food web (Hill *et al.*, 1996). From the base of the food web, MeHg is further transferred to benthic invertebrates and prey fish (Bodaly & Fudge, 1999; Chasar *et al.* 2009). Within aquatic environments the bulk THg, the net production of MeHg, and the resultant quantity of MeHg, all play a strong role in the amount available for uptake into and transfer within the food web (Kidd *et al.*, 1995; Hill *et al.*, 1996). To accurately describe Hg uptake and dynamics in food web compartments, contributing ultimately to fish Hg accumulation, it is important to quantify the amount of Hg that is available to enter the food web (Brigham *et al.*, 2009; Rolfhus *et al.*, 2011). This includes the proportion of the bioavailable MeHg form of THg.

#### 2.1.4 Mercury in the Laurentian Great Lakes Region

The net production and concentrations of MeHg in lake waters and sediment are controlled by a range of factors and conditions; however, it is also influenced by the total amount of Hg that is deposited into the lake's watersheds and surface waters (Weiner *et al.*, 2006; Driscoll *et al.* 2007). Sometimes, instances of elevated Hg in biota are not limited to areas of high atmospheric deposition, which illustrates the complexity of delivery of Hg to an ecosystem (Evers *et al.*, 2007). Mercury emissions in the Laurentian Great Lakes region are declining (U.S.EPA, 2005; Schmeltz *et al.* 2011). This has resulted in a decline in Hg concentrations in lakes and some wildlife in the Laurentian-Great Lakes region over the past 40 years (Evers *et al.*, 2011). Despite the net decline in THg delivery to lake ecosystems in the Laurentian Great Lakes region via atmospheric wet and dry deposition, concentrations in some biota, including certain fish species in select lakes, have not experienced a notable decline in Hg (*Ibid*).

Predatory fish of Lake Erie, one of the Laurentian Great Lakes, experienced increases in their tissue Hg concentrations since the 1990s, following a long declining trend (Bhavsar *et al.*, 2010; Monson *et al.* 2011). As Hg concentrations in fish in other Great Lakes, such as Superior and Huron, continued to decline from the 1970s - onward, Lake Erie stands out as the only lake experiencing a significant increase in fish Hg within recent decades (Bhavsar *et al.*, 2010; Zananski *et al.*, 2011). There are some theories and hypotheses about the drivers of this increase, such as a change in lake trophodynamics due to the introduction of invasive species (Morrison *et al.*, 1998), or indirect effects due to global warming (French *et al.* 2006); however, limited data exist with which to test these ideas.

Three main sources of Hg to Lake Erie are point sources and land run-off, atmospheric deposition, and re-cycling of legacy Hg (Forsythe *et al.*, 2004). Historically, Lake Erie had a high abundance of many metals and persistent organic chemicals (Painter *et al.* 2001; Marvin *et al.* 2002) due to multiple coal burning plants for energy production and chemical chlor-alkali plants along its shore, particularly along major river systems flowing into the Western basin. A fraction of these point sources remain, although the Western shore and the Detroit, Maumee and Sandusky rivers maintain a high level of industrialization.

As a consequence of regional coal combustion, local deposition of gaseous and particulate Hg was once a large contributor to pollution in the watershed basin and lake surface waters (Evers *et al.*, 2011). Both Canada and the United States pledged to Acts that have cleaned the air of Hg and other chemicals. Acts include the Great Lakes Water Quality Agreement of 1978, and the U.S.-Canada Air Quality Agreement of 1991, both of which resulted in the reduction of coal fire plants and waste incineration practices (International Joint Commission, 1978; International Joint Commission, 1991). Regional atmospheric deposition has declined within the past three decades (U.S.EPA, 2005; Driscoll *et al.*, 2007). As gaseous elemental mercury (Hg(0)) has a long atmospheric residence time and an expansive spatial range, global atmospheric deposition remains a long-term and long-range source of Hg to the Great Lakes region (Pacyna *et al.*, 2003).



A third potential source of Hg, which blends historic sources and current inputs, is Hg previously deposited into the lake and settled in the sediments becoming re-suspended and re-entering the Hg cycle of the lake (Walters *et al.*, 1974). In this way, a historic source of Hg that became inaccessible for a time can once again contribute to the current state of Hg cycling in the lake, potentially becoming methylated and contributing to the pool of MeHg in the lake. Identifying the major sources of Hg to the lake is important for understanding the lake-wide availability of Hg to the food web; however, this study does not directly measure the inputs and sources of Hg to the lake.

Concentrations of Hg in fish have changed over recent decades and appear to be variable depending on catch location within the basins of Lake Erie (Azim *et al.*, 2011).

Quantifying the baseline of Hg that is available in the system, including the proportion that is methylated, is a necessary first step in examining the changes in fish Hg and understanding why the changes are occurring. In addition to the spatial patterns, studying potential changes over the summer sampling period may reveal how quickly increases in Hg and MeHg are reflected in the biota. These possible temporal and spatial differences also hold importance for future sampling endeavors by informing seasonal timing and frequency of sampling.

### 2.1.5 Aims and Objectives

In order to explore the drivers behind the spatial variability and recent increases in Hg in biota, this study aims to quantify THg and MeHg in the water, sediments and seston of Lake Erie over a course of the open water season (June to September). To explore my general working hypothesis that non-native species contributed to enhanced trophic transfer of Hg, I first needed to describe variability in the system. Due to historical patterns of Hg input into Lake Erie, and given our understanding of the controls over MeHg production and the physical characteristics of the lake, a number of predictions may be posited:

- The Western basin is expected to have the highest THg concentrations in both water and sediment, with the Eastern basin having the lowest, and the Central basin being intermediate.

- Methylmercury in water and sediment will be higher in the Western basin than the Eastern, with Central being intermediate.
- Methylmercury concentrations in water and sediment are expected to increase over the sampling season, with sampling time therefore being an important consideration for abiotic and biomonitoring programs.
- The preceding changes in Hg in time and space should be reflected in the base of the food web, in suspended coarse particulate matter (seston), which is comprised dominantly of phytoplankton and zooplankton and is a key food source for lower trophic level pelagic fish.

## 2.2 Materials and Methods

### 2.2.1 Study Site

Lake Erie is the most southern of the Laurentian Great Lakes, with its watershed extending into six American states and one Canadian province (Ongley, 1996). It is naturally divided into three major basins, referred to here as Western, Central and Eastern. The Pelee-Lorraine Sill separates the Western basin from the Central basin, and the Long Point-Erie Sill delineates the Central from the Eastern basin (Thomas *et al.*, 1976). The Western basin is the most shallow, with an average depth of 9 m. The lake deepens from West to East, with the Central basin having an average depth of 18.5 m and a maximum of 26 m. The deepest point of the lake is found in the Eastern basin, which has a conical bathymetry with a maximum depth of 64 m (Herdendorf, 1992).

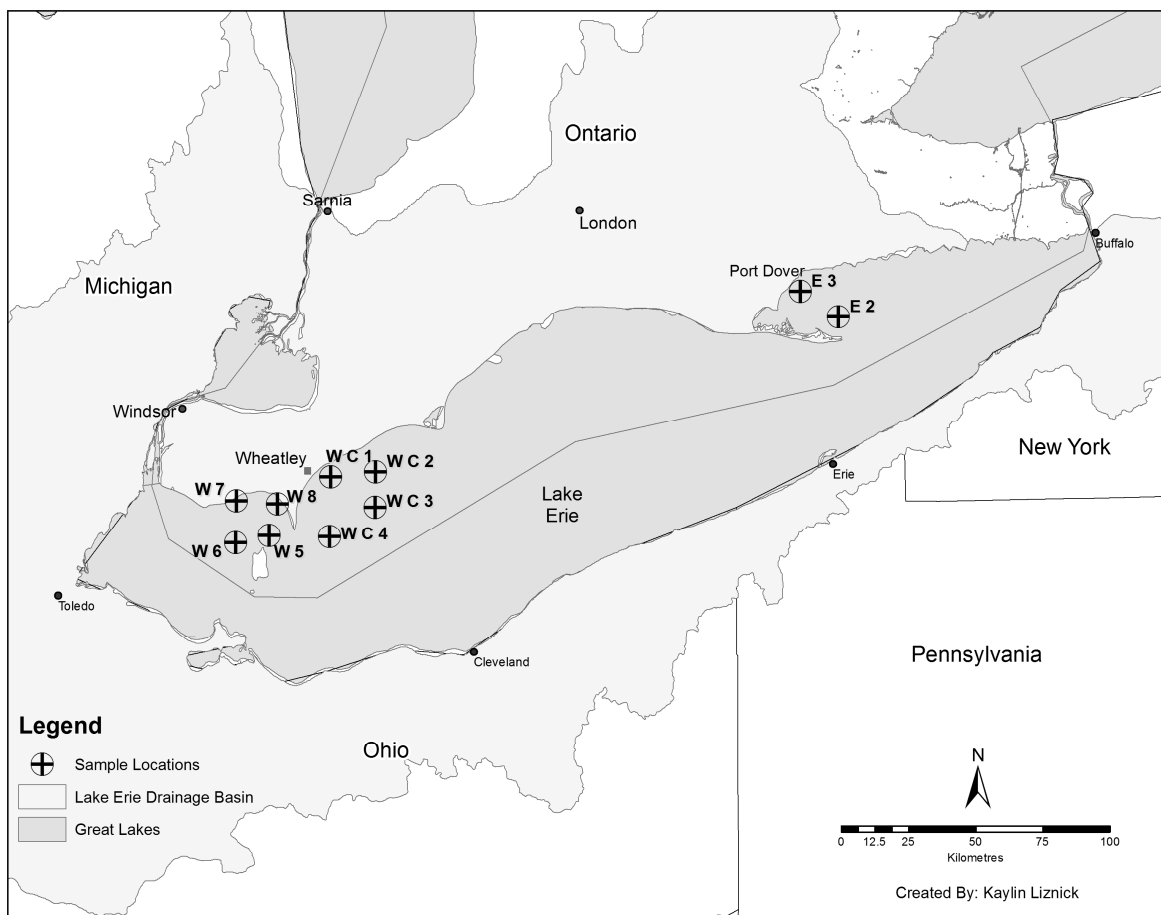
Water from Lake Huron constitutes the major inflow to Lake Erie via Lake St. Clair and the Detroit River. This source contributes approximately 87% of the total inflow of water to the lake (Quinn & Guerra, 1986), and its average annual inflow is estimated to be 5140 m<sup>3</sup>/s (Herdendorf, 1975). Other major riverine inflows include the Maumee River at the city of Toledo, Ohio into the Western basin, and the Grand River at Port Maitland, Ontario into the Eastern. Input from precipitation accounts for a further 11% of water to the lake (Bolsenga & Herdendorf, 1993). The main outflow from Lake Erie into Lake Ontario is via the Niagara River and the Welland Canal, which represent 97% and 3% of the outflow, respectively (Quinn & Guerra, 1986). These two outlets flow at an average

combined rate of 5730 m<sup>3</sup>/s annually (Herdendorf, 1975). The area of Lake Erie is approximately 26 000 km<sup>2</sup>, and being the fourth largest by area and most shallow of the Great Lakes, the water residence time is 2.6 years - the shortest retention time of all the Great Lakes (U.S.EPA, 2012).

### 2.2.2 Sampling Locations and Sampling Regime

In-lake sampling locations were prescribed by the Ontario Ministry of Natural Resources (OMNR) for their routine Lake Erie limnological sampling program and interagency lower-trophic food web monitoring program. Under this program, sites are visited bi-weekly from May-October, weather permitting. Eight sites in the Western and Central basins of the lake were accessed by the Wheatley branch of OMNR and two sites in the Eastern basin were accessed through the Port Dover branch. Sites were accessed via OMNR vessels, diesel-powered 60 ft. fishing tugboats reformed for limnological research. Figure 2.1 outlines site locations, while site latitudes and longitudes can be found in Appendix A.

Four sites in the Western basin (W5, W6, W7, W8), four in the Central basin (WC1, WC2, WC3, WC4) and two in the Eastern basin (E2, E3) were sampled from June to September 2012. Although research was conducted at the Western edge of the Central basin through sampling sites WC1-WC4, a large portion of the Central basin remained un-visited through this sampling program. This is due to the absence of an OMNR office and research vessel on the Northern shore of the Central basin, severely limiting access to this span of open water. Poor October weather conditions also contributed by prohibiting the Port Dover branch from conducting a planned 2-day cruise to sample the Central basin West of the Long Point peninsula.



**Figure 2.1** Outline of Lake Erie and Surrounding Watershed with Sampling Sites and Major Access Points.

## 2.2.3 Water, Sediment and Seston Sampling

### 2.2.3.1 Water

Water samples were collected using clean techniques in accordance with EPA method 1669 (U.S.EPA, 1996). A Niskin-style water sampling device (OceanTest Equipment, Ft. Lauderdale, FL) made from polyvinyl chloride (PVC) coated with Teflon® was deployed using Teflon®-coated cable marked at meter intervals to achieve desired depths. At each site, samples were taken at the surface, 1 meter from surface, and 1 meter above the sediment with 2-3 equally spaced samples collected between those depths, depending on the depth of the site (see Appendix A for details). Water samples were transferred from

the Niskin sampler to new 500 mL polyethylene terephthalate (PETG) plastic bottles that had been environmentalized with sample water. Bottles were then double bagged in polyethylene re-sealable bags. To avoid contamination, the clean hands/dirty hands method was followed, with two individuals donning powder-free nitrile gloves. The first technician handled the sampling equipment and outer bag of the collection equipment, while the bottles and inner bags were handled by a technician other than the sample collector. Samples were stored on ice and transported to the laboratory, where they remained unfiltered and were acidified to a 1% v/v concentration with HCl (OmniTrace®, EDM) within 48 hours of collection. Water samples were kept in cool storage until they were analyzed for THg and MeHg.

### 2.2.3.2 Sediment

At each site, a stainless-steel ponar-style sampler was used to obtain a sediment sample. The grab was emptied into a bucket lined with a clean polypropylene plastic bag, and two samples of sediment were manually removed into small polypropylene re-sealable bags, rolled to expel air, double bagged, and stored on ice. Occasionally, redundancy in sample numbers was unattainable due to a low amount of sediment collected, particularly at sites with consolidated bottom material. Upon return to the laboratory facilities, bagged sediment samples were stored at -20°C until analysis. Prior to analysis, sediments were lyophilized and the dry samples homogenized in their bag using a glass pestle, after which samples were stored at room temperature in the dark until analysis.

### 2.2.3.3 Seston

A 63 µm Nitex mesh plankton net was used to obtain seston samples. The net was deployed to various depths depending on the maximum depth of the site, and pulled upwards through the water column for 10-30 seconds. Collected material was washed into a PVC collection jar at the bottom of the net, and deionized water was used to rinse sample from the jar into environmentalized 500 mL PETG bottles, which were double bagged in polyethylene re-sealable bags and stored on ice until returned to the laboratory. Within 48 hours of collection, samples were filtered through 1.2 µm glass microfiber filter paper (Whatman®). The retentate on the filter paper was transferred into

polypropylene microcentrifuge tubes using clean techniques, and then stored at -20°C until analysis.

## 2.2.4 Mercury Analyses

### 2.2.4.1 Water

Water samples were kept in dark, cool storage until they were analyzed for THg and MeHg. Analysis was performed in the Biotron Centre for Experimental Climate Change Research at the University of Western Ontario. Water samples were analyzed for THg on a Tekran series 2600 ultra-trace mercury analysis system, using the methods described in EPA method 1631 (U.S.EPA, 2002). The minimum detection limit was 0.01 ng/L.

Water samples were analyzed for MeHg on a Tekran series 2700 methylmercury auto-analysis system, using the methods described in EPA method 1630 (U.S.EPA, 1998). The minimum detection limit was 0.02 ng/L.

### 2.2.4.2 Sediment and Seston

Dried, homogenized sediment and seston samples were analyzed for total Hg on a Milestone® DMA-80 Direct Mercury Analyzer using methods described in EPA method 7473 (U.S.EPA, 2007). The calibration detection limit was 1 ng. Every 9 samples, duplicate samples were analyzed (mean % deviation:  $4.82 \pm 8.45$ ,  $n=14$ ). A certified reference material (CRM) was analyzed at the start and end of runs, and every 10 samples (mean % recovery:  $101.19 \pm 9.98$ ,  $n=30$ ), and CRM raw Hg (ng) bounded the lower and upper limits of sample raw Hg (ng). These CRMs included MESS-3 ( $0.091 \pm 0.009$  mg/kg Hg), TORT-2 ( $0.27 \pm 0.06$  mg/kg Hg), and TORT-3 ( $0.292 \pm 0.022$  mg/kg Hg). Blanks were analyzed at the start of runs and after CRMs (mean:  $0.07 \pm 0.07$  ng,  $n=22$ ).

Sediment samples underwent extraction for MeHg as outlined in the USGS method for analysis of MeHg in plant, sediment, and soil samples by cold vapor atomic fluorescence detection (Ogorek & DeWild, 2013). This digestion and extraction method was used in conjunction with EPA method 1630 to carry out sediment sample analysis on a Tekran series 2700 methylmercury auto-analysis system (U.S.EPA, 1998).

Seston samples underwent extraction for MeHg as outlined in the USGS method for analysis of MeHg in biological samples by cold vapor atomic fluorescence detection (DeWild *et al.*, 2004). This digestion and extraction method was used in conjunction with EPA method 1630 to carry out seston sample analysis on a Tekran series 2700 methylmercury auto-analysis system (U.S.EPA, 1998).

### 2.2.5 Quality Assurance, Quality Control, and Statistical Measures

Strict quality assurance and control metrics practices were employed to ensure data integrity. Measures during sample collection included duplicate samples for assessing the repeatability of the collection procedure, travel blanks to assess the effects of transportation, equipment blanks to ensure Niskin and seston equipment trace status, and deionized water field blanks to assess any on-board contamination. Laboratory analysis measures for THg and MeHg in water included duplicates to assess reproducibility of the procedure, method blanks to validate the method procedure and equipment and reagent quality, and matrix spikes to ensure proper recovery. Measures for THg in sediment and seston included blanks, sample replicates, and the use of the CRMs marine estuarine sediment (MESS-3), and lobster hepatopancreas (TORT-2 and TORT-3), from the National Research Council (Canada). Measures for MeHg in sediment and seston included method blanks, sample replicates, matrix spikes, and the use of the CRM Estuarine Sediment (EST-2) from the British Research Council.

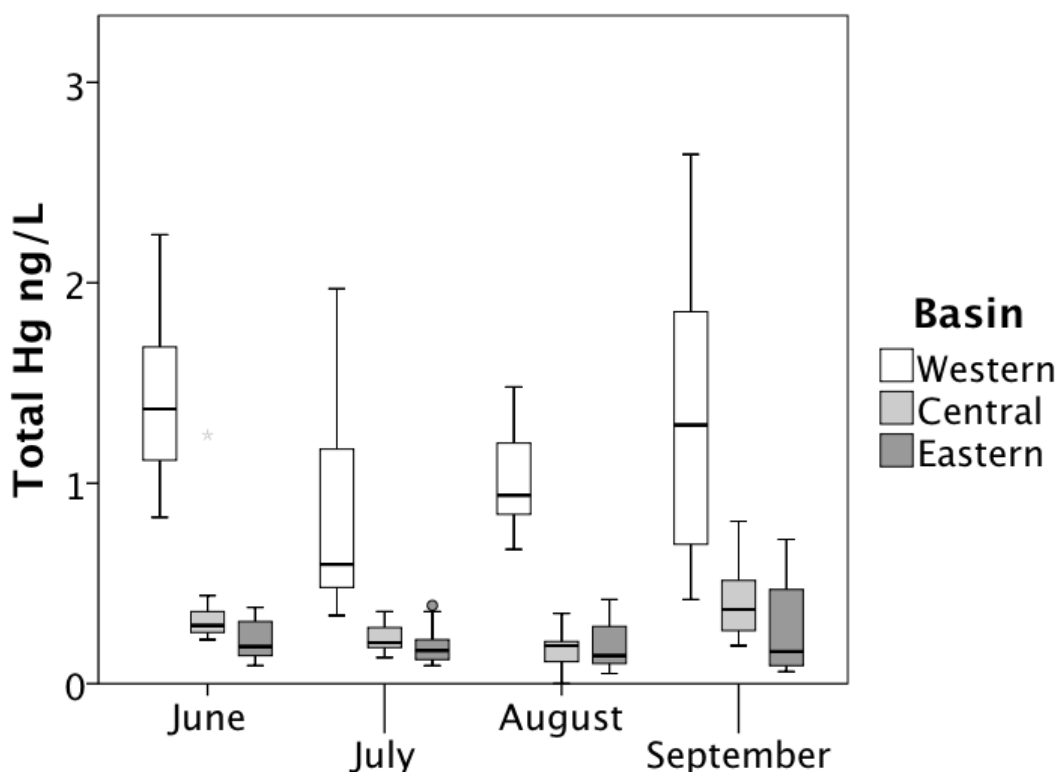
Statistical means and summaries were calculated using SPSS (IBM, 2011). To determine if spatial or seasonal differences in mean THg and MeHg concentrations were significant, analyses of variance (ANOVAs) were performed, and Tukey-Kramer HSD mean comparison tests were calculated using JMP (SAS, 2010).

## 2.3 Results

### 2.3.1 Total Mercury in Water

Water samples were pooled by depth, and by month, to represent depth-averaged and monthly water column THg (Figure 2.2). Exploration of data by depth led to no discernable or regular patterns in THg; therefore, samples were pooled by site to integrate

4-5 samples per site per sampling trip. Sites were further pooled by basin, which resulted in approximately 32 samples per month for the Western basin, 40 per month for the Central basin, and 20 per month for the Eastern basin, including duplicated samples. The seasonal means with standard errors were  $1.13 \pm 0.59$  ng/L for the Western basin,  $0.28 \pm 0.16$  ng/L for the Central basin, and  $0.21 \pm 0.14$  ng/L for the Eastern basin. Fig. 2.2 contrasts the relatively high Hg concentrations in the Western basin to the Central and Eastern basins, which are more comparable to each other in concentration. The Western



**Figure 2.2** Box and whisker plots depicting water THg concentrations over the 2012 sampling months, grouped by basin. 307 individual water samples were pooled by depth at sampling site, and then grouped by month and by basin. Each bar represents an average of 23, 35, and 20 samples for the West, Central and Eastern basins, respectively. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles. Extreme outliers with values of 3 or more times the IQR are denoted by asterisk.



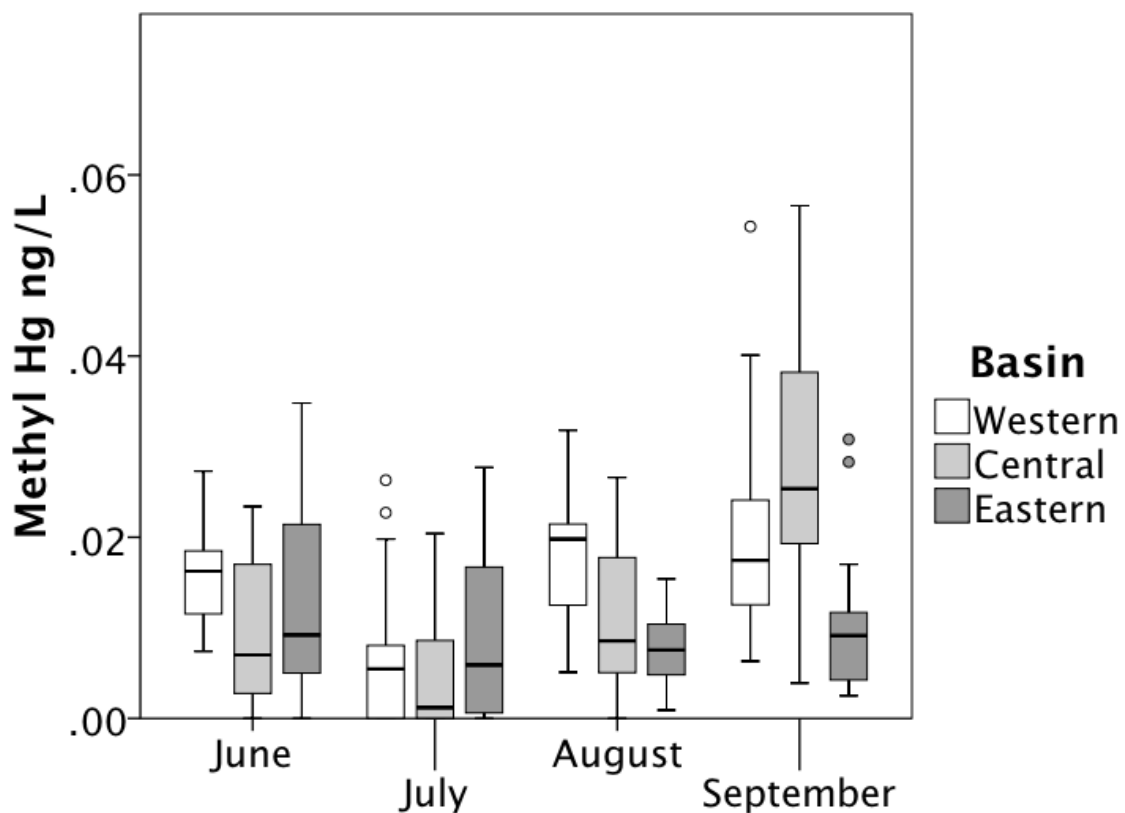
basin exhibited the largest range in Hg concentrations, which may indicate contributions from particulate seston material in the trace THg analysis process. Means among basins were statistically different from one another (One-way ANOVA,  $F_{2,305} = 236.05$ ,  $p = 0.0001$ ). As expected, water THg concentration means from the Western basin were highest, with Central basin means being intermediate and Eastern basin means being lowest (Tukey-Kramer honest significant difference test). Analysis of means by month showed significant differences among the sampling months (One-way ANOVA,  $F_{3,305} = 17.23$ ,  $p = 0.0001$ ). In the Western basin, the September mean was significantly higher than those of other months (One-way ANOVA,  $F_{3,90} = 8.33$ ,  $p = 0.0001$ ; Tukey-Kramer honest significant difference test). In the Central basin, June and July means were statistically similar, with the August mean being significantly different and lowest and the September mean being significantly different and highest (One-way ANOVA,  $F_{3,136} = 35.71$ ,  $p = 0.0001$ ; Tukey-Kramer honest significant difference test). Eastern basin monthly means did not change over the sampling months (One-way ANOVA,  $F_{3,77} = 0.6503$ ,  $p = 0.5852$ ).

### 2.3.2 Methylmercury in Water

Methylmercury concentrations in water followed a similar pattern to THg concentrations in water, but were much lower in concentrations. Seventy-eight percent of all samples fell below the instrument detection concentration of 0.02 ng/L. The three basins contributed to these non-detectable samples unequally. Ninety percent of samples collected in the Eastern basin, 77% of samples collected in the Western basin, and only 71% of samples collected in the Central basin fell below the detection limit of 0.02 ng/L. This indicates that of the three basins, the Central basin had the highest aqueous MeHg concentrations, as measured by having the greatest consistency above the instrument detection limit.

Analysis of seasonal basin means showed a significant difference among basin means (One-way ANOVA,  $F_{2,269} = 9.33$ ,  $p = 0.0001$ ). Western and Central basin seasonal means were significantly higher than the Eastern basin mean (Tukey-Kramer honest significant difference test). Analysis of means by month showed significant differences among the sampling months (One-way ANOVA,  $F_{3,307} = 37.82$ ,  $p = 0.0001$ ). In the Western basin, the July mean was significantly lower than those of the other sampling months (One-way

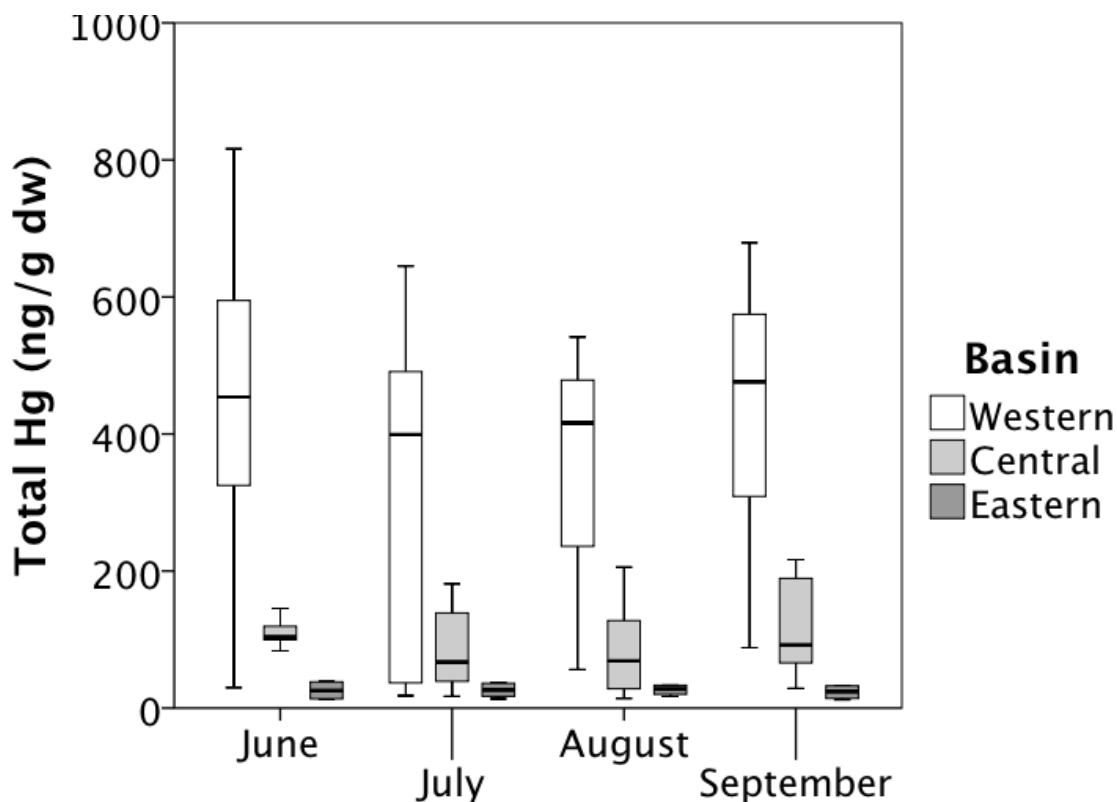
ANOVA,  $F_{3,78} = 9.10$ ,  $p = 0.0001$ ; Tukey-Kramer honest significant difference test). In the Central basin, the July mean was significantly different and lowest, while the September mean was significantly different and highest (One-way ANOVA,  $F_{3,119} = 23.70$ ,  $p = 0.0001$ ; Tukey-Kramer honest significant difference test). The Eastern basin did not experience a change in monthly means (One-way ANOVA,  $F_{3,71} = 1.01$ ,  $p = 0.3924$ ).



**Figure 2.3** Box and whisker plots depicting water MeHg concentrations over the 2012 sampling months, grouped by basin. 308 individual water samples were pooled by depth at sampling site, and then grouped by month and by basin. Each bar represents an average of 23, 35, and 20 samples for the West, Central and Eastern basins, respectively. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles.

### 2.3.3 Total Mercury in Sediment

Sediments from the three basins analyzed for THg exhibited strong spatial heterogeneity. The mean seasonal THg concentrations were  $376.76 \pm 43.72$  ng/g in the Western basin,  $97.23 \pm 11.79$  ng/g in the Central basin, and  $25.59 \pm 2.38$  ng/g in the Eastern basin. Basin means were statistically different from each other (One-way ANOVA,  $F_{2,70} = 34.19$ ,  $p = 0.0001$ ), following the historical pattern of Lake Erie THg concentration gradient, decreasing from West to East (Tukey-Kramer honest significant difference test). Again,

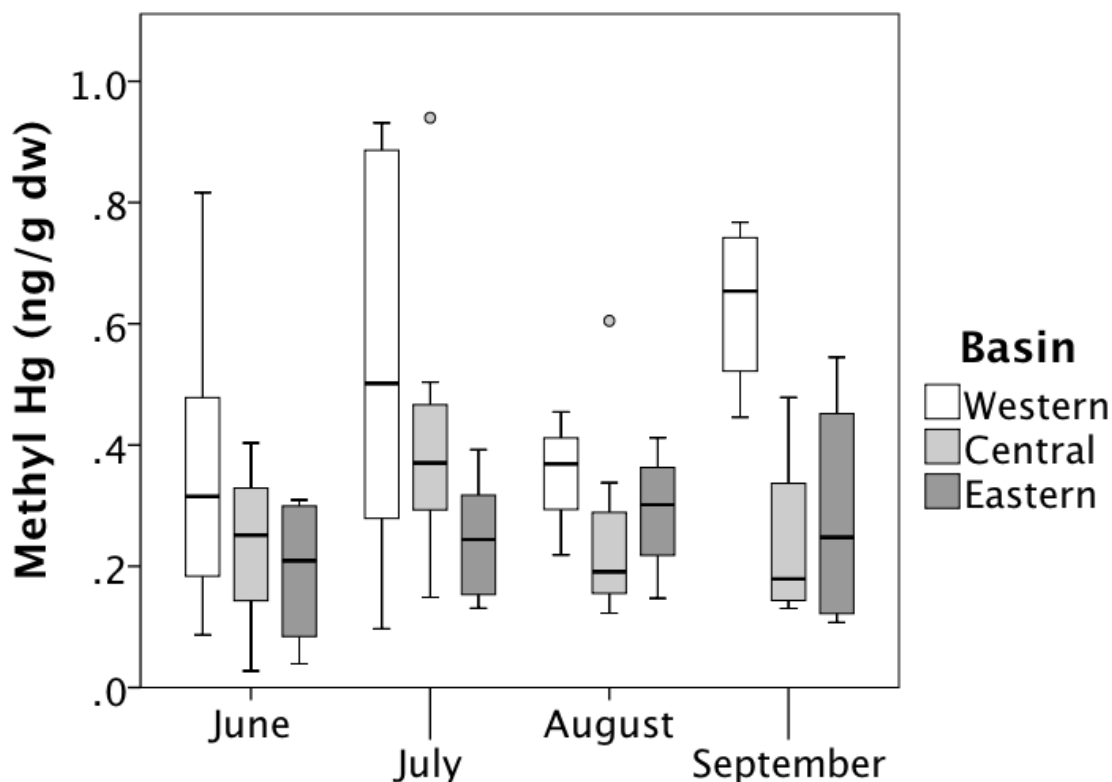


**Figure 2.4** Box and whisker plots depicting sediment THg concentrations over the 2012 sampling months, grouped by basin. 71 individual sediment samples were collected and then grouped by month and by basin. Each bar represents an average of 7, 7, and 5 samples for the West, Central and Eastern basins, respectively. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR.

the largest variability in THg was seen in the Western basin, with sediments ranging from 18.99 to 679.24 ng/g, indicating the four sampling sites within the Western basin were more heterogeneous than the sites in the Central and Eastern basins. As seen in Figure 2.4, THg concentrations in each of the basins remained stable over the summer sampling period, suggesting that sediment THg concentrations did not change within this sampling time frame, which was expected (One-way ANOVA,  $F_{3,70} = 1.14$ ,  $p = 0.3387$ ).

### 2.3.4 Methylmercury in Sediment

Figure 2.5 illustrates MeHg concentrations in the same sediments analyzed for THg, collected from the three basins. The mean seasonal MeHg concentration was  $0.54 \pm 0.07$  ng/g in the Western basin,  $0.29 \pm 0.04$  ng/g in the Central basin and  $0.25 \pm 0.03$  ng/g in the Eastern basin. Analysis of means by basin showed significant differences among basins (One-way ANOVA,  $F_{2,70} = 7.51$ ,  $p = 0.0011$ ). The mean of the Western basin was significantly higher than means from the Central and Eastern basins (Tukey-Kramer honest significant difference test). There were no temporal trends in basin means over the summer sampling months (One-way ANOVA,  $F_{3,70} = 2.33$ ,  $p = 0.0818$ ); however, an apparent increase in the mean Western basin concentration in the latest sampling month, September, is shown in Fig. 2.5. This temporal trend may be obscured in earlier months due to high variability within Western basin samples, particularly in July. This potential increase was not reflected in the other two basins. Mean concentrations followed a declining West-East pattern each month until August, when the Eastern basin mean became higher than the Central basin for the remainder of the season. The Eastern basin sediment MeHg may be further explored by comparing basin percent MeHg data.

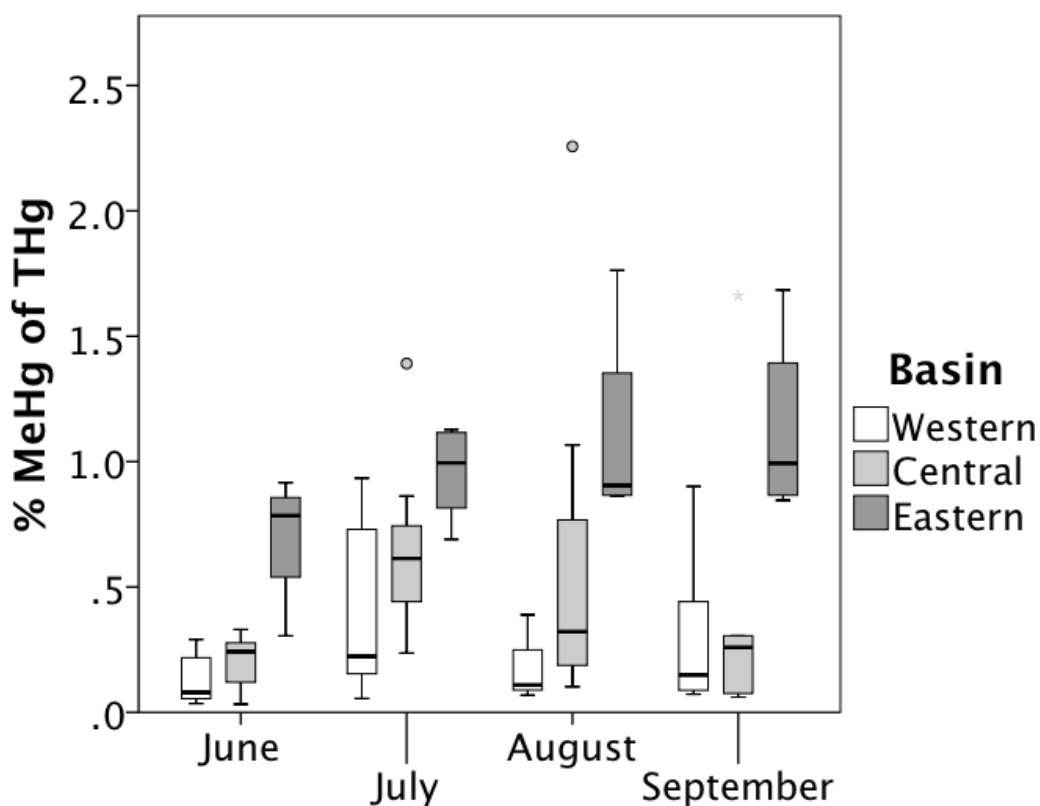


**Figure 2.5** Box and whisker plots depicting sediment MeHg concentrations over the 2012 sampling months, grouped by basin. 71 individual sediment samples were collected and then grouped by month and by basin. Each bar represents an average of 7, 7, and 5 samples for the West, Central and Eastern basins, respectively. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles.

### 2.3.5 Percent Methylmercury in Sediment

The proportion of MeHg to THg in sediment was determined for the three basins and is shown in Figure 2.6. The Western basin had the lowest percent MeHg of  $0.32 \pm 0.08\%$ , surpassed by the Central ratio of  $0.49 \pm 0.10\%$ . The Eastern basin had the highest percent MeHg,  $0.97 \pm 0.08\%$ . The different means indicated that within Lake Erie sediments, those collected in the Eastern basin had a higher methylation potential than sediments from the Central and Western basins. These findings hold important implications for the

amount of THg that is converted to the more bioavailable form, MeHg, for uptake into the base of the food web.

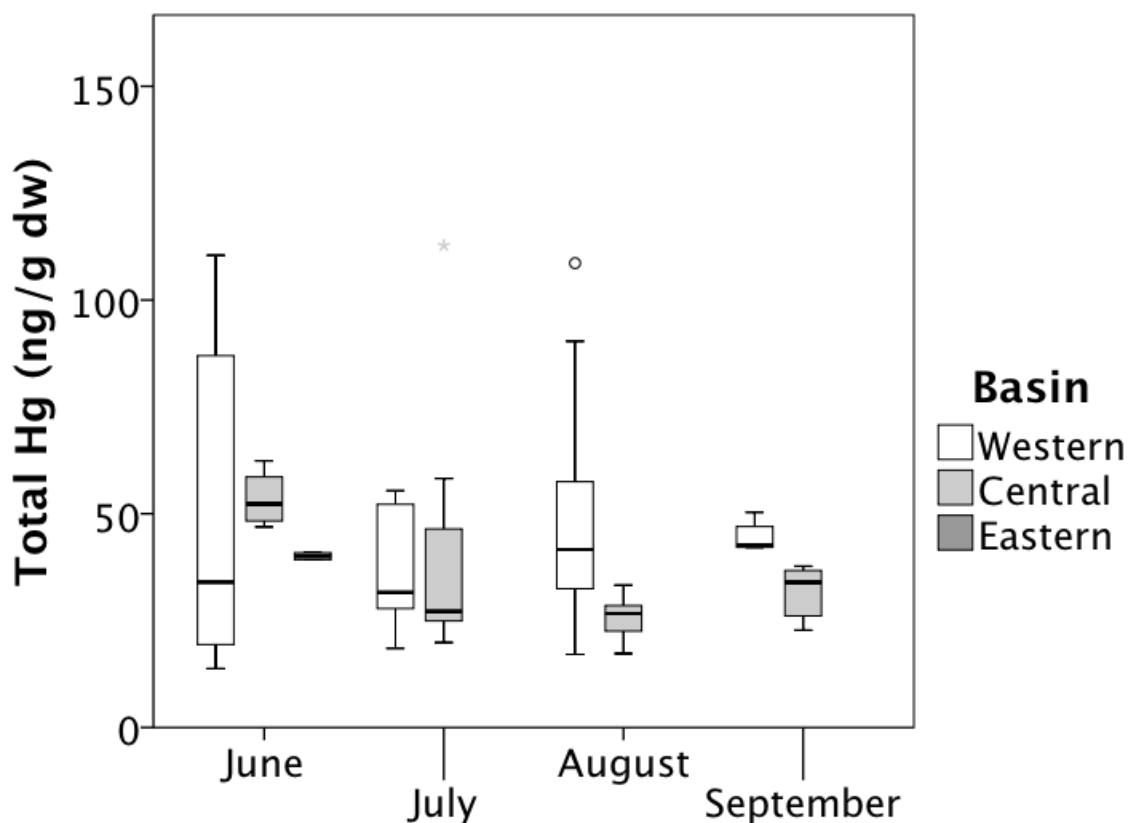


**Figure 2.6** Sediment percent MeHg of THg for sediment samples collected over the 2012 sampling months. 71 individual sediment samples were collected, analyzed for both THg and MeHg, compared relatively, and then grouped by month and by basin. Each bar represents an average of 7, 7, and 5 samples for the West, Central and Eastern basins, respectively. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles.

### 2.3.6 Total Mercury in Seston

Seston from the Western and Central basins were analyzed for THg, with one data entry from the Eastern basin (Fig. 2.7). Seston collected in the Western basin exhibited the most variation in Hg among the basins, with THg concentrations ranging from to 14.49

ng/g to 99.50 ng/g. Average seasonal THg concentrations and standard errors were  $49.69 \pm 5.70$  ng/g for the Western basin and  $35.85 \pm 3.60$  ng/g for the Central basin. Seston abundance was very low in the Eastern basin. Two samples collected in the Eastern basin were pooled and analyzed, to be placed into context with the other two basins. These samples gave the Eastern basin an average Hg concentration of 40.05 ng/g for the month of June. Average seasonal means were not statistically different among basins (One-way ANOVA,  $F_{2,60} = 1.62$ ,  $p = 0.2064$ ); however, there was a unique temporal trend within



**Figure 2.7** Box and whisker plots depicting seston THg concentrations over the 2012 sampling months, grouped by basin. 63 individual seston samples were collected and then grouped by month and by basin. Each bar represents an average of 8, 7, and 2 samples for the West, Central and Eastern basins, respectively. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles. Extreme outliers with values of 3 or more times the IQR are denoted by asterisk.

the Central basin (One-way ANOVA,  $F_{3,27} = 4.15$ ,  $p = 0.0168$ ). The mean in June was higher than that of August, with July and September being intermediate (Tukey-Kramer honest significant difference test). This temporal difference was not observed within the Western basin, where means remained constant throughout the summer sampling period (One-way ANOVA,  $F_{3,32} = 0.1284$ ,  $p = 0.9425$ ). This difference in Western and Central temporal trends may be explained by dominant plankton types and biodilution of Hg, which is explored further in the discussion.

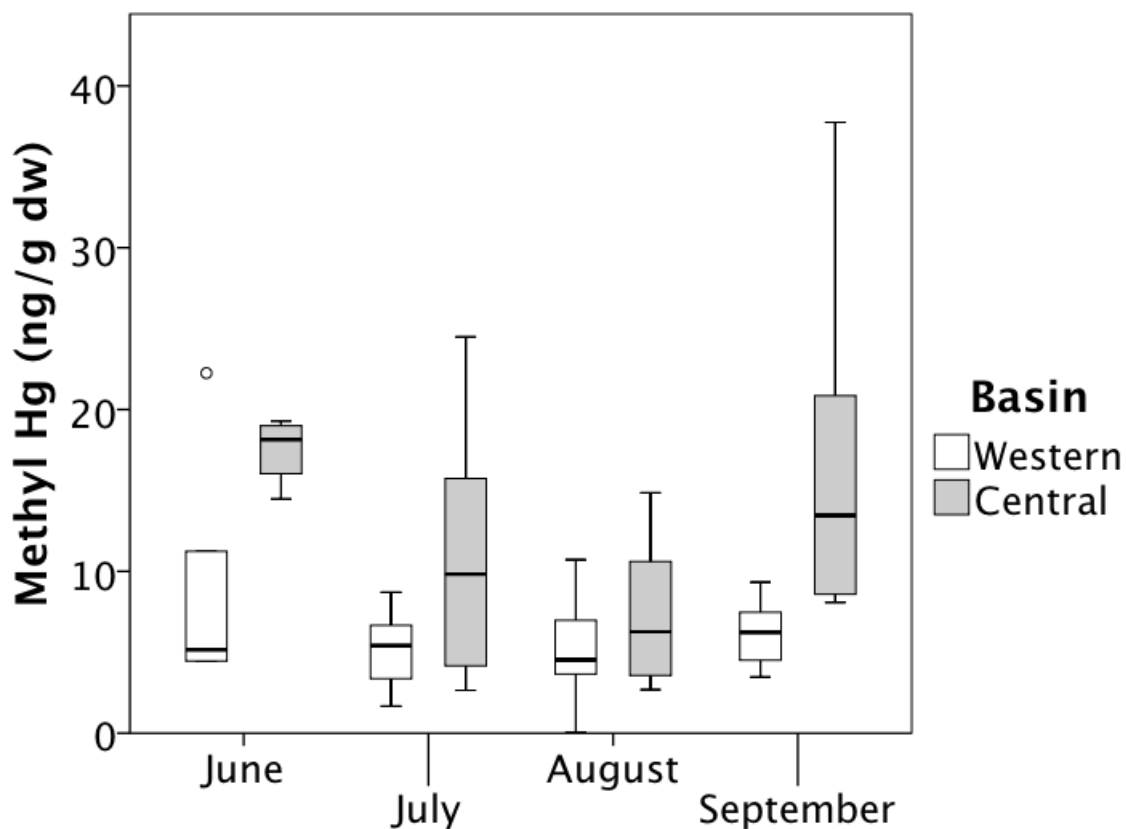
### 2.3.7 Methylmercury in Seston

Seston samples from the Western and Central basins were also analyzed for MeHg, as shown in Fig. 2.8. The average seasonal concentration and standard error in the Western basin was  $6.18 \pm 0.74$  ng/g and was  $12.20 \pm 1.59$  ng/g for the Central basin. The two season-averaged means were different from each other (One-way ANOVA,  $F_{1,109} = 10.97$ ,  $p = 0.0013$ ), and MeHg concentrations within seston collected from the Central basin were higher than seston collected in the West. Concentrations in the Western basin did not change with time over the sampling months (One-way ANOVA,  $F_{3,57} = 0.9414$ ,  $p = 0.4271$ ); however, analysis of the Central means did show significant differences among months (One-way ANOVA,  $F_{3,51} = 2.81$ ,  $p = 0.0450$ ). August and September had the lowest and highest mean concentrations, respectively, with June and July being intermediate (Tukey-Kramer honest significant difference test). This indicates that MeHg concentrations in Central basin seston may increase late in the summer.

### 2.3.8 Percent Methylmercury in Seston

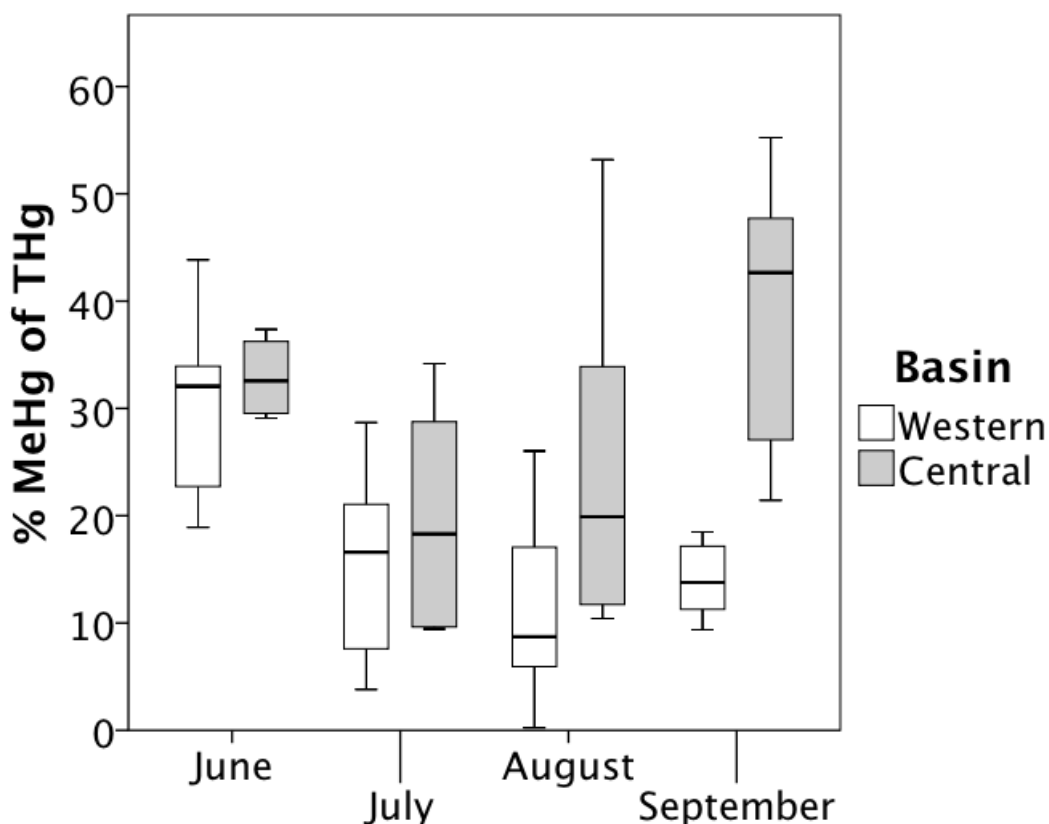
The proportion of THg that is MeHg in Western and Central basin seston samples was determined, and the results give us insight into bioaccumulation within the base of the food web for each basin. Figure 2.9 illustrates that the Central basin had a higher percent MeHg of  $28.55 \pm 2.78$  in seston, with the Western basin's percent MeHg lower at  $16.43 \pm 1.85$ . This difference in means indicated that seston in the Central basin had a higher





**Figure 2.8** Box and whisker plots depicting seston MeHg concentrations over the 2012 sampling months, grouped by basin. 55 individual seston samples were collected and then grouped by month and by basin. Each bar represents an average of 7 samples for both the Western and Central basins. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles.

portion of THg that is in the methylated form, suggesting that seston from the Central basin bioaccumulated more MeHg than seston in the West. These findings hold important implications for bioaccumulation of MeHg in organisms that consume seston and forage in different basins of the lake.



**Figure 2.9** Seston percent MeHg of THg for seston samples collected over the 2012 sampling months. 96 seston samples were collected, analyzed for THg, MeHg, or both if sample size was large enough, compared relatively, and then grouped by month and by basin. Each bar represents an average of 7 samples for the Western and Central basins. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR.

## 2.4 Discussion

### 2.4.1 Total Mercury in Water

Examining the THg concentrations of the water of Lake Erie provides a fundamental understanding of the available Hg that may enter the lake food web. Results for THg indicate a clear difference in the concentrations of water collected from the Western basin, compared to samples collected in the Central and Eastern basins. The observed pattern of water THg concentrations decreasing West to East was in agreement with

previous studies, although current samples exhibited a lower range and mean concentration than those studies (Dove *et al.*, 2012). Dove *et al.* (2012) reported on Environment Canada (2006) and Flett (2009) findings, stating THg concentrations from the Western basin ranged between  $4.26 \pm 3.27$  ng/L in 2006 and  $12.44 \pm 3.57$  ng/L in 2009. The same report stated that the Central basin ranged between  $0.88 \pm 0.24$  ng/L and  $1.84 \pm 0.9$  ng/L, which is higher than my findings, but is more in line than are the results from the Western basin. Finally, yet more comparable to the current Lake Erie findings are the data for samples collected in the Eastern basin, which ranged from  $0.46 \pm 0.06$  ng/L in 2006 and  $0.05 \pm 0.14$  ng/L in 2009 (Dove *et al.*, 2012). The dataset presented in this chapter provides THg concentrations from a wider range of sample locations compared to past research, with a finer and more consistent level of temporal detail, as well as high confidence in the data with low standard error.

#### 2.4.2 Methylmercury in Water

This body of work may be the first to depict the aqueous MeHg concentrations for Lake Erie, as no comparable published data were uncovered. Much of the aqueous MeHg values were below the instrument detection limits of 0.02 ng/L, and this includes the means and medians from each of the basins. Methods for determining the probable value for non-detects could not be employed, as too great a proportion of values were below the detection limits and could not be validated by quality assurance and control measures. These extremely low values were in accordance with aqueous MeHg values observed in other Great Lakes. Rolfhus *et al.* (2003) determined the Lake Superior mean unfiltered lake water MeHg concentration to be 0.0051 ng/L, further stating that MeHg in their study system contributed only 1.1% to the THg concentration. In my experiment, MeHg comprised 1-23% of THg, with the higher percentages originating in the Eastern basin, where MeHg values accounted for a larger proportion of the lowest THg values found among the three basins. The average results for Lake Erie aqueous MeHg concentrations were 0.012 ng/L. Despite being below instrument detection limit and therefore low in confidence of accuracy, the results matched those of Lake Michigan, where the average lake-wide concentration was 0.013 ng/L (Mason & Sullivan, 1997). In comparing with

other great lakes, Lake Erie falls in line or slightly elevated in terms of unfiltered aqueous MeHg concentrations.

### 2.4.3 Total Mercury in Sediments

Determining current surficial sediment THg concentrations at all sites over the summer sampling period provides a good approximation of the amount of Hg to which benthic invertebrates, and subsequently fish, are exposed. Chasar *et al.* (2009) determined that, along with food chain length and trophic transfer efficiencies, differences in the supply and availability of Hg were main drivers of the amount of MeHg bioaccumulation in a food web. The amount of available THg therefore plays an important role in lake-wide bioaccumulation. Sediments collected from each of the basins ranged widely, from 12.14 ng/g from the site E3 to 679.26 ng/g from the site W6, illustrating the vast differences in THg that is available to be potentially methylated. The average concentrations of sediments that were collected in 2012 are lower than published values that were collected in the 1990's. In 2001, Painter *et al.* reported 75<sup>th</sup> percentile concentrations of 650 ng/g in the West, 250 ng/g in the Central and 90 ng/g in the Eastern basin, with an overall lake average of 185 ng/g. Similarly, in 1994 Rossmann and Robbins observed concentrations of 650 ng/g in the Western basin and 140 ng/g in the East (In Marvin *et al.*, 2002). Both studies observed the same eastwardly decreasing concentration gradient; however, the lower THg concentrations observed in my samples suggest the net reduction of THg from the sediments in all basins. This finding is somewhat congruent with those of Drevnick *et al.* (2012), who reported a ~20% decrease in Hg sediment flux in the Great Lakes from the peak deposition timeframe, which is placed in the late 1980s. Although the decline in sediment THg concentrations may be small, obtaining up-to-date values for Lake Erie is important for inferring current bioaccumulation potential of Hg in the basins.

The flux of sediment within Lake Erie is important to consider when examining bulk sediment Hg concentration. In 1977, Kemp *et al.* mapped the sediment budget of each the three Lake Erie basins. Shoreline erosion provided 35% of all new sediments to the lake, and this occurred mainly in the Central basin; however, given the eastward movement of water and sediments, 40% of all inputs to the lake are deposited in the Eastern basin. Consequently, the average sedimentation rates in the basins are 2160 g m<sup>-2</sup> yr<sup>-1</sup> in the

West,  $580 \text{ g m}^{-2} \text{ yr}^{-1}$  in the Central basin, and  $1340 \text{ g m}^{-2} \text{ yr}^{-1}$  in the East (Kemp *et al.*, 1977). Inputs to the Western basin were mainly riverine and not from shoreline erosion. The extent of new sediment deposited in the Eastern basin may serve as a diluting effect to the bulk THg concentrations. This effect was observed in the form of nutrient input to aquatic systems correlating with diluting Hg accumulation in sediments (Rood *et al.*, 1995). Combined with the Eastern basin's lack of strong riverine THg input that exists in the Western basin, these two factors may explain the vast differences in THg sediment concentrations observed between the Western and Eastern basins.

#### 2.4.4 Methylmercury in Surface Sediments

No studies detailing the proportion of THg that is MeHg in Lake Erie were uncovered, and so this dataset of MeHg quantities and percent MeHg for Lake Erie may be the first. Methylmercury concentrations ranged from 0.03 ng/g from the Central basin to 1.91 ng/g in the Western basin. The basal amount of THg gives rise to varying proportions of MeHg, and examining the percent MeHg can reveal the methylating potential in each of the basins. The rate of MeHg production is an important factor in MeHg bioaccumulation in biota, and reporting percent MeHg is a useful means to approximate methylation potential (Gilmour *et al.*, 1998; Heyes *et al.*, 2006). Mean seasonal percent MeHg values from Eastern basin sediments were three times higher than the corresponding value in Western basin sediments. The Eastern basin had the highest percent MeHg, at 0.97, whereas the ratio of MeHg to THg in the Western basin sediments was only 0.32. These findings suggest that although there is much lower THg available in the Eastern basin to be converted to MeHg, a higher proportion is converted, and therefore the methylation potential is higher. This observation is in agreement with the fact that at low levels of sediment THg, MeHg and THg are strongly correlated, as seen in the Eastern basin. However, a large amount of MeHg is not additionally produced at very high levels of THg (Krabbenhoft *et al.*, 1999), as seen in the Western basin. My findings are within the ranges of expected percent MeHg values reported by Gilmour *et al.* (1998) from the Florida Everglades, where MeHg constituted from 0.2% up to 2% of THg in surficial sediments, and with Heyes *et al.* (2006), who reported % MeHg ranges of 0.2-0.7% in the Hudson River and Bay of Fundy.

### 2.4.5 Total Mercury in Seston

Primary producers such as phytoplankton, periphyton, and algae, are the point of entry of inorganic Hg and MeHg into aquatic food webs (Watras & Bloom, 1992). Moreover, the uptake of Hg and MeHg from the water column by the base of the food web constitutes the largest bioaccumulation step in aquatic food webs (Dirscoll *et al.* 2007; Rolffhus *et al.* 2011). For this reason it was important to measure THg in the planktonic portion of the Lake Erie food web, and to quantify the proportion of MeHg and spatial trends in those samples. The vast differences in THg concentrations between sampling trips, even among sites within the same basin, illustrates the variability in seston samples.

Observed seston THg concentrations were lower than values published for zooplankton concentrations. Sorensen *et al.* (1990) and Watras *et al.* (1998) found mean zooplankton THg concentrations of 87.9 and 83 ng/g dry weight, respectively. Although certain samples fell within that range, mean values of half that magnitude suggest my samples consisted mainly of phytoplanktonic species, which are of lower trophic position and accumulate less Hg and MeHg. According to Pickhardt and Fisher (2007), diatom and algae phytoplanktons ranged from 9.7 – 41.8 nmol/g Hg, whereas *Cryptomonad* and *Cyanobacterium*, ranged from 93.5 – 166.0 nmol/g in two contrasting sampling sites within the San Francisco Bay region. These findings all highlight the immense variability, which can potentially be attributed to sampling time, and likely related to the species composition and dominating plankton types.

The Western basin exhibited the highest variability in Hg, particularly in June and August. A partial explanation may be that seston samples were not sorted taxonomically, and the species makeup of the samples likely changed among samples. This variability may account for the observation that means among all three basins are not statistically different. The similarities in mean seston THg among the three basins suggest different rates of bioaccumulation, given the stark water and sediment THg concentrations differences among the three basins.

Concentrations in the Western basin did not change over the sampling period; however those in the Central basin did - bulk seston THg decreased over the sampling period. This

may be explained by the biodilution effect, as observed by Chen & Folt (2005), and on an individual level by the growth dilution effect, as described by Sunda & Huntsman (1998). Because THg availability to the Central basin did not change over the summer sampling period, as confirmed in water and sediment concentrations, the decrease in seston THg may be due to the dilution of a constant amount of THg over a larger biomass, resulting in lower concentrations by weight. Peak values of chlorophyll, a proxy for primary productivity biomass, were historically observed in early August for the site E2 and late August for site E3 (Graham *et al.*, 1996). Assuming comparable findings across basins, this observation agrees with my explanation for the decrease in THg concentrations in the Central basin over the sampling period.

#### 2.4.6 Methylmercury in Seston

Seston samples from the Western and Central basin were analyzed to determine what fraction of THg was in the methylated form. This information is of importance to contaminant studies in lake systems, as MeHg is the bioaccumulating form of Hg, and the amount of MeHg at the base of the food web is a strong variable in the amount found in the top organisms of aquatic food webs (Mason *et al.*, 1996; Stewart *et al.*, 2008). I found that there was no change in MeHg concentrations over the sampling months for seston collected in the Western basin, yet there was an increase in MeHg concentrations at the end of the season in seston collected from the Central basin. It was also found that despite the Western basin having higher abiotic THg concentrations, as seen in the water and sediment, the Central basin consistently had higher MeHg in seston compared to the Western basin.

Both the temporal shift, as well as the occurrence of higher seston MeHg amid lower abiotic THg concentrations in the Central basin, can be partially explained by visual observations made on seston type. This was approximated by colour and size differences. Central basin seston was typically more brown, with individual plankton appearing larger, which suggests composition was predominantly crustaceans, or, zooplankton. Seston from the Western basin was typically smaller, and bright green and blue, suggesting a composition of cyanobacteria and other phytoplankton species. The difference in means, and also the difference in increasing MeHg bioaccumulation

throughout the summer sampling months, may be explained by seston from the Central basin being generally a trophic level above those from the Western basin, constituting higher bioaccumulation of MeHg (Cabana *et al.*, 1994).

Evidence to further support this explanation lies within the percent MeHg for Western and Central basin seston samples. I found that the proportion of MeHg to THg was higher in seston collected from the Central basin, which supports the theory that organisms of a higher trophic status, and thus an additional bioaccumulation step, predominated the Central basin seston assemblage. Considering the known discrepancies in basal abiotic THg that is available to each of the basins, a difference in species assemblages and major trophic status of seston among basins could account for these findings.

Many studies have examined the proportion of THg that is MeHg in phyto- and zooplankton, and percentages are quite variable and appear to be dependent on a number of physical and biological characteristics of the water body. According to Driscoll *et al.* (2007), percent MeHg in phytoplankton from Northeastern American water bodies ranged from 5-40%, whereas in zooplankton the range was higher, from 40-80%. More size-specific studies from Quebec reservoirs found a range of 8-20% in small particles (20-150  $\mu\text{m}$ ), which represent phytoplankton, and from 15% up to 70% in zooplankton. The same study found smaller particles ranging from 15 to 50 ng/g MeHg, lower than the range seen in zooplankton (Plourde *et al.*, 1997). My findings of lower concentrations in phytoplankton-dominated waters, and higher concentrations and accelerated bioaccumulation in zooplankton-dominated waters, agree with these studies. Kainz *et al.* (2006) further focused on the specifics of plankton size and the trophic status of lakes in Victoria, B.C. Seston concentrations were  $13 \pm 15$  ng/g dry weight, which are higher than my finding of 6.18 ng/g in the Western basin and consistent with my finding of 12.20 ng/g in the Central basin. Micro- and meso-plankton had higher concentrations, at  $24-63 \pm 14-28$  ng/g, and macrozooplankton were highest, at  $142 \pm 55$  ng/g dry weight (Kainz *et al.*, 2006). The same study also uncovered that, in a certain size class, MeHg concentrations were lowest in mesotrophic lakes and highest in oligotrophic lakes. These findings were similar to mine given our knowledge of primary production in the three lake basins. This observation may lend further credibility to the possibility of biodilution



occurring in times and areas of high algae and plankton production, namely in the Western basin during late summer.

## 2.5 Conclusions

This study provides a comprehensive analysis of THg and MeHg in various compartments, both abiotic and biotic, of the three Lake Erie basins. A close examination of bulk Hg, as well as the fraction that is methylated, affords us a better understanding of spatial differences in the amount of Hg available to the food web, in addition to where and why certain areas are more susceptible to the bioaccumulating organic form of Hg.

It is clear that within the abiotic sampling compartments of water and sediment, the Western basin remains higher in THg and often MeHg than the Central and Eastern basins. This is especially true in the sediment, which may be acting as a continual source of Hg to both the water column and subsequently the primary biota of the basin. Despite the Western basin having significantly higher Hg in abiotic compartments than both the Central and Eastern basins, the proportion of THg that is MeHg was often lower in the West and increases eastward, indicating that a complex of factors are contributing to higher MeHg production and possibly bioaccumulation in biota in the Central and Eastern basins. This culminates in higher percent MeHg ratios in the Eastern and Central basins for sediment and seston samples. These data can be used further for future reference and input into models that estimate Hg contributions from food sources, which require a certain minimum of accurate empirical data to be of use to aquatic ecology modelers.

Finally, this study has quantified the amount of Hg and MeHg at the base of the food web, which is information that, despite being previously unstudied and un-quantified in this system, is continually shown to be an important factor in understanding differences in Hg within top level predators in aquatic environments. It is intended that this information be coupled with other food web information and extended to further interpret Hg concentrations in different fish species and populations. My aim is to use these data to explain some of the variability in tissue Hg concentrations that is observed among fish caught in different basins, and further explain the recent increasing trend in Lake Erie

fish. In Chapter 3, I invoke the findings of variability of THg and MeHg in the system compartments when examining THg concentrations in benthic invertebrates, and I link THg concentrations in seston when examining the overall food web biomagnification within biotic compartments among the Western and Eastern basins.

## 2.6 References

- Atwell, L., Hobson, K.A., Welch, H.E., 1998. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable nitrogen isotope analysis. *Can. J. Fish. Aquat. Sci.* 55, 1114-1121.
- Azim, M.E., Kumarappah, A., Bhavsar, S.P., Backus, S.M., Arhonditsis, G., 2011. Detection of the spatiotemporal trends of mercury in Lake Erie Fish communities: a Bayesian approach. *Environ. Sci. Technol.* 45, 2217-2226.
- Bhavsar, S.P., Gewurtz, S.B., McGoldrick, D.J., Keir, M.J., Backus, S.M., 2010. Changes in mercury levels in Great Lakes fish between 1970s and 2007. *Environ. Sci. Technol.* 44, 3273-3279.
- Bloom, N.S., 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49, 1010-1017.
- Bodaly, R., Fudge, R., 1999. Uptake of mercury by fish in an experimental boreal reservoir. *Arch. Environ. Contam. Toxicol.* 37, 103-109.
- Bolsenga, S.J., Herdendorf, C.E., 1993. *Lake Erie and Lake St. Clair Handbook*. Wayne State University Press: Detroit, MI.
- Brigham, M.E., Wentz, D.A., Aiken, G.R., Krabbenhoft, D.P., 2009. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. *Environ. Sci. Technol.* 43, 2720-2725.
- Cabana, G., Tremblay, A., Kalff, J., Rasmussen, J.B., 1994. Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (*Salvelinus namaycush*). *Can. J. Fish. Aquat. Sci.* 51, 381-389.
- Campbell, L.M., Hecky, R.E., Nyaundi, J., Muggide, R., Dixon, G.D., 2003. Distribution and food-web transfer of mercury in Napoleon and Winam Gulfs, Lake Victoria, East Africa. *J. Great Lakes Res.* 29, 267-282.

- Chasar, L.C., Scudder, B.C., Stewart, A.R., Bell, A.H., Aiken, G.R., 2009. Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation. *Environ. Sci. Technol.* 43, 2733-2739.
- Chen, C.Y., Folt, C.L., 2005. High plankton densities reduce mercury biomagnification. *Environ. Sci. Technol.* 39, 115-121.
- Cole, D.C., Kearney, J., Sanin, L.H., Leblanc, A., Weber, J., 2004. Blood mercury levels among Ontario anglers and sport-fish eaters. *Environ. Res.* 95, 305-314.
- Dove, A., Hill, B., Klawunn, P., Waltho, J., Backus, S., McCrea, R., 2012. Spatial distribution and trends of total mercury in waters of the Great Lakes and connecting channels using an improved sampling technique. *Environmental Pollution* 161, 328-334.
- Drevnick, P.E., Engstrom, D.R., Driscoll, C.T., Swain, E.B., Balogh, S.J., Kamman, N.C., Long, D.T., Muir, D.G., Parsons, M.J., Rolfhus, K.R., 2012. Spatial and temporal patterns of mercury accumulation in lacustrine sediments across the Laurentian Great Lakes region. *Environ. Pollut.* 161, 252-260.
- Driscoll, C.T., Han, Y., Chen, C.Y., Evers, D.C., Lambert, K.F., Holsen, T.M., Kamman, N.C., Munson, R.K., 2007. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *Bioscience* 57, 17-28.
- Evers, D.C., Han, Y., Driscoll, C.T., Kamman, N.C., Goodale, M.W., Lambert, K.F., Holsen, T.M., Chen, C.Y., Clair, T.A., Butler, T., 2007. Biological mercury hotspots in the northeastern United States and southeastern Canada. *Bioscience* 57, 29-43.
- Evers, D.C., Wiener, J.G., Basu, N., Bodaly, R., Morrison, H.A., Williams, K.A., 2011. Mercury in the Great Lakes region: bioaccumulation, spatiotemporal patterns, ecological risks, and policy. *Ecotoxicology* 20, 1487-1499.
- Forsythe, K.W., Dennis, M., Marvin, C.H., 2004. Comparison of mercury and lead sediment concentrations in Lake Ontario (1968-1998) and Lake Erie (1971-1997/98) using a GIS-Based Kriging approach. *Water Qual. Res. J. Can.* 39, 190-206.

- French, T.D., Campbell, L.M., Jackson, D.A., Casselman, J.M., Scheider, W.A., Hayton, A., 2006. Long-term changes in legacy trace organic contaminants and mercury in Lake Ontario salmon in relation to source controls, trophodynamics, and climatic variability. *Limnol. Oceanogr.* 51, 2794-2807.
- Futter, M.N., 1994. Pelagic food-web structure influences probability of mercury contamination in lake trout (*Salvelinus namaycush*). *Sci. Total Environ.* 145, 7-12.
- Gilmour, C.C., Riedel, G., Ederington, M., Bell, J., Gill, G., Stordal, M., 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* 40, 327-345.
- Graham, D.M., Dahl, J.A., Millard, E.S., Johannsson, O.E., White, L.L. 1996. Assessment of abundance, biomass and production of the lower trophic levels in the eastern basin of Lake Erie, 1994. Great Lakes Laboratory for Fisheries and Aquatic Sciences, Canada Centre for Inland Waters: Burlington, Ontario.
- Hall, B., Bodaly, R., Fudge, R., Rudd, J., Rosenberg, D., 1997. Food as the dominant pathway of methylmercury uptake by fish. *Water Air Soil Pollut.* 100, 13-24.
- Harada, M., 1995. Minamata disease: methylmercury poisoning in Japan caused by environmental pollution. *CRC Crit. Rev. Toxicol.* 25, 1-24.
- Herdendorf, C.E., 1992. Lake Erie coastal wetlands: an overview. *J. Great Lakes Res.* 18, 533-551.
- Herdendorf, C.E., 1975. Shoreline Changes of Lakes Erie and Ontario: With Special Reference to Currents, Sediment Transport and Shore Erosion. Center for Lake Erie Area Research, Ohio State University: Columbus, OH.
- Heyes, A., Mason, R.P., Kim, E., Sunderland, E., 2006. Mercury methylation in estuaries: Insights from using measuring rates using stable mercury isotopes. *Mar. Chem.* 102, 134-147.

- Hill, W.R., Stewart, A.J., Napolitano, G.E., 1996. Mercury speciation and bioaccumulation in lotic primary producers and primary consumers. *Can. J. Fish. Aquat. Sci.* 53, 812-819.
- International Joint Commission. 1978. Great Lakes Water Quality Agreement of 1978. International Joint Commission: Ottawa, Ontario & Washington, D.C.
- International Joint Commission. 1991. U.S.-Canada Air Quality Agreement. International Joint Commission: Ottawa, Ontario & Washington, D.C.
- Kainz, M., Telmer, K., Mazumder, A., 2006. Bioaccumulation patterns of methyl mercury and essential fatty acids in lacustrine planktonic food webs and fish. *Sci. Total Environ.* 368, 271-282.
- Kemp, A., MacInnis, G., Harper, N., 1977. Sedimentation rates and a revised sediment budget for Lake Erie. *J. Great Lakes Res.* 3, 221-233.
- Kidd, K., Hesslein, R., Fudge, R., Hallard, K., 1995. The influence of trophic level as measured by  $\delta^{15}\text{N}$  on mercury concentrations in freshwater organisms. *Water Air Soil Pollut.* 80, 1011-1015.
- Kidd, K.A., Muir, D.C.G., Evans, M.S., Wang, X., Whittle, M., Swanson, H.K., Johnston, T., Guildford, S., 2012. Biomagnification of mercury through lake trout (*Salvelinus namaycush*) food webs of lakes with different physical, chemical and biological characteristics. *Sci. Total Environ.* 438, 135-143.
- Krabbenhoft, D.P., Wiener, J.G., Brumbaugh, W.G., Olson, M.L., DeWild, J.F., Sabin, T.J., 1999. A national pilot study of mercury contamination of aquatic ecosystems along multiple gradients: Bioaccumulation in fish. Biological Science Report USGS/BRD/BSR. 32 pp.
- Marvin, C.H., Charlton, M.N., Reiner, E.J., Kolic, T., MacPherson, K., Stern, G.A., Braekevelt, E., Estenik, J.F., Thiessen, L., Painter, S., 2002. Surficial sediment contamination in Lakes Erie and Ontario: A comparative analysis. *J. Great Lakes Res.* 28, 437-450.

- Marvin-DiPasquale, M., Lutz, M.A., Brigham, M.E., Krabbenhoft, D.P., Aiken, G.R., Orem, W.H., Hall, B.D., 2009. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment– pore water partitioning. *Environ. Sci. Technol.* 43, 2726-2732.
- Mason, R.P., Reinfelder, J.R., Morel, F.M., 1996. Uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Environ. Sci. Technol.* 30, 1835-1845.
- Mason, R.P., Sullivan, K.A., 1997. Mercury in Lake Michigan. *Environ. Sci. Technol.* 31, 942-947.
- Mergler, D., Anderson, H.A., Chan, L.H.M., Mahaffey, K.R., Murray, M., Sakamoto, M., Stern, A.H., 2007. Methylmercury exposure and health effects in humans: a worldwide concern. *AMBIO* 36, 3-11.
- Morel, F.M., Kraepiel, A.M., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 29, 543-566.
- Morrison, H.A., Gobas, F.A., Lazar, R., Whittle, D.M., Haffner, G.D., 1998. Projected changes to the trophodynamics of PCBs in the western Lake Erie ecosystem attributed to the presence of zebra mussels (*Dreissena polymorpha*). *Environ. Sci. Technol.* 32, 3862-3867.
- Moye, H.A., Miles, C.J., Philips, E.J., Sargent, B., Merritt, K.K., 2002. Kinetics and uptake mechanisms for monomethylmercury between freshwater algae and water. *Environ. Sci. Technol.* 36, 3550-3555.
- Ogorek, J., DeWild, J.F., 2013. Analysis of Methylmercury in Plant, Sediment, and Soil Samples by Cold Vapor Atomic Fluorescence Detection with the Brooks-Rand “MERX” Automated Methylmercury Analytical System. U.S. Geological Survey, Reston, VA.
- Ongley, E.D., 1996. Control of water pollution from agriculture – FAO irrigation and drainage paper 55. Food & Agriculture Organization of the United Nations: Rome, Italy.

- Pacyna, J.M., Pacyna, E.G., Steenhuisen, F., Wilson, S., 2003. Mapping 1995 global anthropogenic emissions of mercury. *Atmos. Environ.* 37, 109-117.
- Painter, S., Marvin, C., Rosa, F., Reynoldson, T.B., Charlton, M.N., Fox, M., Lina Thiessen, P.A., Estenik, J.F., 2001. Sediment contamination in Lake Erie: a 25-year retrospective analysis. *J. Great Lakes Res.* 27, 434-448.
- Pickhardt, P.C., Fisher, N.S., 2007. Accumulation of inorganic and methylmercury by freshwater phytoplankton in two contrasting water bodies. *Environ. Sci. Technol.* 41, 125-131.
- Plourde, Y., Lucotte, M., Pichet, P., 1997. Contribution of suspended particulate matter and zooplankton to MeHg contamination of the food chain in midnorthern Quebec (Canada) reservoirs. *Can. J. Fish. Aquat. Sci.* 54, 821-831.
- Quinn, F.H., Guerra, B., 1986. Current perspectives on the Lake Erie water balance. *J. Great Lakes Res.* 12, 109-116.
- Rasmussen, J., Rowan, D., Lean, D., Carey, J., 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. *Can. J. Fish. Aquat. Sci.* 47, 2030-2038.
- Rolfhus, K.R., Sakamoto, H.E., Cleckner, L.B., Back, R.C., Manolopoulos, H., Hurley, J.P., 2003. Distribution and Fluxes of Total and Methylmercury in Lake Superior. *Environ. Sci. Technol.* 37, 865-872.
- Rolfhus, K.R., Hall, B.D., Monson, B.A., Paterson, M.J., Jeremiason, J.D., 2011. Assessment of mercury bioaccumulation within the pelagic food web of lakes in the western Great Lakes region. *Ecotoxicology* 20, 1520-1529.
- Rood, B., Gottgens, J., Delfino, J., Earle, C., Crisman, T., 1995. Mercury accumulation trends in Florida everglades and Savannas Marsh flooded soils, *Water Air Soil Pollut.* 80, 981-990.



- Sandheinrich, M.B., Bhavsar, S.P., Bodaly, R., Drevnick, P.E., Paul, E.A., 2011. Ecological risk of methylmercury to piscivorous fish of the Great Lakes region. *Ecotoxicology* 20, 1577-1587.
- Scheuhammer, A.M., Meyer, M.W., Sandheinrich, M.B., Murray, M.W., 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. *AMBIO* 36, 12-19.
- Schmeltz, D., Evers, D.C., Driscoll, C.T., Artz, R., Cohen, M., Gay, D., Haeuber, R., Krabbenhoft, D.P., Mason, R., Morris, K., 2011. MercNet: a national monitoring network to assess responses to changing mercury emissions in the United States. *Ecotoxicology* 20, 1713-1725.
- Sorensen, J.A., Glass, G.E., Schmidt, K.W., Huber, J.K., Rapp Jr, G.R., 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environ. Sci. Technol.* 24, 1716-1727.
- Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., Krabbenhoft, D.P., 2008. Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir. *Can. J. Fish. Aquat. Sci.* 65, 2351-2366.
- Sunda, W.G., Huntsman, S.A., 1998. Processes regulating cellular metal accumulation and physiological effects: Phytoplankton as model systems. *Sci. Total Environ.* 219, 165-181.
- Thomas, R., Jaquet, J., Kemp, A., Lewis, C., 1976. Surficial sediments of Lake Erie. *J. Fish. Board Can.* 33, 385-403.
- Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. *Crit. Rev. Environ. Sci. Technol.* 31, 241-293.

- U.S.EPA. 1996. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 1998. Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 2005. Technical Support Document for the Final Clean Air Mercury Rule. U.S.EPA Office of Air Quality Planning and Standards: Washington, D.C.
- U.S.EPA. 2007. Method 7473: Mercury In Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. . U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 2012. Great Lakes Basic Information. Retrieved Feb. 5 2014 from <http://www.epa.gov/greatlakes/basicinfo.html>
- Walters Jr, L.J., Kovacik, T.L., Herdendorf, C.E., 1974. Mercury occurrence in sediment cores from western Lake Erie. *Ohio J. Sci.* 74, 1-19.
- Watras, C.J., Bloom, N., 1992. Mercury and methylmercury in individual zooplankton: implications for bioaccumulation. *Limnol. Oceanogr.* 37, 1313-1318.
- Watras, C.J., Back, R., Halvorsen, S., Hudson, R., Morrison, K., Wentz, S., 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219, 183-208.

Wiener, J., Knights, B., Sandheinrich, M., Jeremiason, J., Brigham, M., Engstrom, D., Woodruff, L., Cannon, W., Balogh, S., 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. *Environ. Sci. Technol.* 40, 6261-6268.

Zananski, T.J., Holsen, T.M., Hopke, P.K., Crimmins, B.S., 2011. Mercury temporal trends in top predator fish of the Laurentian Great Lakes. *Ecotoxicology* 20, 1568-1576.

## 3 The Role of Invasive Species in the Enhanced Trophic Transfer of Mercury in Lake Erie

### 3.1 Introduction

#### 3.1.1 Research problem

Due to concerns about the effect of mercury (Hg) in sport fish on human health, public bodies such as the Ontario Ministry of the Environment (OMOE) monitor Hg levels in Ontario lakes including the Laurentian Great Lakes. Public information on large-bodied sport fish from the Great Lakes is provided through fish consumption advisory guidelines by the OMOE, which relies on the Sport Fish Contaminant Monitoring Program. Large provincial and federal monitoring data sets provide long-term Hg information for predatory fish in the Great Lakes, spanning over 40 years up to 2007. From an analysis of temporal trends using this data set, Bhavsar *et al.* (2010) found that Hg concentrations in fish tissue (notably lake trout (*Salvelinus namaycush*) and walleye (*Sander vitreus*)) from Lake Erie had been increasing since the 1990s, whereas Hg levels were concurrently decreasing in all other Great Lakes. Although no specific mechanisms for this change in Lake Erie could be determined from these data, the authors speculated on a range of factors, including changes in air and water temperature due to climate change, changes in global and regional Hg deposition, and changes in the Lake Erie food web coinciding with the arrival of non-native species.

Climate change could impact the delivery of inorganic Hg to Lake Erie due to enhanced mobilization from the watershed, as well as increased deposition (French *et al.*, 2011). While atmospheric Hg is increasing globally, driven by emissions from the continued coal-powered development of large countries in the world, there has been a regional decline in Hg emissions within the Laurentian-Great Lakes region (Pacyna *et al.* 2006; Evers *et al.* 2011). Multiple sources have shown that Hg loading to both terrestrial and aquatic ecosystems in the region has decreased since the 1970s (U.S.EPA, 2005; Schmeltz *et al.* 2011). The Laurentian Great Lakes region would be expected to be evenly affected by changes in global Hg deposition. Therefore, the extent to which changes in loading has influenced the increase in Hg specifically to Lake Erie remains speculative.

Temperature increases due to climate warming could also enhance methylation in both the lake sediments and bottom waters, as well as sites of methylation in the watershed (Hammerschmidt & Fitzgerald, 2004). Although Lake Erie is the shallowest of the Laurentian Great Lakes, there is no evidence in the regional climate record that near-shore temperatures in the Great Lakes have changed by more than 0.01°C, nor that average temperatures in Lake Erie have changed more than 0.037°C (McCormick & Fahnenstiel, 1999; Burns *et al.*, 2005). These observations make climate-driven hypotheses less likely as the major cause of changes in fish Hg concentrations.

The change in Lake Erie's food web that has occurred over the past 25 years is the most compelling explanation for the recent upward trajectory in Hg concentrations in predatory fish. The Lake Erie food web was once dominantly supported by primary production in the pelagic waters. Due to the establishment of non-native species from the Ponto-Caspian area, a new energetic pathway within Lake Erie emerged. The benthic food web became more coupled with the pelagic one, resulting from recent changes in predator-prey interactions attributed to the arrival of non-native benthic species (Johnson *et al.*, 2005, Campbell *et al.*, 2009). With this change in energy dynamics comes a change in contaminant transfer. As certain forms of Hg are highly bioaccumulating, changes in food web structure may also herald new opportunities for contaminants such as Hg to concentrate at the apex of the food web (Vander Zanden & Rasumussen, 1996).

The major species assemblages of Lake Erie prior to the 1990s were grouped here into invertebrates, forage fish and predatory fish. Diets of forage fish were made up primarily of planktonic crustaceans, algae and amphipods (Muth & Busch, 1989). Other invertebrates commonly found in the benthic zone included worms, molluscs, crustaceans and burrowing insect larvae (Barton *et al.*, 1988). Common spiny-rayed forage fish included clupeids such as alewife and shad, and soft-rayed forage fish such as rainbow smelt. These forage fish were eaten by common predators such as walleye, yellow perch (*Perca flavescens*), smallmouth bass (*Micropterus dolomieu*), lake trout, and burbot (*Lota lota*) (Muth, 1985; Forage Task Group, 2001).

The major driver for recent changes to Lake Erie's pelagic and benthic food webs is the arrival of non-native species from the Ponto-Caspian region. The Great Lakes have a history of invasion by non-native species, for example, the arrival of rainbow smelt in Lake Erie in 1931 (Regier & Hartman, 1973). However, a more recent and topical disruption to the lake was the arrival of the dreissenid bivalves zebra (*Dreissenia polymorpha*) and quagga (*Dreissenia bugensis*) mussels (Hebert *et al.*, 1989; Griffiths *et al.*, 1990), and the round goby fish (*Neogobius melanostomus*) (Crossman *et al.* 1991; Jude *et al.* 1992).

The arrival of these non-native species has had consequences on the structure and functioning of Lake Erie's food web. Complex interactions formed among the invaders and their new prey, resulting in their incorporation into the diets of incipient lake organisms. The dreissenid mussels affected the lake's nutrients and energetic cycle through the intense consumption of primary producers (algae and plankton) (Hecky *et al.*, 2004), and the excretion and deposition of feces and pseudofeces on the lake bed. This localized microhabitat effect was shown in Lake Erie's Tropic Collaborative Study, where the benthic invertebrate *Echinogammarus* benefited from the added nutrients to its habitat in the form of zebra mussel pseudofeces, which is high in nutrients previously unavailable to the invertebrate (Van Overdijk *et al.*, 2003). However, in Dermott and Kerec's 1997 study, both positive interactions with meiofauna such as nematodes and ostracods, and negative interactions with native clams due to competition and microhabitat changes, were seen in the Eastern basin. Furthermore, models developed by Bruner *et al.* suggested that the novel ingestion of feces and pseudofeces can increase concentrations of contaminants, specifically PCBs, in gammarids (Bruner *et al.*, 1994). There are clearly many ways that the introduction of these mussels affected nutrient and even contaminant cycling on a local scale. It was primarily the dietary coupling of the round goby and dreissenid mussels that led to local effects manifesting into lake-wide changes to nutrient, contaminant and Hg cycling.

The round goby is a natural predator of the dreissenid mussel, and this predator-prey relationship proliferated in Lake Erie. The round goby remains one of the few consumers

of dreissenid mussels in the lake, along with scant predation by crayfish and freshwater drum (Morrison *et al.* 1997, Forage Task Group, 2001). Zebra mussels remained nearly unchecked in terms of predation for many years until the arrival of the round goby and, thus, when predation began a new energy pathway was created. The zebra mussel had been filtering and consuming primary producers, effectively sequestering energy in their biomass, save for the extra energy expelled through excretion. Both Morrison (2000) and Bunnell (2005) remarked on this new energy pathway in their studies on dreissenid-goby interactions, and the energy pathway was confirmed in Johnson *et al.* (2005). Campbell *et al.* (2009) used  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  to show that the non-native species were firmly integrated in the Lake Erie food web. Not only were round goby consuming mussels to the point of potential top-down control, but they were also being consumed by native fish species of the lake. Round goby appeared in the stomach contents of piscivorous fish including yellow perch, smallmouth bass, and walleye (Forage Task Group, 2011). It is this final linkage that resulted in the connection of the food web from top piscivorous fish down to the mussels that had previously been unmolested. The energy previously inaccessible in the form of large-scale primary production was suddenly directly incorporated in the food web. The vast population sizes of both dreissenid and goby contributed to their fast and efficient inclusion in the Lake Erie food web.

Although these changes in Lake Erie's food web and energy flow were expected to influence the way contaminants transfer among trophic levels, limited information was gathered on Hg specifically. Some research on PCBs showed that contaminant trophic transfer and cycling has indeed changed since recent invasions, and the explanation remains with the introduction of these non-native species (Morrison *et al.*, 2000). Preliminary and limited work by Hogan *et al.* (2007) addressed the question of Hg and lead (Pb) within Lake Erie; however, this research does not address my questions due to inadequate sample sizes and sampling locations. The question of changes to Hg trophic transfer in Lake Erie requires closer examination, with the added benefit of potentially informing the issue of recent increasing trends in fish tissue Hg.

### 3.1.2 Mercury Bioaccumulation in Benthic Invertebrates and Fish

Of the many chemical forms of Hg, divalent inorganic Hg (Hg(II)) is the most common form that enters and exists in aquatic ecosystems. Hg(II) is converted to an organometallic compound called methylmercury (MeHg) primarily by sulphate-reducing bacteria (SRB) (Morel *et al.*, 1998). Once taken into an organism, MeHg has a much longer residence time than its inorganic counterpart due to its binding to protein and muscle tissue (Mathers & Johansen, 1985; Mergler *et al.*, 2007). Its slow depuration relative to inorganic Hg(II) accounts for the propensity of MeHg to bioaccumulate within organisms and biomagnify within food webs. Over 95% of the total Hg burden in fish is in the methylated form (Bloom, 1992), and the majority of this, over 85%, is accumulated through ingestion from food sources (Hall *et al.*, 1997). Accumulation occurs throughout the lifespan of a fish and as a result Hg concentrations and fish age are tightly correlated (Bache *et al.*, 1971).

Hg enters aquatic food webs at the level of primary producers, such as phytoplankton, periphyton and algae (Watras & Bloom, 1992; Hill *et al.*, 1996). In 1992, Watras and Bloom showed that the total Hg in freshwater periphyton and zooplankton was comprised of 13-18 and 29-57% MeHg, respectively (Watras & Bloom, 1992). Studies on freshwater benthic invertebrates reveal up to 50% of THg is in the methylated form (In Hill *et al.*, 1996). Fish species that consume organisms with higher Hg concentrations accumulate Hg at faster rates, and will themselves have higher Hg concentrations (Phillips *et al.*, 1980; Wyn *et al.*, 2009).

### 3.1.3 Importance of Basal Food Web Organisms in Fish Mercury Concentrations

There is a disparity between the amount of information collected on Hg concentration in fish, and Hg concentrations in the supporting food web within the Great Lakes. Studies historically focused on top predatory fish and other organisms of higher trophic level, mainly due to their importance with respect to inclusion and regional reliance in human diets, but also because of ease of sampling. Impetus to characterize Hg at the base of the food web has been driven by the discovery that the largest bioconcentration step occurs between the water column and primary particulate matter (Watras & Bloom, 1992;



Driscoll *et al.*, 2001). The role of zooplankton and invertebrates in Hg transfer was largely unknown, and remains under-studied. Research within the Great Lakes provides an important glimpse of percentages of MeHg in zooplankton and benthic invertebrates, which leads to a greater understanding of fish Hg concentrations (Mason & Sullivan, 1997; Back *et al.*, 2003).

Despite the scarcity of research, some studies have investigated the implication and importance of the base of the food web in top predator Hg concentrations. In freshwater inland lakes on the Minnesota-Ontario border, Hg concentrations in predatory fish were influenced by food web structure affecting trophic position, as well as ecosystem factors that result in a greater amount of MeHg in lower trophic levels (Wiener *et al.*, 2006). Differences among food webs of contrasting water bodies may be due to the amount of Hg available at the base of the food web, and this is especially likely due to the discovery that there is uniformity in MeHg uptake in biota of similar trophic position. As a consequence of fish deriving a majority of Hg through diet, minor differences among bioconcentration factors at the base of the food web can result in measurable differences in concentrations in higher organisms (Pickhardt & Fisher, 2007). Studies focusing on the base and benthic elements of aquatic food webs suggest that small perturbations in these amounts of MeHg, often influenced by lake-specific traits that promote MeHg production, can result in a bottom-up control on Hg concentrations in top predatory fish (Rolfhus *et al.*, 2011). In fact, MeHg concentrations at the base of the food web were proposed by some to be one of the most useful predictors of Hg concentrations in organisms of highest trophic levels, such as piscivorous fish (Stewart *et al.*, 2008; Wyn *et al.* 2009). Conceivably, changes in the way that MeHg at the base of a food web is transferred can have an impact on Hg concentrations in higher organisms.

### 3.1.4 Food Web Changes Affect Mercury Bioaccumulation

The effects of food web structure and trophic level variation on contaminant bioaccumulation are well established in aquatic sciences. Upon understanding the bioaccumulative qualities of Hg, the connection between Hg and more bioaccumulation steps in longer food chains was formed in the literature in the 1990s. This was first shown

using observational experiments with the presence and absence of key prey food items, such as zooplankton or a forage fish, in Ontario lakes (Cabana *et al.*, 1994). By examining the effect of food chain lengthening on both PCB and Hg concentrations in lake trout, bioaccumulation was enhanced in the top predator in lakes with “longer” food chains - in other words, more bioaccumulation steps overall were a determinant of higher contaminant concentrations (Rasmussen *et al.*, 1990; Cabana *et al.*, 1994; Futter, 1994).

These rather simplified experiments focused on single insertions into food webs to validate the hypothesis that trophic transfer plays a strong role in contaminant accumulation. Food webs are very complex, and further studies examined or modeled the intricate relationship between trophic transfer and contaminant concentrations (Vander Zanden & Rasmussen, 1996). Food chain length as a determinant of contaminants in top predators had been further explored and well described using  $\delta^{15}\text{N}$  isotope analysis in both aquatic and terrestrial ecosystems (Atwell *et al.*, 1998; Campbell *et al.*, 2003). These holistic studies attempted to capture the complexity and interconnectedness of aquatic food webs in order to better understand contaminant transfer as it relates to trophic transfer. An isotopic study in Lake Erie specifically, including some 30 species from the Eastern basin alone, explored the role that the recently introduced species blood shrimp, quagga mussels and round goby played in the transfer of energy through new food web pathways, confirming that these non-native species are integrated into the food web (Campbell *et al.*, 2009).

With the establishment of insertions and increasing food web complexity influencing contaminant concentrations, the consideration of recent invasion by non-native species the state of contaminant trophic transfer in Lake Erie is clearly relevant. A study focused on just this in the Western basin of Lake Erie, and modeled changes in PCB concentrations in pelagic fish such as alewife and walleye resulting from food web structure changes following the invasion of the round goby. Although it was found that exposure to older, more PCB-laden sediment was the main driver for changes in concentrations in fish, the presence of the round goby did result in an effect as early as the mid-1990s (Morrison, 2000). A further study aimed to determine how non-native

species contribute to the trophic transfer of Hg and Pb in Lake Erie smallmouth bass, although focus was placed on the predatory fish, with sparse sampling of dreissenid mussels and gobies, and no attention to native benthic species (Hogan *et al.*, 2007). To tease out the role that these non-native species play in the trophic transfer of Hg, a more comprehensive study in terms of study species and spatial and temporal detail is required.

### 3.1.5 Aims and Objectives

To understand why Hg is increasing in Lake Erie sport fish we must first clearly describe the potential drivers that are particular to Lake Erie at this time. The role of non-native species seems a strong starting point, given the evidence that insertions and increasing complexity of aquatic food webs influences the trophic transfer of bioaccumulative contaminants. There is limited research on the benthic communities of Lake Erie, including recently introduced non-native species, and their relation to the cycling and transfer of Hg to top predatory fish. This paucity of information directed the research questions of this project.

The purpose of this study is to determine if the introduction of non-native dreissenid mussels and round goby is wholly or in part responsible for the recent increase in Lake Erie sport fish mercury concentrations. Based on current knowledge of dreissenid mussel and round goby feeding behavior, and abiotic environmental concentrations garnered in Chapter 2, predictions about THg and MeHg concentration native and non-native species can be made:

- Invasive dreissenid mussels in Lake Erie have higher total and methylmercury concentrations relative to indigenous benthic invertebrates due to their tight coupling with their abiotic environment via their filter feeding mechanism.
- Round goby will have higher mercury concentrations than predicted by their trophic position due to their consumption habits.
- The differences in mercury between dreissenid mussels and other invertebrates, as well as among dreissenid mussels from the three basins, will increase over my sampling time as methylmercury concentrations increase in water, sediment, and plankton. The tissue concentrations of these demersal organisms will reflect the seasonal changes in methylmercury concentrations seen in the sediment.

## 3.2 Materials and Methods

### 3.2.1 Study Site

The study site is Lake Erie, one of the Laurentian Great Lakes. It is situated between Southern Ontario and the American states of Michigan, Ohio, Pennsylvania and New York, and is between Lakes Huron and Ontario. Its drainage basin of 58 800 km<sup>2</sup> extends across one Canadian province and six American states (Fuller *et al.*, 1995). Many physical qualities distinguish Lake Erie from the other Laurentian Great Lakes. It is the southernmost lake of the group, the shallowest, and also the smallest by surface area as well as by volume, but is still 9<sup>th</sup> by area and 15<sup>th</sup> by volume amongst the world's large lakes (Herdendorf, 1990). Lake Erie is partitioned into three basins delineated by large sediment deposits or bedrock outcrops: the Western basin is separated from the Central basin by the Pelee-Lorraine Sill, which is separated from the Eastern basin by the Long Point-Erie Sill (Thomas *et al.*, 1976). The basin bathymetry grows incrementally deeper from West to East. The Western basin has an average depth of 7.5 m and a maximum depth of 19 m. The Central basin has an average depth of 18.5 m and a maximum depth of 26 m. The Eastern basin has an average depth of 24.5 m, driven high by a deep conical bathymetry of 64 m (Herdendorf, 1992; Bolsenga & Herdendorf, 1993).

Lake Erie is a holomictic lake, with stratification and thermocline development strongly related to bathymetry. Stratification is seen in the Eastern and Central basins, beginning in May and lasting into September, when the lake overturns. Due to the shallow state of the Western basin, it remains mixed throughout the summer, barring periodic episodes of stratification that can be associated with calm weather (Mortimer, 1987). Historically, Lake Erie is  $\geq 90\%$  ice covered overwinter. Less is known of winter temperature conditions, but a reverse stratification is believed to occur between December and February, with the lake reaching isothermal status at 1° from mid-February to mid-March. Mixing is more likely to occur in areas without ice cover, or in years when ice cover is reduced (Schertzer *et al.*, 1987).

Accompanying thermocline formation is oxygen depletion to colder levels of the water column. This occurs when mixing and diffusion due to turbulence no longer deliver

oxygen to the hypolimnion. The most important factors controlling oxygen depletion are vertical mixing, temperature differences, thickness of the hypolimnion, and seasonal variability, resulting in a fluctuation of deep-water oxygen levels over time (Rosa & Burns, 1987). In addition to the natural depletion of oxygen due to these physical factors, cultural eutrophication due to agricultural intensification in Lake Erie's watershed and coastal areas has led to further oxygen depletion, to the point where the Central basin of the lake was pronounced "dead" in the 1960s (Mortimer, 1987). These episodes of hypoxic conditions resulted in extreme responses from lake biota, for example the extirpation of burrowing mayfly larvae *Hexagenia* spp. in the 1950s (Britt, 1955) as well sub-lethal and lethal effects on fish species (Arend *et al.*, 2011).

### 3.2.2 Sampling Locations and Sampling Regime

Field data collection was facilitated by the Ontario Ministry of Resources (OMNR) in conjunction with their routine Lake Erie limnological sampling program and interagency lower-trophic food web monitoring program. Ten sites throughout the lake basins were visited bi-weekly from May-October, weather permitting. Four sites in the Western basin and four in the Central basin were accessed through the Wheatley office branch of OMNR, and two sites in the Eastern basin were accessed through the Port Dover office branch. Sites were accessed and sampling conducted on 60 ft. diesel-powered tugboats, reformed by OMNR for limnological research. A map of the study site, Lake Erie, including sampling site locations is provided in Figure 2.1, and site coordinates can be found in Appendix A.

The 10 sampling sites consisted of four in the Western basin (W5, W6, W7, W8), four in the Central basin (WC1, WC2, WC3, WC4) and two in the Eastern basin (E2, E3). These sites were sampled from June to September 2012. As per Figure 2.1, a large portion of the Central basin, beyond its Westerly edge, remained un-sampled in conjunction with the OMNR programs. This was due to the absence of an OMNR office and vessel on the North shore of the Central basin. In addition, a planned October 2-day sampling cruise of the Central basin West of the Long Point peninsula was cancelled due to poor weather conditions. Please refer to Figure 2.1 in section 2.2.2 for a map of Lake Erie with sampling sites.

### 3.2.3 Benthic Invertebrate and Fish Sampling

#### 3.2.3.1 Benthic Invertebrates

Benthic invertebrate samples were collected in accordance with clean sampling techniques. At every site, a stainless-steel ponar-style sampling device was used to obtain a sediment sample. The sediment grab was emptied into a bucket lined with a clean polypropylene plastic bag, and after sediment sub-samples were removed using a double-gloved hand, the sediment and lake water mixture was processed for benthic invertebrate removal. Aboard the vessel accessing the Western and Central basins, the mixture was poured into a sieve of 500  $\mu\text{m}$  mesh size, and the plastic bag was rinsed thoroughly with lake water into the same sieve. Dreissenid mussels were removed by gloved hand, rinsed thoroughly with deionized water, and double bagged in polypropylene re-sealable bags. Sieved material was transferred to a sieve of smaller mesh size (154  $\mu\text{m}$ ) using lake water for processing of smaller invertebrates. Aboard the vessel accessing the Eastern basin, a 500  $\mu\text{m}$  sieve was used to separate dreissenid mussels, following sieving through a 240  $\mu\text{m}$  mesh size bucket on to a 150  $\mu\text{m}$  mesh size sieve. Multiple sieving with plenty of rinses with lake water was required in the Eastern basin due to its much finer sediment grain size. After this point, processing on each vessel remained the same.

Organisms remaining on the final sieve were further rinsed of debris, such as lingering sediment, rocks, and crushed dreissenid mussel shells, using deionized water. Living organisms were identified by colour, movement, shape, and other defining features unique to each family. Organisms were identified to the family level and were pooled together, transferred using stainless-steel forceps into polypropylene microcentrifuge tubes, after thorough cleaning with deionized water. Remaining debris from each site was placed in acid-washed jars for further analysis in the lab. Sorted benthic invertebrate samples and unsorted debris jars were held in coolers on ice until arrival at the lab.

Upon arrival at the lab, samples were stored at 4°C until immediate processing of debris was completed. Debris was placed onto 20  $\mu\text{m}$  pore size rayon-polyester Miracloth® and examined under a dissecting microscope at 10-40  $\times$  magnification. Any benthic invertebrate specimens were thoroughly rinsed and pooled appropriately with on-board

sorted samples using acid-washed stainless steel forceps. Fully sorted samples were then stored at -20°C. Prior to analyses, specimens were lyophilized until they reached a constant dry weight, after which point samples were stored at room temperature in the dark until analysis.

### 3.2.3.2 Fish Sampling

Yellow perch, walleye, and round goby (the non-native benthic fish) were chosen as the fish study species for this project. Yellow perch and walleye were primarily chosen for analysis of muscle tissue Hg, in continuation of the OMOE Sport Fish Contaminant Monitoring Program (Bhavsar *et al.*, 2010). Round goby was chosen as little is known of its Hg body burden, and because of the linkage between the benthic and pelagic food web as described in section 3.1.1.

Yellow perch and walleye were obtained through bi-weekly OMNR subsampling commercial fishery catches. Twenty yellow perch and 10 walleye from the Western and Central basins were frozen at -20°C after biometric information was recorded, gonad removal, and liver removal in select fish. Dorsal muscle tissue was left undisturbed by OMNR personnel. Yellow perch between 250 and 350 mm and walleye between 550 and 650 mm were used to comprise the requested fish quota, in order to maintain consistency in accordance with the OMOE Sport Fish Monitoring Program (Bhavsar *et al.*, 2010).

Round goby was not a key species in any lake biomonitoring program, and consequently all round goby collection was incidental. In the Western basin, goby were subsampled from a local fishing derby, and collected as by-catch from mid-summer bottom trawling programs. In the Eastern basin, round goby were collected as by-catch from near-shore netting and trawling efforts. No consistency in size range was achieved, as neither office plentifully sampled round goby. As a potential consequence of the discrepancies between catching procedures, round goby from the Eastern basin were generally smaller than those caught in the Western basin.

In yellow perch and walleye specimens, muscle from the left dorsal area above the lateral line was removed with an acid-washed, stainless steel scalpel. Muscle tissue samples of

approximately 1 g in weight were cleaned of skin and scales. Fillets were placed in polypropylene microcentrifuge tubes, double bagged in re-sealable polypropylene bags, and frozen at  $-20^{\circ}\text{C}$  until analysis. In the case of the round goby, the same procedure was followed; however, dorsal muscle tissue was removed from each side to ensure sufficient sample size for analyses.

The OMNR provided further data on fish age for Lake Erie yellow perch and walleye. Data described mean total length of fish aged through otolith aging processes for both the same sampling year, 2012, as well as long term data spanning the length of their partnership index fishing, 1989-2011. Length information for fish caught in the Western and Eastern basins was used to calculate mean ages for fish in the range of sizes I subsampled.

### 3.2.4 Mercury Analyses

#### 3.2.4.1 Benthic Invertebrates

Dried samples were analyzed for THg on a Milestone® DMA-80 Direct Mercury Analyzer using methods described in EPA method 7473 (U.S.EPA, 2007). The calibration detection limit was 1 ng. Duplicates were analyzed every 9 samples (mean % deviation:  $10.26 \pm 12.63$ ,  $n=11$ ). A CRM was analyzed at the beginning and end of runs, and every 10 samples after duplicates (mean % recovery:  $96.16 \pm 11.08$ ,  $n=28$ ). CRM raw Hg (ng) bounded the lower and upper limits of sample raw Hg (ng). CRMs included MESS-3 ( $0.091 \pm 0.009$  mg/kg Hg), TORT-2 ( $0.27 \pm 0.06$  mg/kg Hg), and TORT-3 ( $0.292 \pm 0.022$  mg/kg Hg). Blanks were analyzed at the start of runs and following CRMs (mean:  $0.16 \pm 0.12$  ng,  $n=23$ ). Results are presented on a dry weight basis.

Following the completion of all necessary THg analysis, remaining benthic invertebrate samples of sufficient mass were analyzed for MeHg. Besides dreissenid tissue, few benthic invertebrates remained or were of sufficient mass for this analysis. Select benthic invertebrate samples underwent extraction for MeHg as outlined in the USGS method for analysis of methylmercury in biological samples by cold vapor atomic fluorescence detection (Ogorek & DeWild, 2013). This digestion and extraction method was used in



conjunction with EPA method 1630 to carry out invertebrate sample analysis on a Tekran series 2700 methylmercury auto-analysis system (U.S.EPA, 1998).

#### 3.2.4.2 Fish Tissue

Fish muscle tissue samples were analyzed for total Hg on a Milestone® DMA-80 Direct Mercury Analyzer using methods described in EPA method 7473 (U.S.EPA, 2007).

Frozen samples were prepared using acid-washed stainless steel forceps and scalpel on an acid-washed watch glass, and 0.1 g – 0.8 g of muscle tissue was used for analysis. The calibration detection limit was 1 ng. Duplicates were analyzed every 9 samples (mean % deviation:  $2.05 \pm 5.45$ ,  $n=15$ ). A CRM was analyzed at the beginning and end of runs, and every 10 samples after duplicates (mean % recovery:  $92.87 \pm 7.97$ ,  $n=28$ ). CRM raw Hg (ng) bounded the lower and upper limits of sample raw Hg (ng). CRMs included MESS-3 ( $0.091 \pm 0.009$  mg/kg Hg) and TORT-2 ( $0.27 \pm 0.06$  mg/kg Hg). Blanks were analyzed at the start of runs and following CRMs (mean:  $0.005 \pm 0.031$  ng,  $n=31$ ).

Results are presented on a wet weight basis, except when they are converted to a dry weight for Figure 3.2, where moisture content of 80% was assumed.

#### 3.2.5 Quality Assurance, Quality Control, and Statistical Measures

Strict quality assurance and control metrics practices were employed to ensure data integrity. Laboratory analysis measures for THg in benthic invertebrates and fish included blanks, samples duplicates, and the use of certified reference materials (CRMs) marine estuarine sediment (MESS-3), and lobster hepatopancreas (TORT-2 and TORT-3), from the National Research Council (Canada). Measures for MeHg in benthic invertebrates included method blanks, sample triplicates, matrix spikes, and the use of the CRM lobster hepatopancreas (TORT-3) from the National Research Council (Canada). Statistical means, medians and 95% confidence interval summaries were calculated using SPSS (IBM, 2011).

## 3.3 Results

### 3.3.1 Total and Methyl Mercury in Benthic Invertebrates

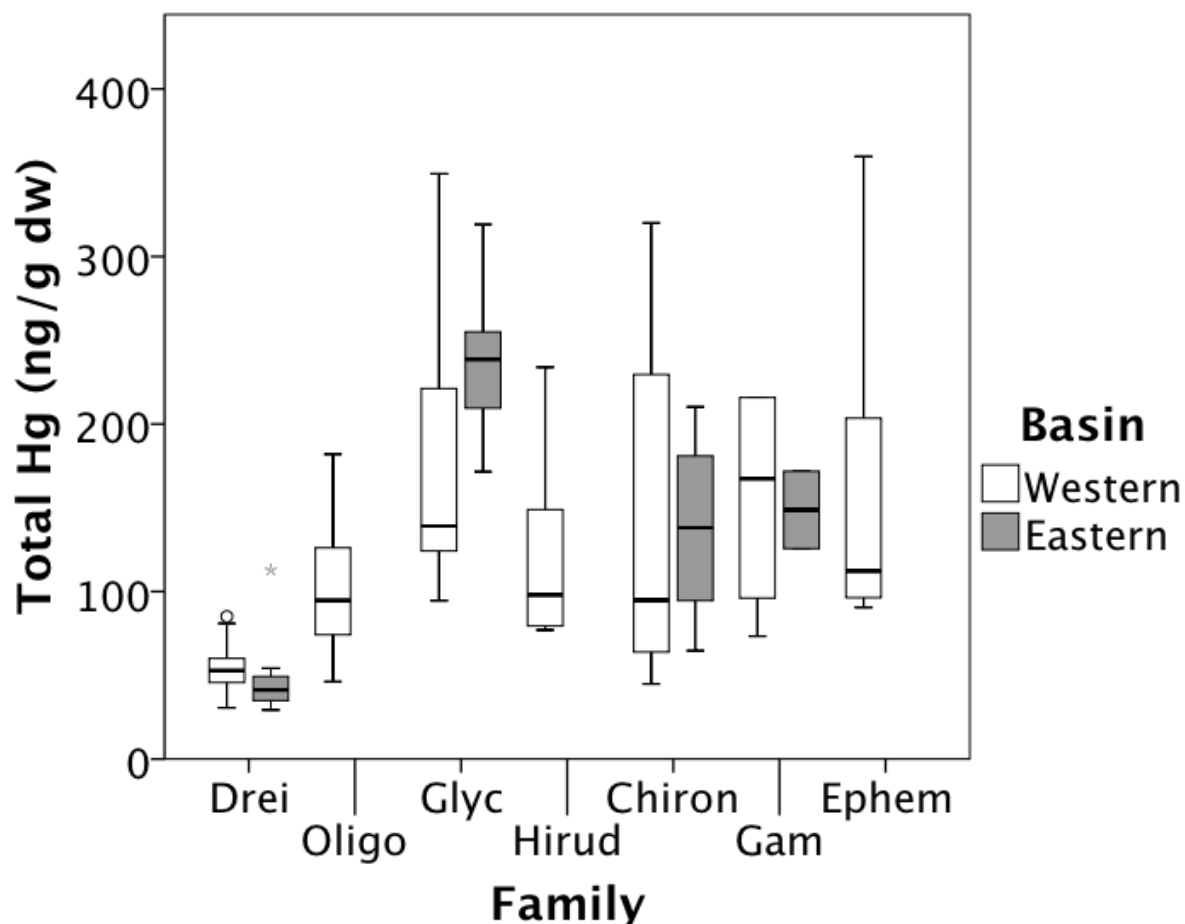
The most commonly collected organisms were dreissenid mussels, *Glycera* worms and chironomid larvae in both basins. Other oligochaete worms, hirudinea leeches and ephemeroptera *Hexagenia* were also present in the Western basin, but not found in the Eastern basin, and so they are presented without spatial comparison. Also important to note is the timing of appearance of benthic invertebrates; for example, dreissenid mussels and chironomids were present throughout each sampling month, whereas ephemeroptera were not present in sediment grabs until September. The THg values for all invertebrates collected over the sampling months with sufficient mass to analyze are shown in Figure 3.1.

Median seasonal THg values were computed for comparison across species. The median seasonal dreissenid mussel THg concentration (47.57 ng/g d.w.) was lower than all other benthic organisms analyzed (Figure 3.1). Chironomids, oligochaete worms, hirudinea and ephemeroptera exhibited similar median THg concentrations to each other. *Glycera* worms exhibited the most elevated seasonal median THg concentration, followed by gammarids. *Glycera*, chironomids and ephemeroptera all showed the greatest range in THg concentrations, whereas dreissenid data had the lowest variability.

The 95<sup>th</sup> percentiles of THg concentrations were compared among the invertebrates. There was no overlap between the upper bound of dreissenid mean THg concentrations, which was 61.52 ng/g, and the lower bounds of all of other invertebrates. The only exception to this was overlap between the lower bound (45.31 ng/g) in the confidence interval of the invertebrate hirudinea. Therefore, of all invertebrates analyzed, hirudinea was the only invertebrate whose 95% percentiles of mean THg concentrations overlapped with that of dreissenid mussels.

There were few differences in median concentrations between Western and Eastern benthic invertebrates of the same family. The median THg concentrations for the Western and Eastern basin dreissenid mussels were 52.88 and 41.32 ng/g, respectively. The median THg concentration of *glycera* worms was 1.7 times higher in the Eastern basin

than in the West. Eastern basin chironomids had a higher median than Western basin chironomids, as well. Glycera worms appeared to exhibit the greatest difference in median THg concentrations between the basins, although due to violation of sample number evenness, statistical measures could not be employed to confirm this.



**Figure 3.1** Box and whisker plots of THg concentrations in 118 benthic invertebrate specimens collected over the sampling months, June-September 2012. Organisms were identified to the family level and pooled for analysis. Drei = dreissenid; Oligo = oligochaete; Glyc = glycera; Hirud = hirudinea; Chiron = Chironomidae; Gam = gammarid; Ephem = ephemeroptera. Families were further split into area collected; Western for sampling sites WC1-W8, and Eastern for sampling sites E2 and E3. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles. Extreme outliers with values of 3 or more times the IQR are denoted by asterisk.

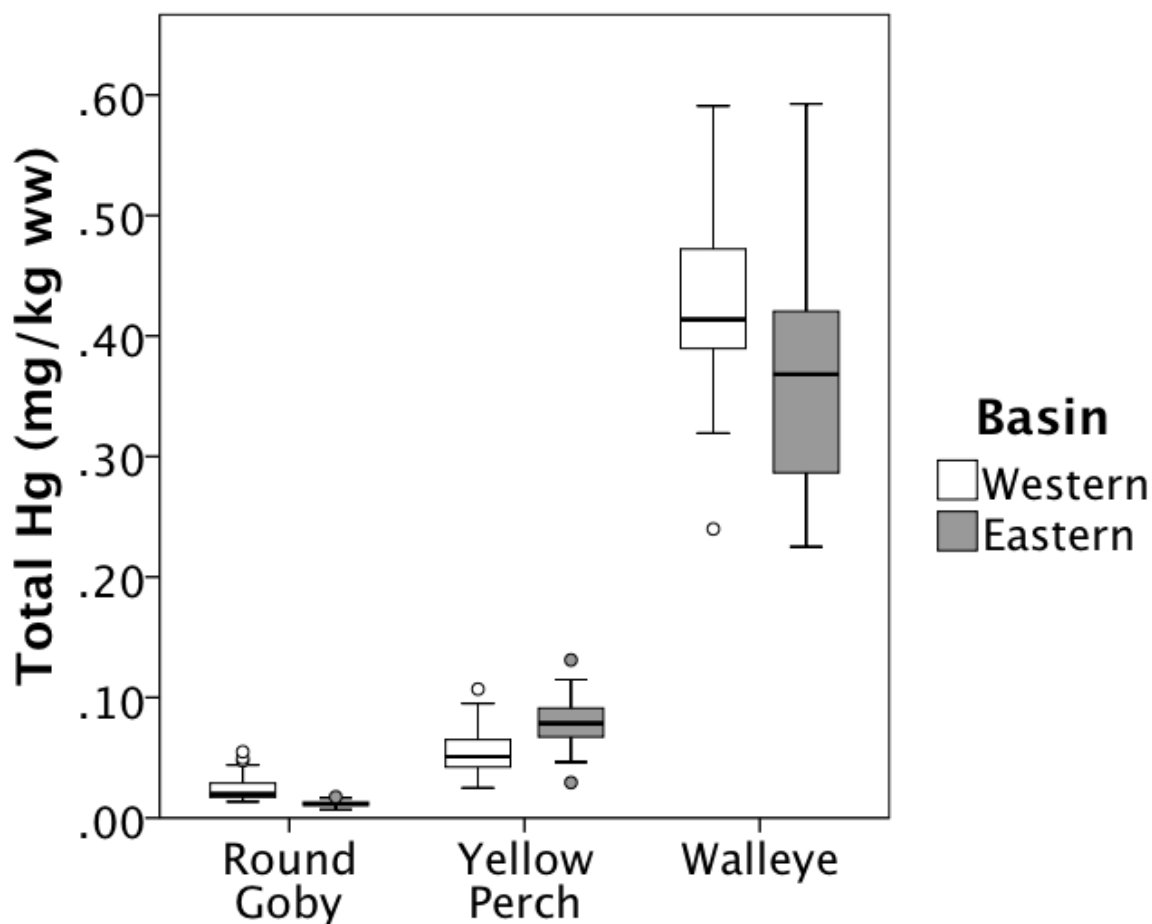
When all benthic invertebrates were combined, overall difference in median THg concentrations between basins was minimal. The median THg concentration of pooled benthic invertebrates collected in the Western basin was 93.98 ng/g. The same calculation for benthic invertebrates from the Eastern basin was 112.90 ng/g. Although there is greater variation in data from the East, there are more outliers in data from the West.

In addition to THg, MeHg was also measured in benthic invertebrates with sufficient mass (notably dreissenid mussels). Median seasonal MeHg concentrations exhibited a West to East decreasing gradient, with a Western basin median of 15.83 ng/g and an Eastern median of 10.20 ng/g. The 95% percentiles for the mean seasonal MeHg concentrations did overlap between these two basins, with the Eastern basin upper bound being 14.48 ng/g and the Western basin lower bound being 13.41 ng/g. However, when data collected from the West-Central basin was removed from the Western basin group, the median seasonal MeHg concentration raised to 17.83 ng/g, with its lower bound, now 15.68 ng/g, no longer overlapping with the Eastern basins upper 95% confidence interval bound. Thus, by separating out only samples collected from sites W5-W8, the mean seasonal MeHg concentration in the Western basin confidence interval does not overlap with that of the East's, suggesting differences in median seasonal dreissenid mussel MeHg tissue concentrations. The remaining benthic invertebrate tissue analyzed was that of Western basin ephemeroptera, which had a MeHg value of 15.92 ng/g. This value was comparable to Western basin dreissenid mussel concentrations. Mean percent MeHg of THg values for dreissenid mussels were  $34.17 \pm 2.09\%$  in the Western basin,  $27.55 \pm 2.95\%$  in the Eastern basin, and 14.56% for Western basin ephemeroptera.

### 3.3.2 Total Mercury in Fish

As all fish species studied were not caught at my sampling sites and catch numbers varied among sites, a basin-wide comparison was the best method of examining spatial trends in all fish species collected. Fish collected in the Western or the West-Central basin were not distinguished upon sampling, and so the data were pooled and referred to collectively as Western basin.

Figure 3.2 shows the relative similarity of round goby and yellow perch THg concentrations compared to walleye. The boxplots also reveal little difference in between-basin THg medians for any fish species. Round goby THg concentrations appeared higher in the Western basin than in the Eastern. In the East, yellow perch appeared to have higher THg concentrations than perch caught in the Western basin, and potential differences will be addressed using tables 3.1 and 3.2. through examining age and growth data. Little difference in median is apparent for walleye from the two basins.



**Figure 3.2** Box and whisker plots depicting THg concentrations in three fish species collected over May-September, 2012. Forty round goby, 60 yellow perch and 15 walleye specimens were grouped by basin in which they were collected or caught. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles.

Table 3.1 highlights the mean ages of both female and male yellow perch sized 25-35 mm for both the 2012 sampling year, as well as long-term data, comprised of 23 years of ageing data. Perch sampled in 2012 were younger compared to long-term data for both females and males from both basins. The younger age of Eastern basin female perch compared to those from the Western basin, both in 2012 and in long-term data, is also important to note, as this holds implications in the amount of time Hg body burdens were developed in fish. Data are not available for male perch caught in the Western basin in 2012, however given long-term data it appears, as with the females, that perch of the same size range caught in the Western basin were older than those from the Eastern basin. In the case of Eastern basin male perch, 2012 age means matched long-term age means, which gives us more confidence in this assumption.

**Table 3.1** Mean ages in years  $\pm$  SE for yellow perch of size range 250-350 mm, as assessed by OMNR otolith aging process for fish collected in both my sample year (2012), as well as long-term data spanning from 1989-2011

	Female		Male	
	West	East	West	East
Ages of fish sampled 2012	6.8 $\pm$ 1.7	5.5 $\pm$ 1.3	N/A	8.0 $\pm$ 1.4
Ages of fish sampled 1989-2011	8.5 $\pm$ 2.5	7.5 $\pm$ 2.5	11.7 $\pm$ 2.1	8.5 $\pm$ 1.9

Table 3.2 shows the mean ages for female and male walleye between 550 and 650 mm in length, caught in both the Western and Eastern basins in 2012, as well as long-term data. In 2012, females between 55 and 65 centimeters that were caught in the West seemed to be 2 years older than those caught in the East, although this trend was reversed when looking at the long-term data. In males of the same size, walleye caught in the Eastern basin appeared to be 4-5 years older than their counterparts in the West, both in 2012 and long-term. While examining long-term ages, mean age tended to drop significantly and fall more in line with 2012 data if some higher ages, where lengths appeared to be affected by senescence, were excluded. The majority of fish caught by the MNR and analyzed in this study were female.

**Table 3.2** Mean ages in years  $\pm$  SE for walleye of size range 550-650 mm, as assessed by OMNR otolith aging process for fish collected in both my sample year (2012), as well as long-term data spanning from 1989-2011

	Female		Male	
	West	East	West	East
Ages of fish sampled 2012	8.0 $\pm$ 2.6	6.0 $\pm$ 1.0	11.0 $\pm$ 2.0	14.6 $\pm$ 4.5
Ages of fish sampled 1989-2011	9.0 $\pm$ 2.8 <sup>a</sup>	10.3 $\pm$ 8.5 <sup>b</sup>	11.7 $\pm$ 3.4 <sup>c</sup>	15.5 $\pm$ 5.5

a Age range of 6-10 and 14 years. Mean age is 8.0  $\pm$  1.6 if age 14 excluded

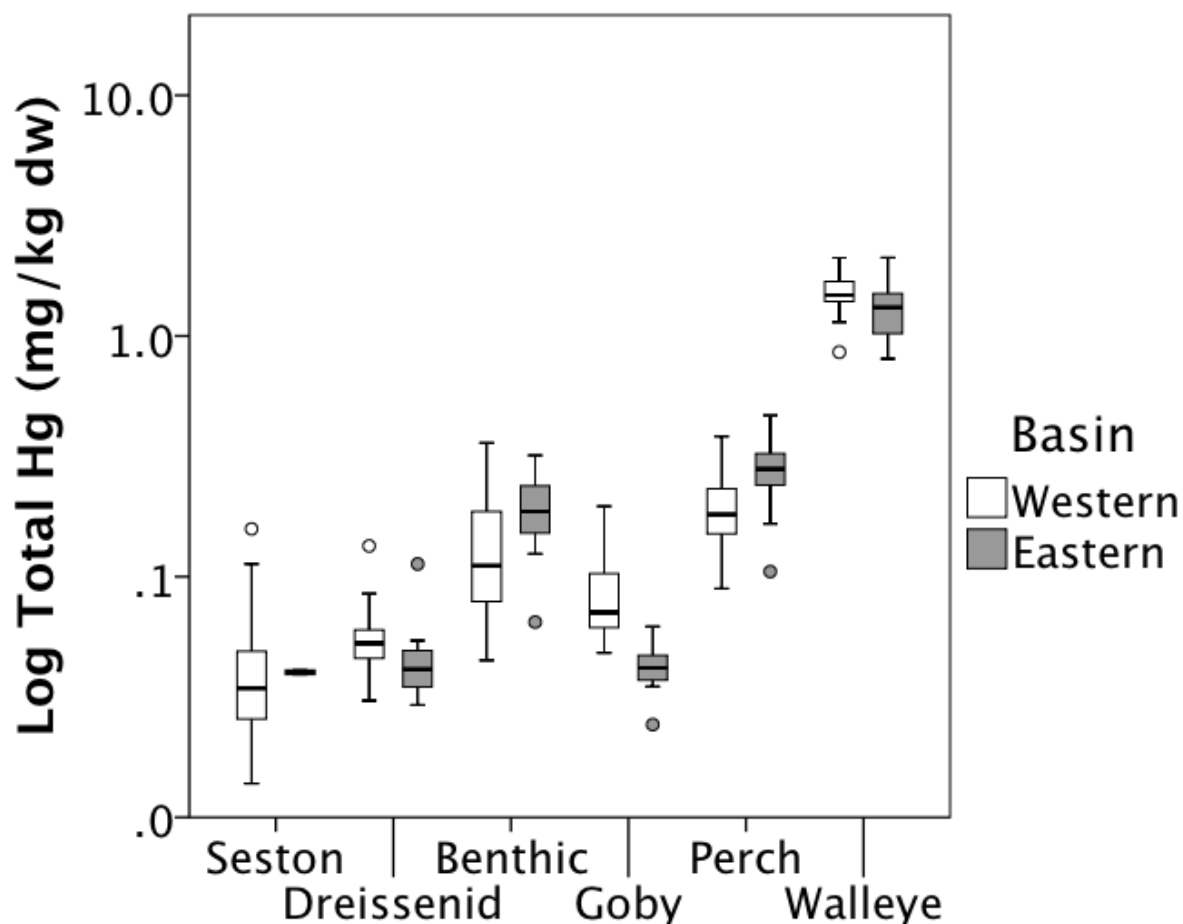
b Age range of 5-7 and 23 years. Mean age is 6.0  $\pm$  1.0 if age 23 excluded

c Age range of 8-12, 14 and 18 years. Mean age is 10.7  $\pm$  2.2 if age 18 excluded and 10.0  $\pm$  1.6 if 14 and 18 excluded.

### 3.3.3 Comparison of Mercury Concentrations Across Trophic Levels

Figure 3.3 depicts THg concentrations on a dry weight basis for all biotic samples collected, including seston, the in-depth analysis of which can be found in Chapter 2. A logarithmic scale was used to facilitate comparison across biotic compartments, which varied greatly in THg concentrations. Generally, this figure depicts a similar pattern in biomagnification across all compartments collected between the Western and Eastern basins. Some variability in THg concentrations existed between basins within a given biotic compartment. Seston and dreissenid THg concentrations were similar.

Differences in THg concentrations between basins were most apparent with benthic invertebrates other than dreissenid mussels, particularly those that live and feed almost exclusively in the sediment. For example, pooled benthic invertebrates, excluding dreissenid mussels, had higher median THg concentrations in the Eastern basin than the Western. Yellow perch THg concentrations also exhibit this pattern; however, the opposite was seen in the round goby, which have higher THg concentrations in the Western basin.



**Figure 3.3** Box and whisker plots depicting log THg concentrations across the range of all biotic specimens collected over the sampling months, June-September 2012. Seston was comprised of living and non-living matter, mainly phyto- and zooplankton with some detritus and debris. Dreissenid mussels included both zebra and quagga species. Benthic was comprised of all benthic invertebrate specimens that were not in the dreissenid family. The fish specimens were divided by species: round goby, yellow perch and walleye. Specimens were further grouped by basin where caught or collected. The 25<sup>th</sup>, 50<sup>th</sup> (median line) and 75<sup>th</sup> percent of values comprise the interquartile range (IQR). Projected whiskers are 1.5 times the IQR, with outliers denoted by circles.



## 3.4 Discussion

### 3.4.1 Total and Methyl Mercury in Benthic Invertebrates

In comparing THg concentrations between dreissenid mussels and other native benthic invertebrates of the basins of Lake Erie, the dreissenid mussel was consistently lower in Hg tissue concentration. THg concentrations in dreissenids closely reflected THg concentrations found in seston, which is primarily composed of their main food source phytoplankton. Mean seston THg concentrations of  $49.69 \pm 5.70$  and  $35.85 \pm 3.60$  ng/g in the Western and Central basin, determined in Chapter 2, are very similar to mean dreissenid THg concentrations of  $57.30 \pm 5.02$  and  $46.85 \pm 6.41$  ng/g in the Western and Eastern basin. The inter-basin differences in dreissenid THg concentrations reflect inter-basin differences in seston THg concentrations.

Other benthic invertebrates that live directly in the sediment, such as oligochaete and glycera worms and chironomids, had THg concentrations that more directly reflected the sediment environment in which they live. Each of the other benthic invertebrate families measured had higher THg concentrations than dreissenids, which is the only example of a filter feeder in this study. As per the findings in Chapter 2, mean sediment THg concentrations were  $376.76 \pm 43.72$  ng/g in the Western basin and  $25.60 \pm 2.38$  ng/g in the Eastern basin. Sediment THg seems to provide a better explanation for high benthic invertebrate THg in the Western basin than the East, as much of the observed benthic THg concentrations in the Eastern basin are above the mean sediment concentration. Although MeHg in Western basin sediment was twice that of the Eastern basin, the difference in concentrations between the basins was not as pronounced as was seen in THg concentrations. Mean sediment MeHg concentrations were  $0.54 \pm 0.07$  ng/g in the Western basin and  $0.25 \pm 0.03$  ng/g in the Eastern basin. Because the abundance of the more bioavailable MeHg may have a larger impact on accumulation in sediment-dwelling organisms, the greater similarity in inter-basin MeHg concentrations than THg concentration may explain why Western and Eastern basin organisms do not generally exhibit different concentrations.

Hogan *et al.* (2007) were the first to quantify THg and MeHg in Lake Erie dreissenid mussels and round goby, although no comparison to native species were made. It is difficult to compare with current findings, as their dreissenid mussel THg concentrations were not reported but appeared to be between 0.01 and 0.1 mg/kg wet weight, with MeHg concentrations between 0.001 and 0.01 mg/kg wet weight (Hogan *et al.*, 2007). Assuming an 80% moisture content in freeze-dried dreissenid mussel as per Zhang *et al.* (2012), my THg and MeHg concentrations would be 10.68 and 2.20 ng/g wet weight, respectively. Therefore, current findings of both forms of Hg in dreissenid mussels are elevated compared to Hogan *et al.* (2007). Although no further studies on THg and MeHg in Lake Erie dreissenids or other benthic invertebrates were uncovered, a study similar conducted in Lake Ontario can be used to contextualize my THg findings if an 80% moisture content conversion is applied to approximate wet weight. Zhang *et al.* (2012) found that dreissenid THg concentrations ranged from 5.6-8.6 ng/g wet weight, which approaches my wet weight findings as approximated above. Amphipod concentrations peaked at  $16.5 \pm 0.4$  ng/g wet weight, which is nearly half my approximate wet weight mean of  $30.71 \pm 4.69$ , and oligochaete concentrations appear in-line with dreissenid concentrations. The differences in benthic invertebrate THg concentrations from Lake Ontario may be due to lower environmental Hg available for food web uptake.

It is important to note that dreissenid mussel Hg concentrations do appear to reflect their environment, namely water and seston, and can potentially be used as biomonitors of contamination. In 2013, Blackwell *et al.* reported mean THg concentrations of 440 ng/g dry weight in the Hg-inundated Onondaga Lake, whereas a less historically contaminated Otisco Lake showed dreissenid mean THg concentrations of 61 ng/g. Mean MeHg concentrations of 217 ng/g and 29 ng/g were also found in dreissenids of the respective lakes (*Ibid*).

An examination of dreissenid mussels in the diets of Lake Erie burbot and yellow perch found that both fish did prey on mussels, but not as much as expected given the morphology and muscle capabilities of their mouthparts. Consumption of small (3-6 mm) zebra mussels by yellow perch was likely due to inadvertent swallowing because of the

preferential habitat they shared with amphipods. Further, dreissenids were only relied upon as a food source during the spring, when dreissenid energy content is at its highest and the abundance of preferential food sources is low (Morrison *et al.*, 1997). The most common prey items of young perch are zooplankton, amphipods and trichoptera. Yellow perch undergo an ontogenic dietary shift as they age, becoming more reliant on other fish species such as gizzard shad, shiners, and small round goby (Morrison *et al.*, 2000, Fowlie *et al.*, 2008). Adult fish in the size range selected for this study likely consume all of the aforementioned food items, with a focus on prey items other than dreissenid mussels. Since the THg concentrations in all other invertebrates were higher than those of dreissenid mussels, and dreissenid consumption by perch appears incidental, it is likely that invertebrates other than dreissenid mussels contribute THg from the benthic food web to my study species yellow perch. Comparing the amount of the more bioavailable MeHg in other benthic invertebrates to the now-known concentrations in dreissenid mussels is required to clarify the contributions of each species to the Hg burden in upper food web organisms.

### 3.4.2 Total Mercury in Fish Species

In comparing fish of various species caught in the Western and Eastern basins, scant spatial trends emerged. Round goby collected from the Western basin had higher THg concentrations, but this is likely due to a lack of size specification, leading to larger gobies from the West being older. Yellow perch from the Eastern basin had slightly higher THg concentrations than Western ones, and this is in contrast with the findings of Azim *et al.* (2011). Walleye concentrations from this study also differ from Azim *et al.* (2011), who found Eastern basin walleye to have higher mean and median concentrations. These differences may be due to length, sampling times, variability in populations, as well as mobility of the Lake Erie walleye between basins (Zhao *et al.*, 2011; Lake Erie Walleye Task Group, 2012).

Age may be the explaining factor for differences in THg concentrations in walleye caught in the two basins. Female walleye between 550-650 mm that were caught in the Western basin were, on average, 2 years older than walleye of the same length caught in the

Eastern basin (Table 3.2). Given that fish Hg concentrations are a function of age (Bache *et al.*, 1971), which is often approximated by length, the higher mean and median values for THg in older Western basin walleye were to be expected. Age does not appear to be a driver of the differences in perch tissue THg concentrations between basins – in fact, the higher THg concentrations corresponded with younger fish cohorts in perch (Figure 3.2 and Table 3.1). Both female and male Eastern basin perch in my selected size range are a year or more younger than Western perch of the same length. The observation of older fish with lower Hg concentrations contradicts what we understand about Hg and age-length relationships.

It is more likely that food web differences are driving the spatial discrepancies in perch THg concentrations. Considering primary production in the basins, a potential explanation for observed diminished THg in Western perch is faster growth rates and biodilution of THg body burden. This can occur by one or a combination of Hg dilution mechanisms. Dilution can occur at the level of primary producers, within blooms due to increased algae, phyto- and zooplankton density. This results in plankton of higher density with lower mass-specific Hg burdens, and their predators, such as fish, are also likely to have lower Hg burdens due to lower food item Hg concentrations (Chen & Folt, 2005). A second mechanism is growth dilution within fish, where fast growth rates due to an abundance of prey resources results in lower relative Hg body burdens (Trudel & Rasmussen, 2006; Kidd *et al.*, 2012).

The greatest algae blooms and plankton density were observed in the Western basin, as evidenced by the lack of sample size to quantify MeHg in seston in the Eastern basin (Chapter 2). Dilution of Hg at the level of primary producers in the Western basin may explain why length-specified perch are of different ages between the basins, and yet perch from the Western basin have lower Hg body burdens. Fish from the Eastern basin seem to reach the target length of 250-350 mm at a younger age, suggesting faster growth rates. Less biodilution from blooms and plankton density may account for elevated THg in Eastern basin perch; however, the reason for seemingly faster growth rates, coupled with no evidence of growth dilution in the less-productive Eastern basin, remains to be

explained. A comparison of diet, showing yellow perch of the Eastern basin reliant on a more energy- and Hg-rich prey item, compared to perch of the Western basin being more reliant on planktonic species encountering Hg dilution, may be the driver of this inter-basin Hg discrepancy.

### 3.4.3 Role of the Round Goby in Mercury Transfer in the Lake Erie Food Web

The establishment of the round goby within the Lake Erie food web led to speculation about contaminant trophic transfer. Studies of round goby gut content in all areas of the lake showed a heavy reliance of the fish on dreissenid mussels as a food source (Ray and Corkum, 1997; Andraso *et al.*, 2011). Many studies and exercises by management groups confirmed that the round goby is found in the stomach contents of important lake predators such as yellow perch, smallmouth bass and walleye, and effectively became a new prey fish (Jude *et al.*, 1992; Forage Task Group, 2001; Campbell *et al.*, 2009). Few studies examined the in-lake ramifications of the goby invasion on contaminant transfer, and one such study determined that the round goby did not play as great a role in changing PCB dynamics in the Western basin of Lake Erie as much as sediment perturbation did (Morrison *et al.*, 2000).

The round goby likely plays a larger role in Hg transfer to top predatory fish than do dreissenid mussels. The diet of the goby is quite diverse, incorporating almost every benthic invertebrate sampled in this study (Johnson *et al.*, 2005; Kornis *et al.*, 2012). Younger round gobies, especially, rely on smaller prey items, such as zooplankton, amphipods and chironomids. Larger gobies depend more on dreissenid mussels, but also maintain a diverse diet of benthic invertebrates (Campbell *et al.*, 2009). This ontogenic shift may account for differences in basin THg concentrations I observed, as smaller Eastern basin gobies may not yet be feeding voraciously on larger prey items. Findings from this chapter suggest that the round goby receive a large body burden of THg from their prey species, particularly those that reside completely in the sediment where gobies choose to feed, despite the fact that mussels, one of its main prey food, has the lowest concentrations of THg of all benthic organisms measured here.

According to Campbell *et al.* (2009), round goby diet in the Eastern basin of Lake Erie consisted of chironomids, dreissenids and amphipods, with dreissenid feces and detritus comprising a minimal proportion of the diet. Johnson *et al.* (2005), who examined round goby diet in the Central basin, found diets were comprised of dreissenids, mollusks, chironomids, zooplankton, fish, and other benthos. In this study, the sampling spread of benthic invertebrate species in Western basin sediment was the most varied. Exclusive to Western basin collection, I encountered isopods, leeches, ephemeroptera, and caddisfly larvae, some of which were not included in the results due to low sample size and lack of comparison to the Eastern basin. The diets of round gobies in the Western basin may be more varied due to a broader array of food items. This could be in contrast to the diets of Eastern basin round gobies, which may rely more on dreissenid mussels due to decreased variety in prey items. In addition, the incidental consumption of detritus while feeding exclusively in the sediment likely contributes to higher goby THg concentrations in the Western basin, especially considering the magnitude of difference between Western and Eastern basin sediment THg concentrations (Chapter 2). Studies examining the relationship between THg and various size classes of goby given diet shifts, and also studies comparing round goby THg concentrations to other prey fish of similar trophic levels, are required to determine if round goby does contribute greatly to higher trophic level THg concentrations.

#### 3.4.4 Comparison of Overall Biomagnification Patterns Among Basins

Analyzing the pattern of biotic THg concentrations in Figure 3.3, biomagnification within the Western and Eastern basin food webs appear similar across species and between basins sampled. Slight discrepancies between basins within certain species are seen; however, the general pattern of biomagnification persists lake-wide. Despite the significant and sometimes remarkable differences in inter-basin water, sediment and seston THg and MeHg concentrations as determined in Chapter 2, inhabitants of opposite basins of the lake appear to accumulate Hg to similar concentrations at the top of the food web. This further solidifies the importance of differing methylation potential within the basins, as well as biodilution of contaminants in highly productive systems.

### 3.5 Conclusions

The results from this chapter provide the first comprehensive examination of THg in the benthic community of Lake Erie. These data were necessary to evaluate the role that two non-native species played in the increase in fish tissue Hg, coinciding with their arrival. It was found that dreissenid mussels likely do not play a strong role in Hg transfer within the lake food web for two reasons:

- a) total dreissenid Hg concentration reflects very similarly that of their food source, phytoplankton, and dreissenids do not bioconcentrate to higher levels as initially expected. They contain the lowest body burden of Hg of all benthic invertebrates sampled. And,
- b) round goby THg concentrations were lower than expected, given the bioconcentration theory of dreissenid mussels and their low THg levels. Evidence of the delivery of large quantities of Hg from dreissenid mussels, which too were expected to be elevated in Hg, to top predators via the round goby was not found.

More evidence is required to evaluate the efficacy of dreissenid mussels reflecting their environmental THg and MeHg concentrations over the sampling months and more importantly relative to other benthic invertebrates. In light of other studies the presented evidence suggest that dreissenid MeHg concentrations track that of their food sources.

It remains a possibility that the round goby plays a role in increasing fish Hg concentrations, as their diets are varied and contain many species of available benthic invertebrates, which were found to have high THg concentrations relative to dreissenid mussels and organisms in other lakes. It is possible that the lack of control of round goby age and size class confounded these results, leading to lower observed round goby THg concentrations than true values. For these reasons, the round goby likely plays a larger role in the transfer of Hg to predatory fish, and consequently played a larger role in their increasing Hg concentrations, than did dreissenid mussels. However, as lake food web systems are complex, it is important to recognize that the establishment of the round goby likely would not have been as strong if not for the earlier arrival and ensuing abundance of dreissenid mussels.

My results support the earlier findings that greater concentrations of Hg at the base of the food web and in benthic invertebrates result in higher concentrations in fish (Chasar *et al.*, 2009; Wyn *et al.*, 2009; Kidd *et al.*, 2012). My findings suggest that fish THg

concentrations remain relatively similar among lake basins, and any incongruities between lake basins are more likely due to differences in food web MeHg biomagnification than age discrepancies.

Further studies of Hg concentration differences at the base of the food web, especially in prey fish of similar trophic level to the round goby, will be required to further clarify the roles that non-native species had in influencing and enhancing Lake Erie's Hg trophic transfer.



### 3.6 References

- Andraso, G.M., Ganger, M.T., Adameczyk, J., 2011. Size-selective predation by round gobies (*Neogobius melanostomus*) on dreissenid mussels in the field. *J. Great Lakes Res.* 37, 298-304.
- Arend, K.K., Beletsky, D., Depinto, J.V., Ludsin, S.A., Roberts, J.J., Rucinski, D.K., Scavia, D., Schwab, D.J., Höök, T.O., 2011. Seasonal and interannual effects of hypoxia on fish habitat quality in central Lake Erie. *Freshwat. Biol.* 56, 366-383.
- Atwell, L., Hobson, K.A., Welch, H.E., 1998. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable nitrogen isotope analysis. *Can. J. Fish. Aquat. Sci.* 55, 1114-1121.
- Azim, M.E., Kumarappah, A., Bhavsar, S.P., Backus, S.M., Arhonditsis, G., 2011. Detection of the spatiotemporal trends of mercury in Lake Erie fish communities: a Bayesian approach. *Environ. Sci. Technol.* 45, 2217-2226.
- Bache, C.A., Gutenmann, W.H., Lisk, D.J., 1971. Residues of total mercury and methylmercuric salts in lake trout as a function of age. *Science* 172, 951-952.
- Back, R.C., Gorski, P.R., Cleckner, L.B., Hurley, J.P., 2003. Mercury content and speciation in the plankton and benthos of Lake Superior. *Sci. Total Environ.* 304, 349-354.
- Barton, D.R., 1988. Distribution of some common benthic invertebrates in nearshore Lake Erie, with emphasis on depth and type of substratum. *J. Great Lakes Res.* 14, 34-43.
- Bhavsar, S.P., Gewurtz, S.B., McGoldrick, D.J., Keir, M.J., Backus, S.M., 2010. Changes in mercury levels in Great Lakes fish between 1970s and 2007. *Environ. Sci. Technol.* 44, 3273-3279.

- Blackwell, B.D., Driscoll, C.T., Spada, M.E., Todorova, S.G., Montesdeoca, M.R., 2013. Evaluation of zebra mussels (*Dreissena polymorpha*) as biomonitors of mercury contamination in aquatic ecosystems. *Environ. Toxicol. Chem.* 32, 638-643.
- Bloom, N.S., 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49, 1010-1017.
- Bolsenga, S.J., Herdendorf, C.E., 1993. *Lake Erie and Lake St. Clair Handbook*. Wayne State University Press: Detroit, MI.
- Britt, N.W., 1955. Stratification in western Lake Erie in summer of 1953: effects on the *Hexagenia* (Ephemeroptera) population. *Ecology* 36, 239-244.
- Bruner, K.A., Fisher, S.W., Landrum, P.F., 1994. The role of the zebra mussel, *Dreissena polymorpha*, in contaminant cycling: II. Zebra mussel contaminant accumulation from algae and suspended particles, and transfer to the benthic invertebrate, *Gammarus fasciatus*. *J. Great Lakes Res.* 20, 735-750.
- Bunnell, D.B., Johnson, T.B., Knight, C.T., 2005. The impact of introduced round gobies (*Neogobius melanostomus*) on phosphorus cycling in central Lake Erie. *Can. J. Fish. Aquat. Sci.* 62, 15-29.
- Burns, N.M., Rockwell, D.C., Bertram, P.E., Dolan, D.M., Ciborowski, J.J., 2005. Trends in temperature, Secchi depth, and dissolved oxygen depletion rates in the central basin of Lake Erie, 1983–2002. *J. Great Lakes Res.* 31, 35-49.
- Cabana, G., Tremblay, A., Kalff, J., Rasmussen, J.B., 1994. Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (*Salvelinus namaycush*). *Can. J. Fish. Aquat. Sci.* 51, 381-389.
- Campbell, L.M., Hecky, R.E., Nyaundi, J., Muggide, R., George Dixon, D., 2003. Distribution and food-web transfer of mercury in Napoleon and Winam Gulfs, Lake Victoria, East Africa. *J. Great Lakes Res.* 29, 267-282.

- Campbell, L.M., Thacker, R., Barton, D., Muir, D.C., Greenwood, D., Hecky, R.E., 2009. Re-engineering the eastern Lake Erie littoral food web: the trophic function of non-indigenous Ponto-Caspian species. *J. Great Lakes Res.* 35, 224-231.
- Chasar, L.C., Scudder, B.C., Stewart, A.R., Bell, A.H., Aiken, G.R., 2009. Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation. *Environ. Sci. Technol.* 43, 2733-2739.
- Crossman, E., Holm, E., Cholmondeley, R., Tuininga, K., 1992. First record for Canada of the rudd, *Scardinius erythrophthalmus*, and notes on the introduced round goby, *Neogobius melanostomus*. *Can. Field Nat.* 106, 206-206.
- Dermott, R., Kerec, D., 1997. Changes to the deepwater benthos of eastern Lake Erie since the invasion of *Dreissena*: 1979-1993. *Can. J. Fish. Aquat. Sci.* 54, 922-930.
- Driscoll, C., Kalicin, M., Lindeman, M., Liuzzi, C., Newton, R., Munson, R., Yavitt, J., 2001. Chemical and biological control of mercury cycling in upland, wetland and lake ecosystems in the Adirondack region of New York. Abstracts of Papers of the American Chemical Society 2002, 223 (Pt 1), U526-U526.
- Evers, D.C., Wiener, J.G., Basu, N., Bodaly, R., Morrison, H.A., Williams, K.A., 2011. Mercury in the Great Lakes region: bioaccumulation, spatiotemporal patterns, ecological risks, and policy. *Ecotoxicology* 20, 1487-1499.
- Forage Task Group. 2001. Report of the Forage Task Group, March 2001. Lake Erie Committee, Great Lakes Fishery Commission: Windsor, Ontario.
- Forage Task Group. 2011. Report of the Forage Task Group, March 2011. Lake Erie Committee, Great Lakes Fishery Commission: Windsor, Ontario.
- Fowlie, A.R., Hodson, P.V., Hickey, M.B.C., 2008. Spatial and seasonal patterns of mercury concentrations in fish from the St. Lawrence River at Cornwall, Ontario: implications for monitoring. *J. Great Lakes Res.* 34, 72-85.

- French, T.D., Petro, S., Reiner, E.J., Bhavsar, S.P., Jackson, D.A., 2011. Thirty-year time series of PCB concentrations in a small invertivorous fish (*Notropis Hudsonius*): an examination of Post-1990 trajectory shifts in the Lower Great Lakes. *Ecosystems* 14, 415-429.
- Fuller, K., Shear, H., Wittig, J., 1995. *The Great Lakes: an environmental atlas and resource book*, third ed. United States Environmental Protection Agency Great Lakes National Program Office: Chicago, IL.
- Futter, M.N., 1994. Pelagic food-web structure influences probability of mercury contamination in lake trout (*Salvelinus namaycush*). *Sci. Total Environ.* 145, 7-12.
- Griffiths, R.W., Schloesser, D.W., Leach, J.H., Kovalak, W.P., 1991. Distribution and dispersal of the zebra mussel (*Dreissena polymorpha*) in the Great Lakes region. *Can. J. Fish. Aquat. Sci.* 48, 1381-1388.
- Hall, B., Bodaly, R., Fudge, R., Rudd, J., Rosenberg, D., 1997. Food as the dominant pathway of methylmercury uptake by fish. *Water Air Soil Pollut.* 100, 13-24.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* 38, 1487-1495.
- Hebert, P.D., Muncaster, B., Mackie, G., 1989. Ecological and genetic studies on *Dreissena polymorpha* (Pallas): a new mollusc in the Great Lakes. *Can. J. Fish. Aquat. Sci.* 46, 1587-1591.
- Hecky, R., Smith, R.E., Barton, D., Guildford, S., Taylor, W., Charlton, M., Howell, T., 2004. The nearshore phosphorus shunt: a consequence of ecosystem engineering by dreissenids in the Laurentian Great Lakes. *Can. J. Fish. Aquat. Sci.* 61, 1285-1293.
- Herdendorf, C.E., 1992. Lake Erie coastal wetlands: an overview. *J. Great Lakes Res.* 18, 533-551.

- Herdendorf, C.E., 1990. Distribution of the world's Large Lakes. Springer: Heidelberg, Berlin.
- Hill, W.R., Stewart, A.J., Napolitano, G.E., 1996. Mercury speciation and bioaccumulation in lotic primary producers and primary consumers. *Can. J. Fish. Aquat. Sci.* 53, 812-819.
- Hogan, L.S., Marschall, E., Folt, C., Stein, R.A., 2007. How non-native species in Lake Erie influence trophic transfer of mercury and lead to top predators. *J. Great Lakes Res.* 33, 46-61.
- Johnson, T.B., Bunnell, D.B., Knight, C.T., 2005. A potential new energy pathway in central Lake Erie: the round goby connection. *J. Great Lakes Res.* 31, 238-251.
- Jude, D.J., Reider, R.H., Smith, G.R., 1992. Establishment of Gobiidae in the Great Lakes Basin. *Can. J. Fish. Aquat. Sci.* 49, 416-421.
- Kidd, K.A., Muir, D.C.G., Evans, M.S., Wang, X., Whittle, M., Swanson, H.K., Johnston, T., Guildford, S., 2012. Biomagnification of mercury through lake trout (*Salvelinus namaycush*) food webs of lakes with different physical, chemical and biological characteristics. *Sci. Total Environ.* 438, 135-143.
- Kornis, M.S., Mercado-Silva, N., Vander Zanden, M.J., 2012. Twenty years of invasion: a review of round goby *Neogobius melanostomus* biology, spread and ecological implications. *J. Fish Biol.* 80, 235-285.
- Lake Erie Walleye Task Group. 2012. Report for 2011 by the Lake Erie Walleye Task Group. Great Lakes Fisheries Commission: Windsor, Ontario.
- Mason, R.P., Sullivan, K.A., 1997. Mercury in Lake Michigan. *Environ. Sci. Technol.* 31, 942-947.
- Mathers, R.A., Johansen, P.H., 1985. The effects of feeding ecology on mercury accumulation in walleye (*Stizostedion vitreum*) and pike (*Esox lucius*) in Lake Simcoe. *Can. J. Zool.* 63, 2006-2012.

- McCormick, M.J., Fahnenstiel, G.L., 1999. Recent climatic trends in nearshore water temperatures in the St. Lawrence Great Lakes. *Limnol. Oceanogr.* 44, 530-540.
- Mergler, D., Anderson, H.A., Chan, L.H.M., Mahaffey, K.R., Murray, M., Sakamoto, M., Stern, A.H., 2007. Methylmercury exposure and health effects in humans: a worldwide concern. *AMBIO* 36, 3-11.
- Morel, F.M., Kraepiel, A.M., Amyot, M., 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 29, 543-566.
- Morrison, H.A., Whittle, D.M., Haffner, G.D., 2000. The relative importance of species invasions and sediment disturbance in regulating chemical dynamics in western Lake Erie. *Ecol. Model.* 125, 279-294.
- Morrison, T.W., Lynch Jr, W.E., Dabrowski, K., 1997. Predation on zebra mussels by freshwater drum and yellow perch in western Lake Erie. *J. Great Lakes Res.* 23, 177-189.
- Mortimer, C., 1987. Fifty years of physical investigations and related limnological studies on Lake Erie, 1928–1977. *J. Great Lakes Res.* 13, 407-435.
- Muth, K.M., 1985. Changes in prey fish abundance in western Lake Erie during periods of high and low predator abundance. Presented papers from the Council of Lake Committees plenary session on Great Lakes predator–prey issues , 85-83.
- Muth, K.M., Busch, W.N., 1989. Food of forage fishes in western Lake Erie, 1975–76. *J. Great Lakes Res.* 15, 217-222.
- Ogorek, J., DeWild, J.F., 2013. Analysis of Methylmercury in Biological Samples by Cold Vapor Atomic Fluorescence Detection with the Brooks-Rand “MERX” Automated Methylmercury Analytical System. U.S. Geological Survey, Reston, VA.
- Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ.* 40, 4048-4063.

- Phillips, G.R., Lenhart, T.E., Gregory, R.W., 1980. Relation between trophic position and mercury accumulation among fishes from the Tongue River Reservoir, Montana. *Environ. Res.* 22, 73-80.
- Pickhardt, P.C., Fisher, N.S., 2007. Accumulation of inorganic and methylmercury by freshwater phytoplankton in two contrasting water bodies. *Environ. Sci. Technol.* 41, 125-131.
- Rasmussen, J., Rowan, D., Lean, D., Carey, J., 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. *Can. J. Fish. Aquat. Sci.* 47, 2030-2038.
- Ray, W.J., Corkum, L.D., 1997. Predation of zebra mussels by round gobies, *Neogobius melanostomus*. *Environ. Biol. Fishes* 50, 267-273.
- Regier, H.A., Hartman, W.L., 1973. Lake Erie's fish community: 150 years of cultural stresses. *Science* 180, 1248-1255.
- Rolfhus, K.R., Hall, B.D., Monson, B.A., Paterson, M.J., Jeremiason, J.D., 2011. Assessment of mercury bioaccumulation within the pelagic food web of lakes in the western Great Lakes region. *Ecotoxicology* 20, 1520-1529.
- Rosa, F., Burns, N.M., 1987. Lake Erie central basin oxygen depletion changes from 1929–1980. *J. Great Lakes Res.* 13, 684-696.
- Schertzer, W., Saylor, J., Boyce, F., Robertson, D., Rosa, F., 1987. Seasonal thermal cycle of Lake Erie. *J. Great Lakes Res.* 13, 468-486.
- Schmeltz, D., Evers, D.C., Driscoll, C.T., Artz, R., Cohen, M., Gay, D., Haeuber, R., Krabbenhoft, D.P., Mason, R., Morris, K., 2011. MercNet: a national monitoring network to assess responses to changing mercury emissions in the United States. *Ecotoxicology* 20, 1713-1725.

- Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., Krabbenhoft, D.P., 2008. Influence of plankton mercury dynamics and trophic pathways on mercury concentrations of top predator fish of a mining-impacted reservoir. *Can. J. Fish. Aquat. Sci.* 65, 2351-2366.
- Thomas, R., Jaquet, J., Kemp, A., Lewis, C., 1976. Surficial sediments of Lake Erie. *Journal of the Fisheries Board of Canada* 33, 385-403.
- Trudel, M., Rasmussen, J.B., 2006. Bioenergetics and mercury dynamics in fish: a modelling perspective. *Can. J. Fish. Aquat. Sci.* 63, 1890-1902.
- U.S.EPA. 1996. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 1998. Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 2002. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- U.S.EPA. 2005. Technical Support Document for the Final Clean Air Mercury Rule. U.S.EPA Office of Air Quality Planning and Standards: Washington, D.C.
- U.S.EPA. 2007. Method 7473: Mercury In Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. . U.S. Environmental Protection Agency Office of Water: Washington, D.C.
- Van Overdijk, C.D., Grigorovich, I.A., Mabee, T., Ray, W.J., Ciborowski, J.J., Macisaac, H.J., 2003. Microhabitat selection by the invasive amphipod *Echinogammarus ischnus* and native *Gammarus fasciatus* in laboratory experiments and in Lake Erie. *Freshwat. Biol.* 48, 567-578.



- Vander Zanden, M.J., Rasmussen, J.B., 1996. A trophic position model of pelagic food webs: Impact on contaminant bioaccumulation in lake trout. *Ecol. Monogr.* , 451-477.
- Watras, C.J., Bloom, N., 1992. Mercury and methylmercury in individual zooplankton: Implications for bioaccumulation. *Limnol. Oceanogr.* 37, 1313-1318.
- Wiener, J., Knights, B., Sandheinrich, M., Jeremiason, J., Brigham, M., Engstrom, D., Woodruff, L., Cannon, W., Balogh, S., 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): importance of atmospheric deposition and ecosystem factors. *Environ. Sci. Technol.* 40, 6261-6268.
- Wyn, B., Kidd, K.A., Burgess, N.M., Curry, R.A., 2009. Mercury biomagnification in the food webs of acidic lakes in Kejimikujik National Park and National Historic Site, Nova Scotia. *Can. J. Fish. Aquat. Sci.* 66, 1532-1545.
- Zhang, L., Campbell, L.M., Johnson, T.B., 2012. Seasonal variation in mercury and food web biomagnification in Lake Ontario, Canada. *Environ. Pollut.* 161, 178-184.
- Zhao, Y., Einhouse, D.W., MacDougall, T.M., 2011. Resolving some of the complexity of a mixed-origin walleye population in the East basin of Lake Erie using a mark-recapture study. *N. Am. J. Fish. Manage.* 31, 379-389.

## 4 Discussion and Conclusions

The purpose of the research presented in this thesis was to contribute to the understanding of Hg cycling in a lake system undergoing long-term biotic Hg changes in sport fish, the causes of which had been hitherto examined in detail. The objectives of this study were to provide an empirical account of THg and MeHg in Lake Erie abiotic and biotic compartments, with the goal of clarifying the roles of recently introduced non-native species in the trophic transfer of Hg to top predatory fish. This was accomplished through quantifying THg and MeHg in water, sediment, seston, and benthic invertebrates including dreissenid mussels. Mercury was also quantified in the benthic fish round goby, and biomonitoring species yellow perch and walleye, with age analysis for the latter two fish species.

Samples of the abiotic compartments water and sediment and the biotic compartment seston were obtained with both spatial and temporal variation in order to assess THg and MeHg quantities in the environment and the base of the Lake Erie food web. Water THg concentrations were highest in the Western basin and were similar in the Central and Eastern basins, and September means for both Western and Central basins were statistically highest, although Eastern basin showed no change over the summer months. Methylmercury concentrations were similar across basins and throughout the summer, and more than three quarters of the data fell below instrument quantification limits, suggesting that aqueous MeHg concentrations in Lake Erie were extremely low. It is possible that THg and MeHg concentrations in water samples may be attributed to particulate matter, such as seston, as lake water was unfiltered, which was consistent with the methods and observations of Rolffhus *et al.* (2003).

In smaller lakes and rivers, the abundance of proximal wetlands is strongly linked to the production and presence of MeHg (Brigham *et al.*, 2009). Lake Erie has the least amount of wetlands (149 total) of the five Great Lakes, and along with Lake Ontario, has the largest amount of moderately to highly degraded wetlands (Cvetkovic & Chow-Fraser, 2011). Much of the wetlands on Lake Erie's shores have been urbanized or converted to agriculture, with the most notable exceptions being The Kettle Lakes and Delta wetlands,

situated in the Western basin, and the Point Pelee area, which extends between the Western and Central basin on the North shore (Herdendorf, 1992). The loss of shoreline wetlands over time may contribute to the exceptionally low MeHg concentrations in Lake Erie water, with sediment pore water and riverine inputs being the major key sources of THg and MeHg to the water column. Given the high concentrations of THg in the Western basin water and surficial sediment relative to the other basins and to other great lakes, inferential evidence is indicative of ongoing particulate loading of Hg, likely through riverine systems. Analysis of water Hg in this study would be greatly supplemented by measuring THg and MeHg in both inflowing waters and pore water. Marvin-Dipasquale *et al.* (2009) found that as pore water dissolved organic carbon (DOC) increases and as sediment grain size decreases, THg and MeHg produced in the sediments partition more readily into pore water. These measurements would confirm our suspicion that Lake Erie sediments are a source of Hg to the water column, in addition to riverine inputs.

Sediment THg and MeHg analysis also revealed significantly higher concentrations in Western basin, decreasing from West to East, which is a spatial gradient consistent with Painter *et al.* (2001), although no significant temporal patterns were uncovered. Considering the low concentrations in water and sediment THg, the Eastern basin exhibited relatively high sediment MeHg concentrations. The Eastern basin's percent MeHg was two or more times higher than both the Central and Western basins, suggesting that Eastern basin sediments have a higher methylation potential. The strong spatial gradient in THg samples ends with the abiotic compartments, as THg and MeHg in seston indicate a more even distribution of Hg across the basins at the base of the food web. I determined that the Western and Central basin's seston have similar THg concentrations throughout the sampling period, and MeHg concentrations in Central basin seston were twice that of seston from the Western basin. This is likely due to the species assemblages of seston sampled, as Central basin seston was comprised of more zooplankton of higher trophic position than seston from the Western basin, with higher MeHg due to biomagnification. Percent MeHg of THg was higher in Central basin seston, which also peaked late in the sampling season, congruent with our understanding of conditions favoring methylation of Hg (Ullrich *et al.*, 2001).

Mercury concentrations in biota higher in the food web, including the non-native species of interest, were determined in Chapter 3 and address the question of the role of the species in enhanced trophic transfer. Dreissenid mussels exhibited the lowest Hg concentrations of all benthic invertebrates sampled, and so the notion that they may bioconcentrate Hg and contribute to enhanced trophic transfer of Hg through high tissue concentrations, as described in Kwan *et al.*, 2003 and Azim *et al.*, 2011, is dispelled in this system. The non-native fish round goby had low Hg concentrations, comparable to prey fish of similar trophic positions in other aquatic systems (*e.g.* Choy *et al.*, 2008), however Hg concentrations relative to other prey fish of Lake Erie were not attained in this study. Since their introduction to the lake and during their establishment in the lake's food web, dreissenid mussels and round goby may have contributed to enhanced trophic transfer through increasing the trophic position of lake fish, and seen in Rennie *et al.* (2011) with the invasion of *Bythotrephes* in Ontario lakes. Further data on the change in trophic position of top predatory fish over time, likely using stable nitrogen isotope analysis as developed by DeNiro & Epstein (1981), and employed by Kidd *et al.* (1995) and Cabana & Rasmussen (1996), among many others, would be required to better comprehend the role of dreissenids and round goby.

The abiotic THg and MeHg concentrations collected under Chapter 2 were required to inform biotic levels at the base of the food web and in benthic species. There is a higher percentage of THg that is in the MeHg form in both water and sediment from the Eastern portion of the lake. The finding of less variation in MeHg, the more bioavailable form of Hg, is in contrast with the significant differences in THg concentrations among basins. This finding may explain why seston and benthic biota have similar Hg concentrations regardless of location. The higher production of MeHg in the Eastern basin, coupled with the apparent increase in the later sampling months, appear to balance the THg concentrations at the base of the food web across basins. Using two commonly sought fish species I found that this phenomena translates through the food web, amounting in similar Hg concentrations in top predators of the lake basins. Although perch have a smaller home range than walleye, estimated to be approximately 9174 m<sup>2</sup> (Minns, 1995), perch that were collected and likely lived in the Western basin did not exhibit higher THg concentrations, as would be expected if they reflected abiotic environmental conditions.

Age did not appear to be an explanation of any inter-basin discrepancies, as perch collected in the Western basin were typically older. The explanation for similar THg concentrations in perch, with slightly higher concentrations in the Eastern basin, likely lies with my previous observation that benthic biota amass similar concentrations of THg, in addition to the biodilution effects on both the levels of primary production within the lake and growth biodilution within fish (Chen & Folt, 2005; Trudel & Rasmussen, 2006). A likely explanation for a lack of spatial differentiation of walleye caught in different basins is the extensive home range of the fish species (Lake Erie Walleye Task Group, 2012).

The outcomes of this study would be strengthened by complete MeHg analysis in seston from the Eastern basin and in a higher variety of benthic invertebrates, both of which were unattainable due to small sample sizes. A comparison of THg in prey and forage fish would strengthen my conclusions on the role of round goby in the transfer of Hg by contextualizing the mean THg concentrations of fish of the same trophic position or similar feeding habits. Further analysis of trophic position and their changes over the preceding decades in my fish species using stable nitrogen isotope analysis would clarify a supposed trophic shift that may have heralded enhanced Hg transfer. In addition, determination and confirmation of suspected food sources of benthic invertebrates and fish species using stable carbon isotope analysis would aid in pinpointing the role of non-native species in enhanced Hg transfer in Lake Erie through clarifying and confirming the suppositions invoked in this thesis.

## 4.1 References

- Azim, M.E., Kumarappah, A., Bhavsar, S.P., Backus, S.M., Arhonditsis, G., 2011. Detection of the spatiotemporal trends of mercury in Lake Erie fish communities: a Bayesian approach. *Environ. Sci. Technol.* 45, 2217-2226.
- Brigham, M.E.; Wentz, D.A.; Aiken, G.R.; Krabbenhoft, D.P., 2009. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. *Environ. Sci. Technol.* 43, 2720-2725.
- Cabana, G., Rasmussen, J.B., 1996. Comparison of aquatic food chains using nitrogen isotopes. *P. Nat. Acad. Sci. U.S.A.* 93, 10844-10847.
- Chen, C.Y., Folt, C.L., 2005. High plankton densities reduce mercury biomagnification. *Environ. Sci. Technol.* 39, 115-121.
- Choy, E.S., Hodson, P.V., Campbell, L.M., Fowlie, A.R., Ridal, J., 2008. Spatial and temporal trends of mercury concentrations in young-of-the-year spottail shiners (*Notropis hudsonius*) in the St. Lawrence River at Cornwall, ON. *Arch. Environ. Contam. Toxicol.* 54, 473-481.
- Cvetkovic, M. and Chow-Fraser, P., 2011. Use of ecological indicators to assess the quality of Great Lakes coastal wetlands. *Ecol. Ind.* 11, 1609-1622.
- Deniro, M.J., Epstein, S., 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochim. Cosmochim. Acta.* 45, 341-351.
- Herdendorf, C.E., 1992. Lake Erie coastal wetlands: an overview. *J. Great Lakes Res.* 18, 533-551.
- Kidd, K., Hesslein, R., Fudge, R., Hallard, K., 1995. The influence of trophic level as measured by  $\delta^{15}\text{N}$  on mercury concentrations in freshwater organisms. *Water Air Soil Pollut.* 80, 1011-1015.

- Kwan, K.H.M., Chan, H.M., De Lafontaine, Y., 2003. Metal contamination in zebra mussels (*Dreissena Polymorpha*) along the St. Lawrence River. *Environ. Monit. Assess.* 88, 193-219.
- Lake Erie Walleye Task Group. 2012. Report for 2011 by the Lake Erie Walleye Task Group. Great Lakes Fisheries Commission: Windsor, Ontario.
- Marvin-DiPasquale, M.; Lutz, M.A.; Brigham, M.E.; Krabbenhoft, D.P.; Aiken, G.R.; Orem, W.H.; Hall, B.D., 2009. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment– pore water partitioning. *Environ. Sci. Technol.* 43, 2726-2732.
- Minns, C.K., 1995. Allometry of home range size in lake and river fishes. *Can. J. Fish. Aquat. Sci.* 52, 1499-1508.
- Painter, S., Marvin, C., Rosa, F., Reynoldson, T.B., Charlton, M.N., Fox, M., Lina Thiessen, P.A., Estenik, J.F., 2001. Sediment contamination in Lake Erie: a 25-year retrospective analysis. *J. Great Lakes Res.* 27, 434-448.
- Rennie, M., Strecker, A., Palmer, M., 2011. *Bythotrephes* invasion elevates trophic position of zooplankton and fish: implications for contaminant biomagnification. *Biol. Invasions* 13, 2621-2634.
- Rolfhus, K.R., Sakamoto, H.E., Cleckner, L.B., Back, R.C., Manolopoulos, H., Hurley, J.P., 2003. Distribution and fluxes of total and methylmercury in Lake Superior. *Environ. Sci. Technol.* 37, 865-872.
- Trudel, M., Rasmussen, J.B., 2006. Bioenergetics and mercury dynamics in fish: a modelling perspective. *Can. J. Fish. Aquat. Sci.* 63, 1890-1902.
- Ullrich, S.M., Tanton, T.W., Abdrashitova, S.A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. *Crit. Rev. Environ. Sci. Technol.* 31, 241-293.

## Appendix

**Appendix A** Site Codes with Latitude and Longitude Coordinates in Decimal Degrees,  
Maximum Site Depths and Water Sampling Depths

Site Name	Latitude (dec deg)	Longitude (dec deg)	Maximum Depth (m)	Sampling Depths (m)
E2	42.62288	-80.05168	38.0	0, 1, 10, 17, 23
E3	42.70895	-80.22388	8.5	0, 1, 3, 5, 8
WC1	42.083056	- 82.343889	16.2	0, 1, 5, 10, 15
WC2	42.108333	- 82.143611	21.2	0, 1, 7, 13, 20
WC3	41.983056	- 82.143333	22.0	0, 1, 7, 13, 21
WC4	41.883056	- 82.345278	16.0	0, 1, 5, 9, 15
W5	41.883333	- 82.616389	10.8	0, 1, 5, 10
W6	41.856111	- 82.766389	11.4	0, 1, 4.5, 9
W7	41.996667	- 82.766389	9.5	0, 1, 4, 8
W8	41.989167	- 82.580833	9.5	0, 1, 4, 8



## Glossary of Acronyms and Abbreviations

<b>ANOVA</b>	Analysis of Variance
<b>CRM</b>	Certified Reference Material
<b>DOC</b>	Dissolved Organic Carbon
<b>DMA-80</b>	Direct Mercury Analyzer 80
<b>d.w.</b>	Dry Weight
<b>ft.</b>	Feet
<b>HCl</b>	Hydrochloric Acid
<b>Hg</b>	Mercury
<b>HSD</b>	Honest Significant Difference
<b>IQR</b>	Interquartile Range
<b>MeHg</b>	Methylmercury
<b>OMNR</b>	Ontario Ministry of Natural Resources
<b>OMOE</b>	Ontario Ministry of the Environment
<b>Pb</b>	Lead
<b>PCB</b>	Polychlorinated Biphenol
<b>PETG</b>	Polyethylene Terephthalate
<b>pH</b>	Measure of acidity
<b>PVC</b>	Polyvinyl Chloride
<b>SRB</b>	Sulphate-reducing Bacteria
<b>THg</b>	Total Mercury
<b>U.S.EPA</b>	United States Environmental Protection Agency
<b>USGS</b>	United States Geological Survey
<b>w.w.</b>	Wet Weight
<b>v/v</b>	Volume Percent Concentration

## Curriculum Vitae

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