Causes and Consequences of a Collapsing Food Web in Lake huron

Mark Ryder
University of Windsor

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CAUSES AND CONSEQUENCES OF A COLLAPSING FOOD WEB IN LAKE HURON

By

Mark Ryder

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

Windsor, Ontario, Canada

2013

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CAUSES AND CONSEQUENCES OF A COLLAPSING FOOD WEB IN LAKE HURON

by

Mark Ryder

APPROVED BY:

______________________________________________
Dr. Rajesh Seth
Engineering

______________________________________________
Dr. Ken G Drouillard
GLIER

______________________________________________
Dr. G Douglas Haffner, Advisor
GLIER

______________________________________________
Dr. Joel Gagnon, Chair of Defense
GLIER / Earth and Environmental Science

June 6, 2013
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ABSTRACT

Lake Huron has undergone significant declines in abundance at multiple trophic levels. These declines are demonstrated to be the result of a decrease in the overall primary production, from an estimate of 100 g C m\(^{-2}\) yr\(^{-1}\) in the 1970s, to 32 g C m\(^{-2}\) yr\(^{-1}\) in this study. It is hypothesized that these declines are the result of increased photo-inhibition and nutrient bioavailability. These declines have the potential to not only affect energy transfer, but contaminant transfer as well. Bioaccumulation patterns in lake trout differed significantly across the three basins, with Georgian Bay revealing the most significant increase in bioaccumulation potential. These differences are demonstrated to be the result of differences in trophic efficiencies in lake trout. This research confirms that the collapse of the Lake Huron food web is related to both a decrease in primary production, as well as declines in trophic efficiency.
DEDICATION

To my family, who have supported me throughout my university career. I am forever in your debt.
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CHAPTER 1
BIOACCUMULATION OF ORGANIC CONTAMINANTS IN A COLLAPSING FOOD WEB

Overview

Bioaccumulation is the sum of processes that regulate the uptake and elimination of chemicals within an organism. It was not until Rachel Carson's book "Silent Spring" (1962), that the concept of biomagnification was proposed. Prior to her work, it was well known that specific chemicals were capable of causing harm to humans and other living organisms, but there was no evidence of biomagnification of persistent, toxic chemicals such as pesticides and herbicides. For several decades the process of biomagnification was regarded as being thermodynamically impossible (Leblanc, 1995). Carson's book was one of the first examples of how the application of a chemical in the environment for a specific purpose, can have a dramatic and unintentional effect on the ecosystem as a whole. Although Carson's book focused on terrestrial systems, particularly birds and humans, the fundamental message was applicable to aquatic systems. Based on the premise that 'the dose makes the poison', kinetic modeling of contaminant dynamics within an aquatic ecosystem became very important in order to quantify chemical dose for organisms occupying different trophic levels.

One of the first measurements to quantify the potential of a chemical to bioaccumulate was the bioconcentration factor (BCF). The BCF measures the equilibrium concentration of the chemical within a living organism, as compared with that with in water. BCF is described as in Equation 1 (Arnot and Gobas, 2006):
(1) \[ \text{BCF} = \frac{C_B}{C_W} = \frac{k_1}{(k_2 + k_E + k_m + k_G)} \]

where \( C_B \) is the concentration (ng g\(^{-1}\)) within the organism, and \( C_W \) is the concentration (ng g\(^{-1}\)) of the chemical found in the water, \( k_1 \) (L g\(^{-1}\) d\(^{-1}\)) is the uptake rate across respiratory surfaces, and \( k_2, k_E, k_m, \) and \( k_G \) are the elimination rates (d\(^{-1}\)) for respiratory surfaces, fecal egestion, metabolism and growth respectively. This model considers uptake and elimination rates that occur only across respiratory surfaces of the organism. This model does not take into account the uptake of chemicals that result from the consumption of food. In order to quantify chemical for uptake from both water and dietary sources, the bioaccumulation factor (BAF) was introduced. The BAF can be expressed as in Equation 2 (Arnot and Gobas, 2006):

(2) \[ \text{BAF} = \frac{C_B}{C_W} = \frac{k_1 + k_D(C_D/C_W)}{(k_2 + k_E + k_m + k_G)} \]

where \( k_D \) is the dietary uptake rate (g g\(^{-1}\) d\(^{-1}\)) and \( C_D \) is the chemical concentration in the diet (ng g\(^{-1}\)). It is important to note that in order to directly measure either a BCF or BAF, one must make the assumption of steady state. Steady state occurs when \( \frac{dC_B}{dt} = 0 \), such that the uptake of the chemical is equal the rate of elimination. Steady state dynamics often assume uptake rates and elimination rates are constant throughout the lifetime of the organism and growth of the organism is also constant. It is important to note however, that not all chemicals have similar potentials to bioaccumulate. Mackay (1982) showed that the hydrophobicity of a chemical, measured by the \( n \)-octanol-water partition coefficient (\( K_{ow} \)) was a good predictor of a chemicals potential to bioaccumulate.

Contaminant modeling has shifted from using BCF’s and BAF’s to fugacity based models. Fugacity was first introduced by G.N. Lewis in 1901 as a tool to study chemical
equilibrium dynamics, however Mackay (1979) modified this concept in order to apply it to biological systems. Fugacity (Equation 3) is simply the partial pressure experienced by a chemical between two phases and is expressed as:

$$f = \frac{C}{Z}$$

Where $f$ is the fugacity (Pa), $C$ is the concentration in a phase (mol m$^{-3}$), and $Z$ is the capacity of that phase (mol m$^{-3}$ Pa) to hold the chemical. For biological systems, $Z$ is often represented by as lipid content of the organism (Hebert and Keenleyside, 1995). At chemical equilibrium, the fugacity of all phases are equal and therefore the rates of exchange between all phases are equal. In the case where fugacities are not equal, a difference in pressure will exist between phases, resulting in chemical partitioning from the phases with higher partial pressure to those of lower partial pressure until equilibrium is reached. These differences in fugacity can persist over time, thus a system can be at steady state but not at chemical equilibrium.

The fugacity concept was critical in quantifying the relative importance of biomagnification as an exposure route. Biomagnification is the increase in chemical fugacity in biota over food as a result of food uptake. Connolly and Pederson (1988) observed fugacity increased in a cold water food web, with organisms at the second trophic level having approximately four times the fugacity than that of the water, while organisms at the fourth trophic level having 14 times the fugacity of water. This phenomenon could not be explained by simple thermodynamic models, since chemicals were predicted to achieve equilibrium, resulting in equal fugacities among organisms of all trophic levels. Gobas et al (1993) were able to explain this phenomenon of increasing
fugacity by showing how the gastrointestinal (GI) tract of fish was able to change the fugacity of the food by absorption of lipids as food travelled through the gut. This uptake of lipid increased the chemical fugacity in the food relative to the fish, leading to an increase in chemical pressure in the food resulting in chemical partitioning into the organism.

Steady state models (Mackay and Hughes, 1984; Petersen and Kristensen, 1998; Morrison et al., 1997) assume that uptake, elimination, and growth rates are constant throughout the lifetime of an organism. This allows for easier estimations of the potential chemical concentration within the organism. The alternative, are non-steady state models (Czub and McLachlan, 2004; Burtnyk et al., 2009), which do not make the same assumptions as steady state models, and although such models are more realistic they are often difficult to calibrate. Steady state models have been shown to be effective with small aquatic organisms including *Daphnia* (Gomes et al., 2004) and phytoplankton (Kola and Wilkinson, 2005), however even phytoplankton models have proven difficult in estimating contaminant levels due to high growth rates (Epplett et al., 2000; Swackhamer and Skoglund, 1993).

The Great Lakes have been exposed to a multitude of organic contaminants, including but not limited to chemicals such as polychlorinated biphenyls (PCB’s), dichlorodiphenyltrichloroethane (DDT) and other pesticides. Many of these chemicals were banned in the early 1970's due to the Great Lakes Water Quality Agreement (GLWQA) between Canada and the United States. As a result the concentrations of these chemicals in fish have declined significantly in the Great Lakes (Bhavsar et al., 2007). These chemicals are still present in the biota and sediment at levels that can negatively
affect the health of both humans and animals. In order to reduce the risk of contaminant exposure to humans, both governments have implemented Great Lakes fish consumption guidelines. These guidelines are designed to inform the public of which species, and from what locations, are most heavily contaminated. For this reason, it is important to understand the relative importance of factors that regulate chemical bioaccumulation in fish in order to accurately measure chemical dose that may be exposed to humans, as it is the dose that makes the poison. Thus, it is essential to determine which model, either steady state or non-steady state, makes the most accurate predictions of dose in aquatic ecosystems.

**State of Lake Huron**

Lake Huron has experienced a large number of perturbations over the last century. One of the first was the invasion of the sea lamprey (*Petromyzon marinus*) in the late 1930's, and their peak abundance occurred just before 1950 (Smith and Tibbles, 1980). Sea lamprey were a primary cause of the major decline in lake trout populations, with the population becoming nearly extirpated during the 1950's. To deal with this issue, the Great Lakes Fishery Commission (GLFC) was formed in 1955. The primary goals of the GLFC were to control the sea lamprey population through the use of lampricides, as well as rehabilitate the lake trout population through stocking programs. The program has been quite successful, with lake trout populations slowly recovering to pre-lamprey invasion levels (Johnson and VanAmberg, 1995; Reid et al., 2001).
Sea lamprey were not the only invasive species to have a profound effect on the ecosystem. Zebra mussels (*Dreissena polymorpha*) and quagga mussels (*Dreissena rostriformis*), were first discovered in the Great Lakes system in 1988 in the Detroit River (Hebert et al., 1989). By 1991 there was already a significant population of zebra mussels in Saginaw Bay in Lake Huron. *Dreissenids* are capable of significantly decreasing chlorophyll *a* in water because of a very high filtering rate (Hebert et al., 1991; Leach 1993). This was a concern for Lake Huron, as it was already considered a highly oligotrophic lake (Vollenweider et al., 1974).

Recently, Lake Huron has undergone several changes to the food web. The largest change occurred in the forage fish populations, which have shown a decrease of 80% in overall abundances as summarized in Figure 1 (Roseman and Riley, 2009). The two species of forage fish with the greatest decline are the rainbow smelt (*Osmerus mordax*) and alewife (*Alosa pseudoharengus*), which constitute the greatest proportion of food to lake trout diets (Madenjian et al., 2006). The main cause of this decline was thought to be overstocking of top predator fish (Paterson et al., 2009), which included lake trout, but also other salmonids as well. The zooplankton community, however, has also shown a decrease in abundances. Barbiero et al. (2009) reported populations of zooplankton species to have decreased upwards of 90%. At the base of the food web, chlorophyll *a* has also shown a significant decrease, with the largest drops occurring between the years 2000 and 2003 (Barbiero et al., 2011).

Lake trout abundances have also decreased between the years 1996 and 2009, with a catch per effort of 16 lake trout per 305 m of gill net in 1996, versus 4 lake trout in 2009 (He et al., 2012). However, there has been a change in the age distribution in lake
trout with 8+ age fish constituting 2% of the population in 1996, to over 5% by 2010 (He et al., 2012). What is more concerning is that both lipid content, and energy densities have declined significantly in lake trout (Paterson et al., 2009) and declines are most notable in older, larger fish. Overall, all trophic levels are declining in abundance, which suggests a bottom-up regulator of the food web associated with decrease in the primary production rate originally measured as being 100 to 120 g C m\(^{-2}\) yr\(^{-1}\) (Glooschenko et al., 1973) or a decrease in trophic efficiencies. Fahnenstiel et al (1995) measured productivity in Saginaw Bay from the years 1990 to 1993 and found that primary productivity in the bay had decreased from approximately 220 to 100 mg C m\(^{-3}\) d as a result of significantly lower chlorophyll \(a\) levels. Chlorophyll \(a\) efficiency (mg C mg chl \(a\) \(^{-1}\) m\(^{-2}\) h\(^{-1}\)) however revealed a significant increase over the three year period from 2 to 4 mg C mg chl \(a\) \(^{-1}\) m\(^{-2}\) h\(^{-1}\). The authors hypothesize that an increase in water clarity, and therefore light penetration allowed for increased photosynthetic efficiency by the algae.

*Top-down and Bottom-up Processes in Ecosystems*

There has been large debate on the processes that control trophic interactions in ecosystems. The two opposing views are that a community is limited by resources (bottom-up) or by predator mediated interactions (top-down). The top-down hypothesis was first proposed by Hairston et al., (1960) in which they argue "green" accumulates in terrestrial systems because herbivores abundances are heavily controlled by predators in the system. Carpenter et al., (1995) provided strong evidence for this argument with work on lakes with piscivorous and non-piscivorous fish. They found that in lakes that
contained piscivorous fish, grazing pressure on planktivores decreased, which subsequently increase grazing pressure on the algal community. Fretwell (1977) expanded on the idea of top-down control by suggesting that food chain length may also play a significant role on the base of the food web. In food webs with an odd number of trophic levels, grazers would be limited by predation and therefore primary production would continue uninterrupted. However, in food webs with even number of trophic positions, primary producers would be grazer limited, and therefore reduce overall primary production.

A counter-argument was suggested by Hunter and Price (1992) in which they state that removal of a species high in the food web may substantially alter the rest of the community, it would not ultimately stop primary production from occurring, thus the community would subsist. However, complete removal of primary producers in the system would eventually lead to system collapse. Hunter and Price (1992) concluded that although food web structure may determine the standing crop of the system, primary producers fundamentally control the biomass produced in the system. A strong case of bottom-up control mechanisms has been observed in Lake Erie (Makarewicz 1993). Following the reduction of phosphorus loadings into the Great Lakes, there was a substantial drop in the abundance of phytoplankton as well as an increase in water clarity in Lake Erie (Makarewicz 1993) although the relationship was confounded by the arrival of the zebra mussel.

**Objectives**
Given the large scale changes observed at multiple trophic levels in Lake Huron, understanding the mechanism in which energy, and consequently contaminants, are transferred from the base of the food web to organisms at higher trophic positions is vitally important for sustainable management of fish in Lake Huron, as well as contaminant advisories associated with the consumption of these fish. This thesis examines energetic dynamics in the Lake Huron food web with respect to top-down and bottom-up processes. Top-down processes are investigated using persistent congeners of PCBs as energetic tracers, while bottom-up processes are examined by measuring temporal changes in primary production.

Objective 1: To determine if Lake Huron primary production is controlled by top-down or bottom-up processes. I hypothesize in chapter 2 that there will be no change in annual primary production rates in Lake Huron. If primary production rates remain constant through time, then changes observed at higher trophic levels are a result of top-down processes acting on lower trophic levels. However, if declines are observed in annual primary production rates, then this would suggest that the Lake Huron food web collapse is controlled by bottom-up processes, including such factors as nutrient limitation, mixing regimes and/or thermal dynamics.

Objective 2: To resolve if the steady state or non-steady state bioaccumulation models best reflect changes in trophic efficiencies in the Lake Huron food web. I hypothesize in chapter 3 that there should be no age related changes in chemical fugacity as well as no spatial differences observed in bioaccumulation patterns. If fugacity does change with respect to age and size, then it is evident that non-steady state kinetics determine patterns of bioaccumulation in lake trout and therefore non-steady state models are more
applicable to quantify trophic efficiencies in aquatic food webs. If spatial differences are observed among lake trout, this further supports the non-steady state hypothesis and that the processes regulating non-steady state dynamics are system dependent.

The final chapter provides a comparison of information regarding top down and bottom up processes in Lake Huron, and discusses the relative importance of both processes by summarizing the findings of this thesis.
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CHAPTER 2

PRIMARY PRODUCTION IN THE MAIN BASIN OF LAKE HURON: EVIDENCE OF BOTTOM-UP CONTROL

Introduction

Primary production in aquatic ecosystems is the process in which phytoplankton and other autotrophs take up carbon dioxide (CO$_2$) from the water and convert radiant into chemical energy via the process of photosynthesis. This is a fundamental process in aquatic ecosystems since organisms higher in the food web, including zooplankton, invertebrates and fish rely on the chemical energy fixed by primary producers. Chemical energy can come from either external sources including terrestrial run-off (allochthonous) or from within the system (autochthonous) (Birge and Juday, 1927). This distinction of energy sources is important because in relatively small systems, such as ponds, allochthonous carbon sources dominate the carbon used in secondary production as a result of the ratio of shoreline to lake surface area (Hamilton et al., 2001). In the Great Lakes, however, these edge effects still occur but to a lesser extent because of the large size of the lakes and therefore autochthonous carbon production becomes increasingly more important (Munawar et al., 2011).

In large lake systems, like Lake Huron, phytoplankton contribute the majority of primary production (Fitzpatrick et al., 2007). It is unclear, however, what processes regulate primary productivity in this system. Traditionally, a bottom-up mechanism suggested that phytoplankton were regulated solely by the limitation of resources (Schindler, 1974; Edmondson 1970). Typically either phosphorus (Sterner, 2008) or
nitrogen (Vitousek and Howarth, 1991) have been shown to limit the rates of primary production within lake systems. Although in some cases other nutrients such as iron (Geider and Laroche, 1994) might limit production rates, there is little evidence of this on broader limnological scales.

Top-down mechanisms via predator grazing have also been suggested in regulating primary production rates by limiting the abundance of phytoplankton through predation (Carpenter et al., 1995). Carpenter et al. (1995) showed this process by comparing lakes that either contained, or did not contain, piscivorous fish. The lakes that did not have piscivorous fish showed much higher abundances of edible algae as a result of decreased predation pressures on the algae from zooplankton.

Lake Huron was described as an oligotrophic lake with daily primary production rates of approximately 150 - 700 mg C m\(^{-2}\) d\(^{-1}\) (Glooschenko et al., 1973), in comparison to Lake Erie (Western basin), Lake Michigan and Lake Superior which have daily production rates of 300 - 2000 (Fitzpatrick et al., 2007), 600 - 800 (Fahnenstiel et al., 2010), and 200 - 350 mg C m\(^{-2}\) d\(^{-1}\) (Sterner, 2010) respectively. Despite having low production rates relative to other Great Lakes, Lake Huron has supported a freshwater fishery with annual yields of approximately 5 to 7 million kg, with lake whitefish (Corogonis clupeaformis) constituting the majority of the catch (Ebener et al., 2008). Lake Huron is also stocked extensively with sport fish which include Altantic Salmon (Salmo salar) and lake trout (Salvelinus namaycush) (Ebener et al., 2008). In recent years, there has been a significant decline in the forage fish populations that these top predator fish rely on (Roseman and Riley, 2009). These declines have the potential to alter consumption rates in the top predator (Pothoven and Madenjian, 2008). Similar
changes have also been observed in lower trophic levels of Lake Huron, with zooplankton abundances and size distribution decreases reported in (Barbiero et al., 2009). Additionally, Hebert et al. (2009) reported declines in herring gull (*Larus argentatus*) diet and egg size, as these birds feed on Lake Huron forage fish, primarily alewife (*Alosa pseudoharengus*) and smelt (*Osmerus mordax*).

In this study, primary production rates as well as nutrient and chlorophyll a levels were measured in the main basin of Lake Huron. These measurements are compared to previous measurements of annual primary production rates of 100 g C m$^{-2}$ yr$^{-1}$ (Vollenweider et al., 1974; Glooshenko et al., 1973) to determine, what, if any, changes have occurred to the primary production rates in Lake Huron. Understanding the processes that regulate primary production in large lake ecosystems is critical to managing the food web as a whole. It is hypothesized that Lake Huron is controlled by bottom-up processes that a decline in primary production will regulate the changes observed in the higher trophic levels. If primary production rates have not significantly changed, then it would suggest that the food web changes are the result of decreased trophic efficiencies in zooplankton and fish. If primary production rates have declined significantly, then this observation would support the conclusion of Lake Huron being regulated by bottom-up processes.

*Materials and Methods*

*Sample Collection*
All samples were collected between May 2011 and September 2012 from a site approximately 15 km off the coast of Goderich, Ontario (N43 44.260, W81 54.679). The location was chosen to obtain an offshore, open water measurement that would represent conditions for the majority of the main basin of Lake Huron. Water samples were collected at 0, 3, 5, 10, and 15 meter depths using a 2 litre Kemmerer sampler. From these samples, a sub-sample of water was collected for primary productivity measurements, nutrients and chlorophyll a.

*Light*

The irradiance of the water column was measured using a Li-Cor Spherical Quantum Sensor and LI-1000 Data Logger at every 1 metre interval from 0 to 9 metres. These measurements were used to calculate the vertical attenuation coefficient ($\varepsilon_{par}$) for each sampling date using the equation:

$$\varepsilon_{par} = \frac{(\ln I_0 - \ln I_z)}{z}$$

where $I_0$ is the irradiance at the surface, and $I_z$ is the irradiance at depth $z$. Using the vertical attenuation coefficient, the euphotic depth ($Z_{eu}$) was calculated by the equation:

$$Z_{eu} = \frac{4.6}{\varepsilon_{par}}$$

The euphotic depth is the point in the water column where primary production stops due to the lack of available sunlight and is generally accepted to be approximately 0.01 $I_0$.

*Primary Productivity*
Primary productivity was measured using the $^{14}$C method outlined in Strickland and Parsons (1968). Briefly, at each depth, two clear 300 mL biological oxygen demand (BOD) bottles, and one dark BOD bottle were filled with water that had been brought up from specific depths and injected with 1mL of radioactive labeled $^{14}$C (10 μCi) buffer solution. Each bottle was then attached to a buoyant rack that would suspend the bottles at their respective depths for a 2 hour period, at which point the bottles were brought back up and immediately placed inside a dark cooler. All effort was taken to ensure that bottles exposure to direct sunlight was kept to a minimum. Due to the distance of the sampling site from the laboratory, filtration of the samples was conducted in the shade upon returning to shore. All 300 mL from each bottle was filtered through a Whatman nucleopore 0.45 μm filter. The filter was then placed inside a 20 mL scintillation vial, and 15 mL of Ultima Gold Scintillation fluid was added. Radioactivity was measured on a Beckman LS 6500 Scintillation Counter.

Productivity rate (mg C m$^{-3}$) for each depth and date was calculated using the formula from Vollenweider (1974):

$$P = ^{14}\text{C}_{\text{up}} \cdot ^{12}\text{C}_{\text{avail}} \cdot 1.06$$

where $^{14}\text{C}_{\text{up}}$ is the ratio of $^{14}$C taken up by the phytoplankton versus total $^{14}$C injected into the bottles, $^{12}\text{C}_{\text{avail}}$ is 21 mg C l$^{-1}$ (Vollenweider, 1974) and 1.06 is the isotope correction factor. In order to convert this measurement to a time rate, the primary productivity rate was divided by the incubation time in order to obtain a primary productivity rate (mg C m$^{-3}$ h$^{-1}$). Primary production (mg C m$^{-2}$ d$^{-1}$) for a given date was taken by averaging the five depth measurements, and multiplying by the euphotic depth as well as day length. In
order to remain consistent with previous studies (Glooschenko et al., 1973; Fitzpatrick et al., 2007), average day length was assumed to be 10 hours.

Annual primary production rates (mg C m\(^{-2}\) yr\(^{-1}\)) were calculated following the methods of Fitzpatrick et al. (2007). Briefly, seasonal rates were calculated by averaging daily production rates by the number of days in a season (91.25 days). However, samples in this study were only collected during spring and summer, fall measurements were estimated to be equal to spring, and winter production rates were assumed to equal ½ spring production (Fitzpatrick et al., 2007).

**Temperature and Dissolved Oxygen**

Temperature and dissolved oxygen with depth profiles were measured using a Brancker XR-420-CDT by slowly lowering it into the water, down to a depth of approximately 40m while a measurement was recorded every 1 second. Mixing depth (\(Z_m\)) was determined to be when a change in temperature of more than 1°C over a 1m interval, or assumed to be 50m if no such change was apparent. The ratio of \(Z_{eu}\) and \(Z_m\) was then calculated to determine whether primary production is limited by phytoplankton being mixed out of the euphotic zone.

**Total Phosphorus**

Nutrient samples were stored in glass amber jars (500mL) immediately after being pulled from depth. Upon arrival to the laboratory, each depth sample was acidified using concentrated sulfuric acid. Total phosphorus concentrations were measured by taking a sub-sample (50mL) of the acidified nutrient sample using the ascorbic acid
method (Strickland and Parsons 1968) and quantified against a standard using a Beckman DU-530 Spectrophotometer.

*Nitrate*

From the acidified nutrient sample, a 100mL sub-sample was taken for total nitrate determination. Total nitrate samples were collected for both years, however only samples from 2011 have been analyzed and returned thus far. Total nitrates were determined using the continuous flow colorimetric assay method, and was performed at the Soil Biology Laboratory at the University of Georgia, Athens, Georgia.

*Chlorophyll a*

Chlorophyll a concentrations were measured following the methods of Strickland and Parsons (1968). A one litre water sample was filtered through a Whatman GF/C filter (1.2μm) and then analyzed using the acetone pigment extraction and spectrophotometric analysis. Because the distance of the sampling site to the laboratory, filters were not extracted until the following day, however they were kept frozen overnight on dry ice, and wrapped in aluminum foil in order to minimize degradation.

*Chlorophyll a assimilation efficiency*

The assimilation efficiency of chlorophyll a (mg C mg chl a⁻¹ m⁻³ hr⁻¹) was calculated by taking the primary productivity rate calculated for a sampling period and normalizing to the concentration of chlorophyll a in the water sample. An overall average for the sampling day as well as assimilation efficiency with depth were measured to determine whether photo-inhibition was limiting primary productivity at the surface.
Results

Euphotic Depth

Light penetration decreased from spring to summer (Figure 2.1). The vertical attenuation coefficient ranged from 0.14 to 0.19 m$^{-1}$. The May 2011 sampling date had the highest light penetration with a euphotic depth of 32.3 m. In contrast to this, the September 2011 euphotic depth was 23.7 m. On average, the euphotic depth for 2011 and 2012 was 27.7 m for spring and summer.

Primary Productivity

Primary productivity rates ranged from 0.02 to 1.87 mg C m$^{-3}$ h$^{-1}$. Daily primary production rates ranged from 47 to 314 mg C m$^{-2}$ d$^{-1}$ with a steady increase in daily rates from spring to summer (Figure 2.2). Peak productivity rates were recorded midsummer (August) coinciding with peak chlorophyll a levels. Primary productivity with depth is summarized in Figure 2.3 Yearly primary production rate was estimated to be 32.4 g C m$^{-2}$ yr$^{-1}$.

Temperature and Dissolved Oxygen

Water was coldest (4°C) during the spring when the water column was isothermal. Full stratification did not occur until late July to early August (Figure 2.4), where a distinct thermocline formed between a depth of 20 and 25 m. The thermocline persisted into September, however the mixing depth increased as surface waters began to cool. The ratio of $Z_{eu}/Z_{m}$ ranged from 0.6 to 1.3, and increased as the season progressed.
When $Z_{eq}/Z_m$ was high (July and August) primary production occurred in both the epilimnion and metalimnion (Figure 2.4).

Dissolved oxygen ranged from 5.4 to 24.4 mg l$^{-1}$ and oxygen depth profiles can be seen in Figure (2.4). Maximum oxygen concentration occurred in the coldest waters during early spring and minimum concentrations occurred at the surface during the summer months when surface temperature was at its maximum.

**Total Phosphorus**

Total phosphorus had a negative relationship with respect to season (Figure 2.5A). Average spring measurements of 8.1± 0.4 mg TP m$^{-3}$ were significantly higher than those measured during the summer season 6.6 ± 0.6 mg TP m$^{-3}$ ($P < 0.01$, Student t-test). The April 2012 sampling date had the highest total phosphorus measurements of 8.6 mg TP m$^{-3}$, while September 2011 had the overall lowest total phosphorus measured with 4.5 mg TP m$^{-3}$.

**Nitrates**

Nitrate values for Lake Huron ranged from 127.7 to 235.1 mg m$^{-3}$ for the 2011 (Figure 2.5B). The maximum nitrate levels occurred in mid August, while the lowest concentrations were measured during May, however no significant relationship existed (ANOVA, $P > 0.05$).

**Chlorophyll a**
Chlorophyll a measurements for 2011 and 2012 ranged from 0.26 to 2.9 mg C m$^{-3}$ for Lake Huron with peak concentrations occurring late in the growing season (August-September) (Figure 2.6).

**Chlorophyll a Assimilation Efficiency**

Chlorophyll a assimilation efficiency showed no relationship with time or depth ($P > 0.05$, Figure 2.7) and ranged from 0.03 to 3.98 mg C (mg chl a)$^{-1}$ m$^{-3}$ h$^{-1}$. Peak efficiencies were observed during the earliest primary productivity measurements (i.e. late April to early May). Total phosphorus had a positive, but non-significant correlation with chlorophyll a assimilation efficiency, while nitrate had a negative relationship ($P > 0.05$, Figure 2.8). Chlorophyll a assimilation efficiencies did not show any relationship with depth or date (Figure 5), nor was there a relationship with $Z_{eu}/Z_m$ ($P > 0.05$)

**Discussion**

It is evident from these data that the annual primary production rates in the open waters of Lake Huron have decreased by a factor of 4 when compared to previous estimates of (Vollenweider et al. 1974; Glooshenko et al., 1973). Since the lake supports a wide variety of sport and commercial fisheries (Ebener et al., 2008), it is important to understand what factors could cause such a significant drop in primary production rates. Earlier estimates of primary production were performed using on board light incubation which could potentially underestimate the effects of photo-inhibition and photo-oxidation, which can have a significant impact on primary production rates (Cullen and Lesser, 1991). The deepest measurements of primary productivity in this study was at
15m, well above $Z_m$, and since late in the season $Z_{eu}$ was greater than $Z_m$, the daily and annual primary production rates for the water column in this study might be an underestimate of the true value.

Primary production can be limited by light (Jones et al., 1996). In the case of Lake Huron being a highly oligotrophic lake (Vollenweider et al., 1974), light availability should not be limiting for phytoplankton. The data in this study show that as the season progresses, the euphotic depth continually decreases, resulting in a smaller volume for primary production to occur (Figure 2.1). Primary productivity rates, however, increased as the season progresses (Figure 2.2). The ratio of $Z_{eu}/Z_m$ revealed that late in the season the ratio became greater than 1, and which suggests that during mid-late summer primary production reaches into the metalimnion. However in this study, primary production was not directly measured in this layer. The dissolved oxygen profiles, however, demonstrated that late in the summer season (August-September, Figure 2.4D,E), primary production was occurring in the metalimnion due to the presence of peaks of dissolved oxygen, which was not accounted for in the water column estimates. Additionally, there is evidence of photo-inhibition occurring in the first 10 m of the water column during mid-summer (June-July), as the highest productivity rates occur at 15m depth (Figure 2.3B,C). It is likely that because the relative importance of photo-inhibition is low in the deeper (>15m depth) portion of the water column, primary productivity rates are higher.

Nutrient limitation, however, has been shown to be significantly related to primary production rates in the Great Lakes (North et al., 2007; Lehman 2002). The majority of nutrients entering Lake Huron are from terrestrial run-off, particularly for nitrogen and phosphorus (Beeton 1999; Robertson and Saad, 2011). Near shore
phosphorus levels off the coast of Goderich, ON, have decreased from approximately 40 to 20 mg m$^{-3}$ between 1976 and 1999, with levels becoming relatively stable after 1990 (Nicholls et al., 2001). The phosphorus levels in this study were taken more offshore than the Nicholls et al. (2001) study, and were approximately 25 to 50% of those values reported. In this study, there was also a consistent decrease with total phosphorus from spring to summer, suggesting that during the spring mixing event there is a replenishment of phosphorus to the open waters of Lake Huron, and as the season progresses this phosphorus reservoir becomes depleted due to nutritional requirements from phytoplankton to maintain a specific ratio of nutrients (Redfield, 1934) as well as larger particulates settling to the lake bottom (Hamilton and Schladow 1997). Nitrate levels however, increased as the season progresses, likely because of agricultural runoff of nitrogen, as it is more conservative than phosphorus in aquatic ecosystems (Robertson and Saad, 2011) and remains more bioavailable than phosphorus.

In addition to decreased primary productivity levels in Lake Huron, the chlorophyll $a$ assimilation efficiencies are cause for concern. Chlorophyll $a$ efficiencies have been reported, both in Lake Huron and open ocean, to range between 4 to 20 mg C (mg chl $a)^{-1}$ h$^{-1}$ (Fahnenstiel et al., 1995; Curl and Small, 1965). The majority of chlorophyll $a$ efficiencies measured in this study were below 1 mg C (mg chl $a)^{-1}$ h$^{-1}$, and are similar to those measured in an ultraoligotrophic lake (Modenutti et al., 2004), with peak efficiencies occurring early in the season (April and May). If the system was regulated by predation on phytoplankton, a decrease in efficiency as the season progresses would not be expected as it would decrease the competition among phytoplankton for resources, therefore allowing those phytoplankton cells to be more
efficient in their use of resources (Dippner, 1998). However, what is observed in this study is that as phosphorus availability decreases, in addition to chlorophyll $a$ concentrations increasing, the efficiency of chlorophyll $a$ decreases (Figure 6). Although the relationship is not significant, it is important to note that the chlorophyll $a$ assimilation efficiency was highest when phosphorus concentrations were at their peak and $Z_{eu}/Z_m$ was at its lowest. This study only examined total phosphorus, and did not consider the role of soluble reactive phosphorus (SRP). There was no relationship with nitrate concentration and chlorophyll $a$ assimilation efficiency suggesting that the main basin is not nitrogen limited.

The near shore shunt hypothesis, proposed by Hecky et al., (2004), aimed to explain the significant changes in nutrient cycling in lakes due to the presence of Dreissenids. The major changes reported in higher trophic levels in Lake Huron coincide shortly after the arrival of Dreissenids. Rosemann and Riley (2009) reported drops in forage fish populations of nearly 80%, decreases in lake trout energy densities were reported by Paterson et al. (2009), decreases in zooplankton abundances observed by Barbiero et al. (2009), as well as changes in phytoplankton spring abundances between 1998 and 2002, decreasing approximately 25% (Barbiero et al., 2011). The near shore shunt hypothesis predicts that there will be a severe reduction in the nutrients and other particles transported from the near shore to the offshore of lakes. Dreissenids mussels are very efficient at filtering the water (Sprung and Rose, 1988; Silverman et al., 1995) and the feces and pseudofeces of Dreissenids are composed of material and particles that are unusable by most organisms (Klerks et al., 1996). This leads to the near shore being nutrient rich, while the offshore pelagic portion of the lake becomes nutrient limited (Cha
et al., 2011). Total phosphorus levels reported in this study are lower than previous estimates. Because *Dreissenids* have the potential to alter both nutrient flow, as well as nutrient composition, it is possible that rates of SRP reaching the open waters are significantly lower than pre-invasion levels. Additionally, the ratio of SRP/TP may be significantly lower, and this relationship should be examined in future work.

From a top down perspective, predation on phytoplankton via grazing by zooplankton and other predators would be the most likely cause of the decline in primary production. Over consumption of the phytoplankton would lead to decreased abundances, resulting in a decrease in primary production rates overall (Fahnenstiel et al., 1995), but not to decreased assimilation efficiencies. Barbiero et al. (2009) however, have reported significant declines in zooplankton abundances in both the northern and southern basins of Lake Huron. Barbiero et al. (2009) reported peaks in zooplankton abundances of approximately 10 mg m$^{-3}$ (dry weight) in 1999 for cyclopoid and calanoid copepods, but by 2006 abundances had dropped to less than 2 mg m$^{-3}$ (dry weight), and many species of *Daphnia* also showing similar declines. Top-down dynamics would predict an increase in chlorophyll $a$ concentrations with a potential decrease in chlorophyll $a$ efficiencies due to self shading.

Overstocking of lake trout and other salmonids is a potential explanation for the decline in forage fish population as well as a decrease in lake trout and forage fish condition (Paterson et al., 2009). Overstocking, however, does not address the significant drops observed at lower trophic levels including primary producers as seen in this study. A bottom-up control mechanism, either by direct primary production decreases as is observed in this study, or through a decrease in trophic efficiencies, is a more likely cause
of the trophic collapse because it would predict that a large decrease in biomass
production lower in the food web would ultimately lead to decreases in biomass at all
positions in the food web (Carpenter et al., 2001).

The arrival of the *Dreissenids* caused a decrease in the daily primary production
rates of Saginaw Bay from 200 to 100 mg C m\(^{-3}\) d\(^{-1}\) over a 3 year period (Fahnenstiel et
al., 1995). Decreased primary productivity was caused by overgrazing of the *Dreissenids*
on the phytoplankton community. However, because of the increased clarity that resulted,
the efficiency of the remaining phytoplankton community increased greatly (Fahnenstiel
et al., 1995). It is unlikely that this would occur off shore, in the open waters of Lake
Huron as it did in Saginaw Bay. Saginaw Bay is very shallow, ranging from 20 to less
than 1 m, in comparison to the open waters of the main basin where depth can range from
30 to greater than 100 m (National Oceanic and Atmospheric Administration, NOAA).
The presence of the *Dreissenids* may decrease abundances of phytoplankton due to
grazing near shore, however any nutrients that are excreted by the *Dreissenids* remains in
the euphotic zone, and thus partially available for uptake by the phytoplankton (Klerks et
al 1996).

In summary, this study aimed to address if the multitude of changes reported at
multiple trophic levels in Lake Huron could be caused by a potential decrease in primary
production. The annual rates of 32 g C m\(^{-2}\) yr\(^{-1}\) are significantly lower than the 100 g C
m\(^{-2}\) yr\(^{-1}\) reported previously by Vollenweider et al. (1974). It is likely, the the 32 g C m\(^{-2}\)
yr\(^{-1}\) is an underestimate of annual primary production, as an unknown portion of the
primary production in the water column was not directly sampled. The low values of
chlorophyll a assimilation efficiencies strongly supports the hypothesis that Lake Huron
productivity is controlled by bottom-up control mechanisms, likely phosphorus limitations. The decrease in primary productivity is likely the result of the invasion of *Dreissenids* in Lake Huron which have reduced the availability of nutrients, specifically phosphorus, to the off-shore open waters of the lake. It is concluded that the decreases in abundances at higher trophic levels are a result of bottom up processes, specifically, that an overall decrease in primary productivity rates has resulted in a decrease in biomass at higher trophic levels.
Figure 2.1: Euphotic depth with sampling day for 2011 and 2012 combined with day 1 representing January 1.
Figure 2.2: Daily primary production rates for the main basin of Lake Huron for 2011 and 2012
Figure 2.3: Primary productivity with depth profiles for (A) May, (B) June, (C) July, (D) August and (E) September respectively.
Figure 2.4: Temperature and dissolved oxygen with depth profiles for (A) May, (B) June, (C) July, (D), August, and (E) September. Black diamonds and white squares represent temperature and oxygen concentrations respectively. Dashed horizontal lines represent euphotic depths.
Figure 2.5: Concentrations for (A) total phosphorus and (B) total nitrates from primary productivity site on Lake Huron. Combined data for 2011 and 2012 seasons. Nitrates only comprises of 2011 sampling season. The x-axis refers to the day of year, with January 1 as day 1.
Figure 2.6: Chlorophyll $a$ concentrations for the primary productivity site of Lake Huron. Combined data for 2011 and 2012 seasons.
Figure 2.7: Chlorophyll a efficiencies for primary productivity site for Lake Huron main basin. Data is combined for 2011 and 2012 seasons. The symbols □, ■, ○, ×, and + represent assimilation efficiencies at depths 0, 3, 5, 10 and 15 respectively.
Figure 2.8: Chlorophyll a assimilation efficiency in relation to total phosphorus (■) and total nitrate (□) concentrations. Solid and dashed lines represent the line of best fit of total phosphorus and nitrates, respectively.

- Chlorophyll a assimilation efficiency (mg C [mg chl a] \(^{-1}\) m\(^{-3}\) h\(^{-1}\))
- NO\(^3\) concentration (mg m\(^{-3}\))
- Total phosphorus concentration (mg m\(^{-3}\))

R\(^2\) = 0.1155
P > 0.05

R\(^2\) = 0.0867
P > 0.05


References


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CHAPTER 3

BIOLOGICAL AND ECOLOGICAL PROPERTIES INFLUENCE STEADY- AND NON-STEADY STATE PCB BIOACCUMULATION KINETICS IN LAKE HURON LAKE TROUT (*SALVELINUS NAMAYCUS*)

*Introduction*

Bioaccumulation can typically be broken down into three distinct drivers; (i) physical-chemical (ii) biological/physiological and (iii) ecological. Physical chemical properties, such as $K_{ow}$ have been shown to predict the potential of a specific chemical to bioaccumulate (Mackay 1982), such that super hydrophobic chemicals ($K_{ow} > 6.5$) tend to bioaccumulate in the tissues of an organism (Connolly and Pedersen, 1988). Biological and physiological properties regulating chemical accumulation include uptake and elimination rates across respiratory surfaces (Paterson et al., 2007), as well as fecal egestion rates (Paterson et al., 2010) and assimilation efficiencies (Liu et al., 2010) of the food consumed. Growth of the organism has also been identified as a critical component regulating bioaccumulation (Eby et al., 1997) as a result of growth dilution. Lastly, ecological factors including contaminant levels in food and trophic position have been demonstrated to predict the potential of a chemical to bioaccumulate (Vander Zanden and Rasmussen, 1996). It is difficult to quantify the relative importance physical-chemical, biological and ecological drivers on the bioaccumulation of persistent organic pollutants (POPs) within aquatic ecosystems.

Bioaccumulation is associated with three interdependent processes, bioconcentration (Mackay, 1982), biomagnification (Gobas, 1999) and bioamplification
(Daley et al., 2009; Daley et al., 2011). A general model for describing the bioaccumulation of POPs in fish was summarized by Drouillard et al. (2009) and is outlined in Equation 1:

\[
\frac{dC_f}{dt} = \left( \frac{Q_f}{E_{food} \cdot AE_{food}} \right) \cdot AE_{chem} \cdot C_{food} - C_f \cdot \left( \frac{\Delta V_f}{V_f \cdot t} \right) - C_f \cdot (k_r + k_w)
\]

where \( C_f \) is the concentration of chemical in the fish (ng g\(^{-1}\)), \( Q_f \) is the energy requirements of the fish (kJ g\(^{-1}\) d\(^{-1}\)), \( E_{food} \) is the energy density of the food (kJ g\(^{-1}\)), \( AE_{food} \) is the assimilation efficiency of food energy (unitless), \( AE_{chem} \) is the assimilation efficiency of the chemical into the fish, \( C_{food} \) is the chemical concentration of chemical in food (ng g\(^{-1}\)), \( V_f \) is the mass (g) of the fish, \( t \) is time (d), \( k_r \) and \( k_w \) are the respiratory and fecal elimination rates (d\(^{-1}\)) of the fish respectively. Traditionally bioconcentration and biomagnification models have been solved under the assumption of steady state, where growth and elimination rates are often assumed to remain constant throughout the lifetime of the organism, and the model solution would yield Equation 2:

\[
dC_f / dt = 0
\]

Steady state occurs when the elimination rate of a chemical is equal to the uptake rate, resulting in no net change in chemical concentration through time. Recent studies, however, have demonstrated that chemical elimination rates are not necessarily constant, and are influenced by a number of biological and ecological factors, and thus alter the potential for an animal to reach steady state.
The time for an individual to reach steady state is proportional to the elimination rate as defined by Equation 3:

\[ T_{0.95} \approx \frac{3}{(k_r + k_w)} \]

Under the assumption of a constant chemical elimination rate, time to steady state is achievable within the life history of the animal. However, allometric and temperature dependent changes in animal metabolism, and changes in an animal's physiological state such as dormancy, can result in very low chemical elimination rates (Leney et al., 2006; Paterson et al., 2007). Consequently, these processes have the potential to extend the time required for an individual to reach steady state. Additionally, as the elimination rates, \( k_r \) and \( k_w \) approach 0, then Equation 1 becomes a non-steady state dynamic and the rate of uptake is based on energy requirements, assimilation efficiencies and growth rates. In aquatic ecosystems of temperate and northern latitudes, long lived cold blooded species spend much of their lives at levels of basal metabolism, and thus the potential to achieve steady state within a lifetime declines relative to the proportion of the life cycle spent over wintering.

There have been a number of studies that have examined the bioaccumulation of organic contaminants in lake trout (Wszolek et al., 1979; Bache et al., 1972; Borgmann and Whittle, 1992). Typically, studies have tended to examine the magnitude and temporal trends of chemical contaminants and rarely examine the kinetics of individual congeners. In this study, multiple age cohorts of lake trout were collected from the three basins of Lake Huron to investigate and compare PCB congener bioaccumulation and growth rates. It is hypothesized that long lived (15+ years) lake trout will achieve steady
state bioaccumulation kinetics. Secondly, I will examine if there are differences in bioaccumulation patterns observed among the three basins with respect to $K_{ow}$. If the bioaccumulation of PCB’s are controlled by physical-chemical properties then lake trout from all basins will have similar bioaccumulation patterns. If differences in PCB bioaccumulation patterns with respect to $K_{ow}$ are observed among basins, it would support the hypothesis that lake trout bioaccumulation is controlled by ecological processes that lake trout experience uniquely in their respective basins.

**Materials and Methods**

**Sample Collection**

Lake Huron is the second largest of the Great Lakes, with a surface area of approximately 59,600 km$^2$, and consists of three basins. The main basin, which is the largest and deepest of the three basins with an average depth of 59 m. Georgian Bay which is the second largest basin and averages 44 m in depth. Lastly is the North Channel which is a narrow channel that connects Lake Superior to Lake Huron and averages 22 m in depth. These basins have the potential to provide lake trout with distinct habitats. Lake trout generally inhabit waters between 8 to 12$^\circ$C (Martin and Oliver, 1980) and grow slowly, often not reaching maturity until age 5 or older (Madenjian et al., 1998). Because they are a long lived species, typically exceeding 10 years of age, they have the potential to reach a point where growth becomes negligible as a result of increased energetic demands (Stewart et al., 1983). Lake trout are top predators and will typically consume the larger and more abundant forage fish available. Currently the most abundant forage
fish available in Lake Huron are smelt (*Osmerus mordax*) and bloaters (*Coregonus hoyi*), however recent data on the main basin has shown that the populations of these and other forage fish are declining (Roseman and Riley, 2009).

Lake trout were collected between April 2010 and November 2011 from five locations across Lake Huron including the North Channel, Georgian Bay, and Main basins of the lake (Figure 3.1). With the exception of the Douglas Point collections which occurred in November 2011, all fish were collected between the months of April - August. Lake trout collected in April 2010 (Stokes Bay) were acquired as by-catch from a commercial fishery supplier during lake whitefish gill netting operations. Lake trout collected from Goderich, Cape Rich and Frazer Bay between June – August 2011 were provided through the Ontario Ministry of Natural Resources (OMNR) Upper Great Lakes Management Unit’s (UGLMU) index netting program. Forage fish, including rainbow smelt, bloater and round gobies were also collected during these sampling trips. The November 2011 Douglas Point lake trout samples were provided by Bruce Power in collaboration with the OMNR. Gill nets used by the OMNR were 400 m long x 1.83 m deep with 2–25 m panels of 3.2 and 3.8 cm stretch mesh and 7–50 m panels of 5.1–12.7 cm mesh in 1.27 cm increments. Nets were set overnight in water depths ranging from 20 – 45 m depending on the depth of the thermocline. Fish were stored individually in food grade plastic bags and placed on dry-ice during transport to the Great Lakes Institute for Environmental Research (GLIER) where fish were subsequently stored at -20 °C until processed. Refer to Table 3.1.
**Sample Processing**

Biological information collected from each fish included total fork and standard lengths, mass, and sex. Sagittal otoliths were removed from each fish for aging purposes. Following dissection, whole fish were homogenized using a stainless steel commercial meat grinder. Samples were processed through the grinder multiple times to ensure proper homogenization and 3 x 35 g subsamples of the homogenate were stored in solvent rinsed stainless steel containers until chemical analysis. The grinder was thoroughly cleaned and rinsed with soap and water and dried between each fish and solvent rinsed between each of the lake trout collection locations.

Aging of lake trout was completed at GLIER and by the OMNR. Lake trout collected in April 2010 were aged using sagittal otoliths following the general processing methods for preparing otolith thin sections by the Otolith Research Laboratory, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada. All other fish were aged by the OMNR using a combination of fin clip, otolith, coded wire tag, and established length at age relationships for Lake Huron lake trout.

**Chemical Analysis**

Chemical analyses were performed following the procedure outlined in Daley et al. 2009. Briefly, 0.5g of homogenate was mixed and ground with 15g of sodium sulphate in a glass mortar and pestle. The mixture was then transferred to a 20mL glass syringe containing 15mL of 50:50 (v:v) hexane and dichloromethane (DCM) extraction solvent. The syringe was equipped with a sterile 0.45µm glass fibre filter with a small amount of glass wool also placed in the bottom of the syringe. Samples were spiked with 50µL of a PCB 34 recovery standard (125mg mL⁻¹). Samples were allowed to stand for
one hour before opening the columns. An additional 20mL of 50:50 hexane/DCM extraction solvent was added during the procedure for a total extraction volume of 45mL. Following extraction, samples were evaporated under vacuum to approximately 2mL and volume adjusting to 10mL with hexane. Sample lipid contents were determined gravimetrically by transferring 1mL of the extract into a tared aluminum weigh boat drying at 110ºC for 1 hour.

Sample clean-up was performed using 6 g of magnesium silicate (Florisil 60-200 mesh) with a 1 cm cap of sodium sulphate. Samples were eluted with 50mL of hexane, concentrated under vacuum to < 1ml and brought up to a final volume of 1 ml with iso-octane. Method blanks, an in-house reference tissue (Detroit River common carp *Cyprinus carpio*) and an external PCB reference standard (Quebec Ministry of the Environment Congener Standard) were included with every set of six samples.

PCB analysis was performed using an electron capture equipped gas chromatograph (GC-ECD) as described in Lazar *et al.* 1992. The Quebec PCB standard contains forty congeners, however, only 31 of these were consistently measured in all fish. These included PCBs 18/17, 31/28, 33, 44, 48, 52, 70, 74, 87, 95, 99, 101, 105/132, 110, 118, 128, 138, 149, 151/82, 153, 156/171, 158, 169, 170, 177, 180, 183, 187, 191, 194, 195/208, 201, 205, 206, 209 and represent a range of log K<sub>ow</sub> from 5.25 - 8.18 (Hawker and Connell 1988). For co-eluting congeners, the primary congener represents the dominant constituent of each peak. Recoveries of the PCB 34 spiking standard were 77.3 ± 1.1 % (mean ± standard error). Sum PCB concentrations quantified in the reference tissue homogenates averaged (176.1 ± 12.2 ng g<sup>-1</sup>) were within the quality assurance guidelines of GLIER’s organic analytical laboratory (mean ± 2 SD).
**Stable Isotopes**

Carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) stable isotope analyses were completed by the Trophic Ecology Laboratory at GLIER following the methods described in Burtnyk et al., (2009). Approximately 1 g of whole body homogenate was freeze dried for a minimum of 48 hours and then ground to a fine powder using a mortar and pestle. To remove potential bias in carbon isotope values due to lipids (Post et al. 2007), samples were lipid extracted using 5 mL of a 2:1 (v:v) chloroform:methanol extraction solvent. Samples were allowed to stand for a minimum of 48 hours before being centrifuged and then decanting the remaining supernatant and repeating the extraction process. Between 300 - 700μg of the lipid extracted sample was added to a 3.0 x 5.5mm tin capsule and the capsule was folded closed. Isotope values were determined using a continuous-flow isotope ratio mass spectrometer (Finnegan MAT Deltaplus, Thermo Finnegan, San Jose, California) coupled with an elemental analyzer (Costech, Valencia, California). Carbon and nitrogen stable isotope ratios were quantified using at least three reference standards that have been externally validated against National Institutes of Standards and Technology (NIST) standard materials. Precision values (mean ± SD) $\delta^{13}C$ and $\delta^{15}N$ were -25.5 (0.08) and 6.4 (0.1), respectively, based on analyses of at least 100 analysis of a NIST standard (SRM 8414 – bovine muscle standard).

**Data Analysis**

Lake trout growth rates were estimated using the Von Bertalanffy (VBL) growth curve outlined below:

\[
L_t = L_{\infty} \cdot (1 - e^{-k(t-t_0)})
\]
where \( L_t \) is the total length in centimetres at time \( t \) (yrs), \( L_\infty \) is the theoretical maximum total length, \( k \) is the growth rate of the fish (yr\(^{-1}\)), and \( t \) is the age of the fish (yrs). Since fish were not collected at all age classes at all sites, in order to remain consistent across the sampling locations, von Bertalanffy growth calculations were completed using fish between 3 – 9 years of age for the Stokes Bay, Goderich and Frazer Bay collections. For the Douglas Point and Cape Rich collections, VBL model calculations were completed using 2 – 9 and 2 – 8 year old fish. The VBL model predicted length at age values were then converted to mass at age using the length-weight relationships obtained at each site for the respective age ranges of fish. The mass at age values were then used to estimate specific growth rates for lake trout age classes as described below (Ricker 1979):

\[
G = \left[ \frac{W_t}{W_0} \right] \times 100
\]

where \( G \) is the specific growth rate (g g\(^{-1}\) d\(^{-1}\)), \( W_t \) is the mass (g) of the fish at time \( t \) (d), and \( W_0 \) is the mass of the initial age class.

PCB congener bioaccumulation dynamics for the three basins of Lake Huron lake trout were compared by calculating congener bioaccumulation coefficients (CBC) following the method of Burtnyk et al., (2009). For this calculation, lipid corrected PCB congener concentrations quantified in individual lake trout were normalized to the average lipid corrected congener concentration measured in one of the youngest age classes collected at each site in order to correct for background contamination:
\[ f = \frac{[PCB_t]}{A} \]

where \( f \) represents the change in fugacity relative to that in a two or three year old trout, \([PCB_t]\) is the lipid normalized PCB congener concentration at age \( t \), and \( A \) is the average lipid normalized PCB concentration for a two or three year old fish collected at each sampling location. In order to remain consistent and allow comparisons, the same age ranges used to calculate daily growth rates were used to calculate the \( CBC \)'s. PCB congener bioaccumulation coefficients were determined from the linear regression relationship between age normalized PCB congener fugacities and lake trout age outlined below:

\[ f = CBC \,(Age) + c \]

where \( f \) represents the age corrected PCB congener fugacity, the \( CBC \) is the regression slope coefficient, and \( c \) is the regression intercept. Statistically significant \( (P < 0.10) \) \( CBC \) values represented non-steady state bioaccumulation kinetics (Burtnyk et al., 2009).

Estimates of cumulative feeding events (\( CFEs \)) were calculated (Equation 8) in order to examine potential differences in feeding rates among lake trout from the three basins of Lake Huron.

\[ CFE = \frac{M_{180,LT}}{M_{180,FF}} \cdot 0.8 \]

where \( M_{180,LT} \) represents the mass of PCB180 in an individual lake trout, calculated from the product of body mass (gram) and PCB180 concentration (ng g\(^{-1}\)). The mass of
PCB180 in the forage fish $M_{180,FF}$ was estimated based on a composite diet of rainbow smelt and bloater. As a result of their relative abundances, smelt and bloater were assumed to be the primary source of PCB bioaccumulation for lake trout (Cottrill 2012). A dietary assimilation efficiency for PCB180 of 80% was used as per Thomann (1989) and Madenjian et al., (1993). Multiple iterations for each lake trout were completed to generate an average $CFE$ estimate by varying PCB180 concentrations and diet proportions of smelt and bloater. Prey fish PCB180 concentrations were randomized between 0.1 - 100% of the maximum concentration measured in each species. Proportions of smelt and bloater in the diet were randomized from 100% smelt to 100% bloater in 0.1% increments. Model sensitivity was completed using the same range of diet and PCB180 values but while maintaining diet at an equal composition of rainbow smelt (50%) and bloater (50%), or tested using average PCB180 concentrations for each prey type and varying the diet composition over the same range of values outlined above.

Statistical analysis was performed using SYSTAT 11 (SYSTAT 2004). Unless otherwise stated, significance was assumed at the $P < 0.05$ level, and reported values represent mean ± 1 standard deviation. Analysis of variance (ANOVA) were performed to determine if differences exist in size and chemical concentrations in lake trout among sites. Analysis of covariance (ANCOVA) were performed in order to determine if differences exist in the $CBC$’s both among sites and among basins.

**Results**

A summary of the lake trout collection information including biological, PCB and stable isotope data is provided Table 3.1. A total of 158 lake trout ranging from 1 – 15
years of age were collected for this study. All 1 year old fish were collected from Frazer Bay with the oldest individual caught during the Douglas Point collections. Fish mass ranged from 37.5 – 6600 g with these extremes representing fish collected from Frazer Bay and Douglas Point, respectively. With the exception of the fish from the Douglas Point, which were collected during spawning, lake trout lipid contents were positively correlated with age at all other sites. For the Stokes Bay, Goderich and Frazer Bay collections, the relationships between lipid content and age were significant ($P < 0.01$), however, for the Douglas Point and Cape Rich collections these relationships were not significant ($P > 0.05$). Individual lake trout $\Sigma$PCB concentrations ranged from 8.3 – 1842.4 ng g$^{-1}$ (wet weight) among the collection locations (Table 3.1; Figure 3.2). Average $\Sigma$PCB (±SD) concentrations among the collections locations were lowest for fish collected from Frazer Bay (41.9 ± 23.6 ng g$^{-1}$) with fish from Douglas Point having the highest average $\Sigma$PCB concentration (349.4 ± 301.5 ng g$^{-1}$). $\Sigma$PCB was positively correlated with both age and body mass for all fish ($P < 0.01$) (Figure 3.2). Lipid normalized $\Sigma$PCB were also positively correlated with both age and mass ($P < 0.01$).

Data for the forage fish is summarized in Table 3.2. For smelt, total lengths ranged from 10.3 - 25.0 cm, 10.7 - 16.2 cm, and 11.0 - 22.8 cm for Goderich, Cape Rich, and Frazer Bay respectively. Smelt were significantly smaller at Cape Rich compared to the Goderich (ANOVA; $P < 0.05$), but not significantly smaller than fish from Frazer Bay ($P > 0.05$). Total lengths for bloaters ranged from 15.0 - 50.7 cm, 15.5 - 55.1 cm, and 15.0 - 71.3 cm for Goderich, Cape Rich and Frazer Bay respectively. Bloaters captured in Frazer Bay were significantly larger ($P < 0.01$) than the bloaters caught from the other sites. $\Sigma$PCB for bloaters were significantly lower in Frazer Bay versus Cape Rich and
Goderich ($P < 0.03$). ΣPCB for smelt were significantly higher for Goderich smelt ($P < 0.01$) relative to the other sites.

Based on the VBL growth models, $L_\infty$ and $k$ were calculated to be 83.4 and 0.22, 70.1 and 0.251, 68.0 and 0.444, 75.3 and 0.213, and 74.0 cm and 0.259 year$^{-1}$ respectively for Stokes Bay, Goderich, Douglas Point, Frazer Bay, and Cape Rich fish respectively. At all age classes, specific growth rates (Figure 3.3) were highest in the Stokes Bay trout, while the lowest were measured at Douglas Point. For all sites, the greatest decline in specific growth rates was between ages 1 and 2. Stokes Bay had the largest decrease from 0.00544 to 0.00282 (g g$^{-1}$ d$^{-1}$), a difference of 0.00262 (g g$^{-1}$ d$^{-1}$). This is closely matched by that between ages 2 and 9 with a difference of 0.00253 (g g$^{-1}$ d$^{-1}$). By age 5, all daily growth rates were below 0.10% (d$^{-1}$), however trout from Douglas Point were below 0.10% (d$^{-1}$) by year 3.

Lake trout $\delta^{13}$C were most negative for Stokes Bay fish ($P < 0.01$), while Fraser Bay ($P < 0.01$), and Cape Rich ($P < 0.02$) trout were significantly more negative with age (Figure 3.4). Goderich and Douglas Point demonstrated no change in $\delta^{13}$C signature with age. The $\delta^{15}$N showed a significant increase in Stokes Bay ($P < 0.01$), Douglas Point ($P < 0.01$), and Frazer Bay ($P < 0.01$) fish. All sites, with the exception of Douglas Point, had a difference smaller than 2.5‰ between the lowest and highest individual. The greatest difference among individuals at Douglas Point was 4.2‰ (Figure 3.5). Lake trout from the main basin did not differ significantly in both $\delta^{13}$C and $\delta^{15}$N.

Goderich and Cape Rich had 17 congeners ($\log K_{ow} 6.13 - 8.18$) that exhibited significant increases in CBC’s, which was the most among all sites (Figure 3.6). Frazer Bay had the least number of significant CBC with only 2. The only congener with
significant increases in \( CBC \)s at all sites was PCB congener 170. The only site to not demonstrate a significant relationship with \( K_{ow} \) and the congener bioaccumulation coefficient was Frazer Bay (\( P > 0.05 \)). Cape Rich exhibited the strongest relationship between \( K_{ow} \) and the congener bioaccumulation coefficient, and was significantly different than the other sites (ANCOVA, \( P < 0.01 \)). The slope was approximately 3 times greater than any of the other sites located in the main basin, and was 6 times greater than that observed in Frazer Bay. The \( CBC \)'s from the main basin (Goderich, Douglas Point, Stokes Bay) did not differ significantly (ANCOVA, \( P > 0.05 \)). PCB 48 (\( \log K_{ow} \) 5.85) in the Goderich trout was the least hydrophobic congener to reveal a significant \( CBC \). In Stokes Bay, PCB 170 (\( \log K_{ow} \) 7.27) was the least hydrophobic congener to show a significant \( CBC \).

Model cumulative feeding events varied from basin to basin (Figure 3.7). An individual from the main basin was estimated to have the highest cumulative feeding events (not shown on Figure 3.7) with 24,619. The sensitivity analysis however, suggests that, on average, lake trout from Georgian Bay consume more food at a given age, while lake trout from the North Channel have the lowest feeding rates among the three basins.

**Discussion**

PCB bioaccumulation patterns of hydrophobic congeners (\( \log K_{ow} > 6.2 \)) for Lake Huron lake trout are indicative of non-steady state dynamics, whereas those with a lower \( K_{ow} \) revealed steady state dynamics. There were significant site to site differences in both the magnitude of PCB bioaccumulation and also the relationship between \( \log K_{ow} \) and the
congener bioaccumulation coefficients. These differences were basin specific and indicate that other, likely ecological, factors have relatively important roles in the kinetics and patterns of PCB bioaccumulation observed in Lake Huron lake trout.

The data presented in this study clearly demonstrated that lipid corrected chemical concentrations increased significantly with age (Figure 3.2). Bioconcentration, as predicted by Leblanc (1995) would not explain this observation. Factors regulating individual growth dynamics are key factors regulating bioaccumulation. In this study, lake trout growth varied both spatially and temporally, until near zero specific growth rates after 5 - 7 years of age. Consequently, chemical concentrations in older fish increased dramatically as a result of constant uptake from the diet, with little or no chemical elimination, or minimal growth dilution effects.

Diet is the major exposure route for larger, top predator organisms such as lake trout to persistent organic pollutants (Luk and Brockway, 1997). Prey fish abundances have changed significantly in Lake Huron between 1994 and 2007. The overall abundance of total forage fish has decreased by approximately 80%, with alewife (*Alosa pseudoharengus*), a key food source for lake trout since invading the lake in the 1930's, becoming nearly extirpated in Lake Huron (Roseman and Riley, 2009). Among the three basins of Lake Huron, there are also significant differences in the overall abundances of prey fish species (Schaeffer et al., 2011). Prey fish abundances among the three basins revealed that Georgian Bay has the lowest overall abundances of forage fish, approximately 5 times less than what is found in the North Channel, and 8 times lower than the Main Basin of Lake Huron (Schaeffer et al., 2011). If, however, lake trout
abundances are corrected for basin volume, the North Channel has the highest density of forage fish available for lake trout to consume (see Table 3.3).

Lake trout are size selective predators (Christie et al., 1987), and will seek out the largest food source available in order to maximize the amount of energy consumed (Kerr et al., 1971). It is possible that changes in diet and foraging costs explain the significant increases in lipid normalized chemical concentrations with age. If lake trout continually fed on larger forage fish as they grow, it would be difficult to maintain a steady state condition bioaccumulation pattern as a result of larger forage fish tending to be more contaminated than smaller fish (Jackson and Schindler, 1996). Although specific sites did show significant increases in the δ^{15}N signatures with age, with the exception of trout caught from Douglas Point, the difference between the lowest and highest δ^{15}N values were less than one trophic level (3.4‰, Post 2002), thus it is not likely that the increases in chemical concentration with age seen among sites were a function of diet shifts in the lake trout. Frazer Bay and Cape Rich were the only sites where lake trout δ^{13}C changed significantly with fish age. At these sites, lake trout δ^{13}C values became more negative with fish age, suggesting that younger lake trout spawn and forage near shore until they are large enough to be able to feed on offshore forage fish. Lake trout from the main basin (Stokes Bay, Goderich and Douglas Point) had no changes in their δ^{13}C values with age. Relative to the other basins, Frazer Bay had less negative δ^{13}C signatures both in lake trout, but also in forage fish suggesting that the basin overall has a low δ^{13}C signature.

All sites sampled revealed significant differences in their patterns of bioaccumulation with respect to \( K_{ow} \). Trout from the three Main Basin sites revealed a
similar trend of moderate bioaccumulation, whereas the Frazer Bay trout demonstrated minimal bioaccumulation of chemicals. Cape Rich fish however, were clearly accumulating chemicals at a greater rate than measured at the other sites. The highly hydrophobic congeners (log $K_{ow} \geq 6.2$), exhibited higher rates of bioaccumulation. The lower prey fish abundances in Georgian Bay provide a plausible explanation as to why Cape Rich fish are accumulating PCB's at a greater rate than lake trout in the other two basins. Differences in growth rates are primarily due to the increased energetic costs associated with searching and capturing prey, rather than a difference in the overall quality of food (Pazzia et al., 2002). As discussed previously, lake trout will search out the largest food available as this has the greatest energetic benefit. Cape Rich lake trout growth rates were comparable to those determined for the other sites, but prey fish abundances in Georgian Bay are significantly lower, indicating that these lake trout are spending significantly more energy in the search of food. Trout from Georgian Bay eat more food, by mass, in order to achieve similar growth rates measured in the other basins. Consequently, lake trout from the Cape Rich site are accumulating PCBs at a greater rate, as a result of consuming more forage fish to achieve the same size relative to fish in the other basins (Figure 3.7).

Lake trout from Frazer Bay demonstrated no relationship between $CBC$ with $K_{ow}$ indicating that chemicals in these fish are at steady state. Lake trout from this location have the slowest growth rates, therefore these fish are more capable of eliminating chemicals at a faster rate than larger fish (Sijm and Vanderlinde, 1995; Paterson et al., 2007). The feeding analysis, however, suggests that Fraser Bay trout have consumed the
fewest number of meals at a given age, indicating that these lake trout require less food (therefore less PCB uptake) and spend less energy than lake trout in the other basins.

Madenjian et al. (1993) developed an individual based model that explained a large portion of the variability measured in lake trout in Lake Michigan. By changing the variability of contaminant concentrations in the forage fish, the model was better able to predict concentrations in the lake trout. The Madenjian et al. (1993) model simulated random encounters of lake trout and forage fish, and based on size of the lake trout and prey fish, determined whether individual lake trout were successful in capturing prey. The model was able to predict the general trend of PCB bioaccumulation in lake trout, however, it was unable to match the highest predicted PCB values in trout to the highest concentrations observed in wild lake trout. This modeling effort provided further evidence that ecological factors such as diet and feeding efficiency are critical for our understanding of PCB uptake rates and the differences in contaminant burdens observed among individuals.

The feeding analysis (Figure 3.7) suggests that lake trout in Georgian Bay have a greater number of feeding events relative to lake trout from the other two basins. This increased feeding activity supports the hypothesis that trout in this basin are having to feed more often just to maintain a growth rate that is comparable to those fish in the other basins. It is interesting to note that although the Main Basin had the greatest areal abundance of forage fish, lake trout in Frazer Bay were still the most efficient at acquiring prey. Since Frazer Bay had, on average, the largest forage fish, this suggests that Frazer Bay lake trout would need to consume fewer meals on average, as each feeding event would generally result in a greater energetic payoff. Lake trout in Georgian
Bay however, have a severe disadvantage, because overall abundances of forage fish were low compared to the other basins, but also, smelt were significantly smaller. Therefore, even when lake trout capture smelt, they were receiving less of an energetic payoff when compared to either Frazer Bay or the Main Basin. The cumulative feeding estimates in this study are likely underestimates of the true value, as the forage fish were captured using gill nets and may not represent the relative abundance of large and small individuals at their respective sites.

This study clearly demonstrated that bioaccumulation was regulated by ecological processes operating within the three basins of Lake Huron. When feeding rates of lake trout were shown to be high relative to other basins, the CBC’s of those fish, specifically for super hydrophobic chemical ($\log K_{ow} > 6.2$) were significantly higher. The CBC’s at all sites for less hydrophobic congeners ($\log K_{ow} < 6.2$) were similar among all sites, which suggests that for less hydrophobic chemicals, chemical factors are the driving factor in bioaccumulation patterns, as chemical factors cannot vary from site to site. However, for more hydrophobic chemical ($\log K_{ow} > 6.2$), ecological factors become more critical in the bioaccumulation patterns observed. In Burtnyk et al. (2009), bioaccumulation dynamics of bluegill (*Lepomis macrochirus*) and cisco (*Coregonus artedi*) were compared using the CBC method. These fish species inhabit littoral and pelagic habitats of the lake. Bluegill inhabit near shore, warm water habitats, while cisco's prefer much colder, and deep portions of the lake. Burtnyk et al. (2009) observed that differences exist in the bioaccumulation patterns among the species and concluded that these are attributed to ecological differences that exist among the fish. In this study, a single species was compared, but among different basins of Lake Huron. Different
patterns in PCB bioaccumulation in lake trout among the basins supports the hypothesis that ecological differences can determine whether an organism will achieve steady state with the chemical environment.

Overall, this study demonstrates the importance of ecological factors in the bioaccumulation processes in lake trout, as the bioaccumulation patterns differed significantly within each basin of Lake Huron. It is concluded that for high $K_{ow}$ congeners, lake trout bioaccumulation is dominated by non-steady state processes which are strongly regulated by ecological processes such as foraging efficiencies.
Table 3.1: Summary of biological and chemical data from all sampling sites. Values in brackets represent 1 standard deviation. Superscripts represent significant differences (ANOVA, \( P<0.05 \)) with Tukey's *post-hoc* test.

<table>
<thead>
<tr>
<th>Site</th>
<th>Age (yrs)</th>
<th>n</th>
<th>Mass (kg)</th>
<th>Length (cm)</th>
<th>Lipid (%)</th>
<th>( \delta^{13}C ) (‰)</th>
<th>( \delta^{15}N ) (‰)</th>
<th>( \sum \text{PCB} ) (ng g(^{-1}) ww)</th>
<th>( \sum \text{PCB} ) (µg g(^{-1}) lipid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stokes Bay</td>
<td>3-11</td>
<td>36</td>
<td>2.3(1.3)( ^{bc} )</td>
<td>59.4(10.6)( ^{bc} )</td>
<td>8.1(4.3)( ^{a} )</td>
<td>-23.7(0.9)( ^{b} )</td>
<td>12.7(0.6)( ^{a} )</td>
<td>115.8(88.0)( ^{b} )</td>
<td>1.7(1.5)( ^{a} )</td>
</tr>
<tr>
<td>Goderich</td>
<td>3-12</td>
<td>13</td>
<td>2.8(1.6)( ^{cd} )</td>
<td>60.6(11.3)( ^{bc} )</td>
<td>14.8(5.0)( ^{b} )</td>
<td>-23.6(0.6)( ^{b} )</td>
<td>13.1(0.5)( ^{ab} )</td>
<td>252.9(176.4)( ^{bc} )</td>
<td>1.7(1.5)( ^{ab} )</td>
</tr>
<tr>
<td>Douglas Point</td>
<td>2-15</td>
<td>45</td>
<td>3.0(1.0)( ^{d} )</td>
<td>66.3(6.9)( ^{c} )</td>
<td>13.5(3.8)( ^{b} )</td>
<td>-23.7(1.2)( ^{b} )</td>
<td>13.1(0.7)( ^{b} )</td>
<td>349.4(301.5)( ^{c} )</td>
<td>2.7(2.3)( ^{b} )</td>
</tr>
<tr>
<td>Frazer Bay</td>
<td>1-9</td>
<td>51</td>
<td>1.0(0.8)( ^{a} )</td>
<td>44.0(12.3)( ^{a} )</td>
<td>8.3(5.8)( ^{b} )</td>
<td>-21.5(1.3)( ^{a} )</td>
<td>12.6(0.4)( ^{a} )</td>
<td>41.9(23.6)( ^{a} )</td>
<td>0.9(1.0)( ^{a} )</td>
</tr>
<tr>
<td>Cape Rich</td>
<td>2-13</td>
<td>13</td>
<td>1.6(1.5)( ^{ab} )</td>
<td>49.4(13.1)( ^{ab} )</td>
<td>10.2(2.7)( ^{ab} )</td>
<td>-22.8(0.9)( ^{b} )</td>
<td>12.9(0.6)( ^{ab} )</td>
<td>74.6(58.4)( ^{ab} )</td>
<td>0.8(0.7)( ^{a} )</td>
</tr>
</tbody>
</table>
Table 3.2: Summary data on 2011 forage fish from the three basins. Numbers in brackets represent 1 standard deviation. ΣPCB data given is based off 5 randomly selected individuals chosen for extraction. Letters in superscript represent significant differences (ANOVA, $P<0.05$) using Tukey's post-hoc test.

<table>
<thead>
<tr>
<th>Species</th>
<th>Basin</th>
<th>N</th>
<th>Total Length (cm)</th>
<th>Mass (g)</th>
<th>Lipid %</th>
<th>$\delta^{13}$C ‰</th>
<th>$\delta^{15}$N ‰</th>
<th>ΣPCB (ng g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelt</td>
<td>MB</td>
<td>80</td>
<td>15.7(3.2)$^a$</td>
<td>24.1(16.8)$^a$</td>
<td>5.0(1.6)$^a$</td>
<td>−24.5(0.8)$^a$</td>
<td>8.8(0.5)$^a$</td>
<td>56.4(16.0)$^a$</td>
</tr>
<tr>
<td></td>
<td>GB</td>
<td>19</td>
<td>13.6(1.4)$^b$</td>
<td>13.3(4.0)$^b$</td>
<td>1.5(0.3)$^b$</td>
<td>−22.6(0.6)$^b$</td>
<td>9.9(0.3)$^b$</td>
<td>10.2(3.5)$^b$</td>
</tr>
<tr>
<td></td>
<td>NC</td>
<td>30</td>
<td>14.8(3.2)$^a$</td>
<td>22.5(15.6)$^{ab}$</td>
<td>2.9(1.1)$^b$</td>
<td>−20.7(0.7)$^c$</td>
<td>10.7(0.6)$^c$</td>
<td>13.6(3.1)$^b$</td>
</tr>
<tr>
<td>Bloater</td>
<td>MB</td>
<td>57</td>
<td>17.0(1.1)$^a$</td>
<td>34.5(5.3)$^a$</td>
<td>4.7(1.7)</td>
<td>−24.3(0.6)$^a$</td>
<td>8.8(1.1)$^a$</td>
<td>54.8(10.2)$^a$</td>
</tr>
<tr>
<td></td>
<td>GB</td>
<td>10</td>
<td>17.3(1.1)$^a$</td>
<td>42.6(10.3)$^{ab}$</td>
<td>3.9(0.8)</td>
<td>−24.0(0.3)$^a$</td>
<td>10.9(0.5)$^b$</td>
<td>39.4(19.0)$^a$</td>
</tr>
<tr>
<td></td>
<td>NC</td>
<td>16</td>
<td>18.9(1.6)$^b$</td>
<td>49.4(12.8)$^b$</td>
<td>3.7(2.2)</td>
<td>−22.2(1.3)$^b$</td>
<td>10.3(0.5)$^b$</td>
<td>15.4(3.0)$^b$</td>
</tr>
</tbody>
</table>
Table 3.3: Surface area, morphometric characteristics, and prey fish abundance data for the basins of Lake Huron

<table>
<thead>
<tr>
<th>Basin</th>
<th>Surface Area (km²)</th>
<th>Mean Depth (m)</th>
<th>Volume (km³)</th>
<th>Prey Fish Abundance (kg ha⁻¹)</th>
<th>Prey Fish Density (kg km⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Basinᵃ</td>
<td>40,504</td>
<td>59⁺</td>
<td>2,389.7</td>
<td>18</td>
<td>3,050.8</td>
</tr>
<tr>
<td>Georgian Bayᵇ</td>
<td>15,111</td>
<td>44</td>
<td>664.9</td>
<td>2</td>
<td>454.5</td>
</tr>
<tr>
<td>North Channelᵇ</td>
<td>3,950</td>
<td>22</td>
<td>86.9</td>
<td>10</td>
<td>4545.5</td>
</tr>
</tbody>
</table>

ᵃ Main Basin characteristics from the National Oceanic and Atmospheric Administrations' Great Lakes Environmental Research Laboratory website (http://www.glerl.noaa.gov/pr/ourlakes/)
ᵇ Georgian Bay and North Channel basin surface area and average depth information from Ridgeway et al. (2006).
⁺ Represents average depth for Lake Huron's three basins.
ᵈ Prey fish abundance data from Schaeffer et al. (2011).
Figure 3.1: Map of Lake Huron. Stars represent general locations of where lake trout were sampled. Dashed line represents border between Canada and the United States (Image taken from Google Maps, modified by the author).
Figure 3.2: (A) Wet weight and (B) lipid normalized concentration of ΣPCB of all fish collected from (■) Goderich, (□) Stokes Bay, (▲) Douglas Point, (○) Frazer Bay, and (×) Cape Rich.
Figure 3.3: Specific growth rates of the individual sites from Lake Huron. Calculated using only individuals used in congener bioaccumulation coefficient calculations.
Figure 3.4: $\delta^{13}C$ stable isotope signature with age from all sites on Lake Huron. (A) contains both the Goderich and Stokes Bay populations depicted by open and closed squared respectively. (B) Douglas Point. (C) Frazer Bay. (D) Cape Rich
Figure 3.5: $\delta^{15}$N isotope signatures with age from all sampling sites in Lake Huron: (A) contains both Goderich and Stokes Bay lake trout depicted by open diamonds and closed squared respectively. (B) Douglas Point (C) Little Current (D) Cape Rich
Figure 3.6: Congener bioaccumulation coefficients in relation to hydrophobicity for: Stokes Bay (A), Goderich (B), Douglas Point (C), Frazer Bay (D) and Cape Rich (E). Dashed lines represent lines of best fit. Open boxes symbolize significant relationships for CBC's. ANCOVA reveals that the slope of Cape Rich is significantly greater than the other sites ($P < 0.01$)
Figure 3.7: Estimated cumulative number of feeding events for Georgian Bay (▲), North Channel (■), and Main Basin (○) of Lake Huron respectively. Solid, dashed-dotted, and dashed lines represent lines of best fit for Georgian Bay, North Channel and Main Basin respectively. Dotted lines represent 99% confidence intervals.
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CHAPTER 4
GENERAL CONCLUSIONS

The goal of this thesis was to examine the causes of the collapse of the Lake Huron food web by examining annual primary production rates, and by quantifying bioaccumulation patterns in lake trout (*Salvelinus namaycush*) from the three basins of the lake. Understanding the processes that govern energy flow in a system is critical to the implementation of proper food web management strategies.

Bottom-up processes were predicted to be the cause of the significant declines reported at all trophic levels of Lake Huron. It was unclear, however, whether these changes resulted from a decrease in overall primary production, or from a drop in the efficiency of energy transfer up the food web. Open water annual primary production was measured in the main basin of Lake Huron over a span of two years (April to September) and was compared against previous estimates by Vollenweider et al. (1974) of 100 g C m$^{-2}$ yr$^{-1}$. Annual primary production is estimated to be 32 g C m$^{-2}$ yr$^{-1}$, one third of the Vollenweider et al. (1974) study. This large decrease in primary productivity strongly supports the hypothesis that the collapse of the Lake Huron food web is regulated by bottom-up processes, and that these declines are likely the result of changes in nutrient availability and potential effects of photo-inhibition. This argument is strengthened by the fact that overall chlorophyll $a$ assimilation efficiencies of less than 1 mg C mg chl $a^{-1}$ m$^{-3}$ hr$^{-1}$ were much lower than would be expected. Although the study is able to examine temporal trends in primary productivity, light and nutrient availability, it cannot make inferences on potential spatial differences that may exist in the lake because of the
limitation of only a single sampling location. Additionally, it was evident that the primary productivity set-up of a maximum depth of 15 m was clearly not deep enough for Lake Huron. Future studies would benefit from having multiple locations in each basin in order to confirm the overall results of this study as well measure primary productivity at deeper depths than 15 m.

Lake trout from all basins displayed significant increases in their lipid normalized concentrations of PCB's, which supports the hypothesis that non-steady state kinetics dominate bioaccumulation patterns. For an organism like lake trout where growth rates greatly decrease with time, it is demonstrated that as growth rates approach zero, the rate at which PCB's accumulate increases. Understanding the mechanisms which determine PCB bioaccumulation is critical in order to develop models that will accurately predict both the magnitude of contamination, and the individual variation that exists among fish.

The lake trout study also revealed the critical importance of ecological factors on the bioaccumulation dynamics of organic contaminants. Lake trout that are the most efficient at obtaining prey are also the least likely to demonstrate non-steady state dynamics for super hydrophobic (log $K_{ow} > 6.2$) congeners of PCB's. This further supports the hypothesis that Lake Huron is dominated by bottom-up processes, as it provides evidence that differences in the abundance of prey species can greatly influence higher trophic organisms by altering the efficiency in which lake trout obtain energy. This study could have greatly benefitted from a much larger sample size of lake trout, specifically from Georgian Bay. The low sample size, however, does highlight the fact that Georgian Bay has severely low abundances of lake trout, along with the forage fish population, since each site had similar sampling effort. Future studies might incorporate
other species of fish in order to confirm these results, additionally, a lab study conducted in parallel that would alter feeding rates and foraging costs would prove a powerful tool in confirming the observations and interpretations of this study.

In conclusion, both studies recognize the importance of ecological efficiencies to the health of the system. In chapter 2, extremely low chlorophyll a efficiencies are reported in the main basin of Lake Huron which suggests that phytoplankton are either highly nutrient limited, or photoinhibited, which reduces the rate of primary production. In chapter 3, feeding efficiencies differ significantly from site to site resulting in significant differences in the bioaccumulation patterns of PCB's in lake trout.
VITA AUCTORIS

NAME: Mark Ryder

PLACE OF BIRTH: Brampton, ON

YEAR OF BIRTH: 1987

EDUCATION:
Notre Dame Catholic Secondary School, Windsor, ON, 2005
University of Windsor, B.Sc., Windsor, ON, 2010
University of Windsor, M.Sc., Windsor, ON, 2013