Historic patterns of deposition and biomagnification of mercury in selected wetland systems

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titled

Historic Patterns of Deposition and Biomagnification of Mercury in Selected Wetland Systems

by

Brenda Sue Simmers Leady

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in Biology (Ecology Track)

________________________
Johan F. Gottgens, PhD, Committee Chair

________________________
Elliot J. Tramer, PhD, Committee Member

________________________
Frederick Williams, PhD, Committee Member

________________________
Alison L. Spongberg, PhD, Committee Member

________________________
Timothy G. Fisher, PhD, Committee Member

________________________
Patricia R. Komuniecki, PhD, Dean
College of Graduate Studies

The University of Toledo
August 2013
An Abstract of

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Mercury (Hg) is a global pollutant impacting wildlife and humans, even at low levels. I addressed four topics in environmental Hg research that have not been emphasized in the literature. First, I examined the utility of lake sediment cores in documenting Hg input and output from a system. I tested the similarity of records of US industrial Hg consumption (“environmental input”) and tissue levels in walleye (Stizostedion vitreum vitreum) (“biological output”) with Hg stratigraphy in cores from the western basin of Lake Erie. Hg consumption correlated with Hg accumulation rates in one core ($R^2=0.39$, $p<0.001$) but not in the other. Hg accumulation rates correlated with the history of walleye tissue Hg levels in both cores ($p<0.001$). The model for fish tissue levels calculated a 1945 mean of 80 ng Hg g$^{-1}$ (similar to reported results of 75 ng Hg g$^{-1}$) and hind-casted a mean of 17 ng Hg g$^{-1}$ for ca. 1900 fish tissue levels, providing a reasonable restoration target. Second, I compared mercury dynamics in two regions of a tropical wetland differing in their history of mercury contamination. I found a significant impact of Hg in the northern Pantanal (Brazil), an area with a recent history of gold mining, as compared to a 200km distant reference site in the same wetland. Average pre-
1940 Hg accumulation in cores was not significantly different (N=5, p=0.14) between both regions and comparable with rates calculated for global reference sites. Post gold-rush Hg (post-1980) deposition was more than 1.5 times higher than the post-1980 rate in the reference sites, implying a regional Hg effect of gold mining. A significant impact on sediments, plants, and fish was also found. *Salvinia auriculata*, suggested as a biological monitor for Hg pollution, contained almost four times more Hg in the northern Pantanal (90.7 ± 9.1 ng g$_{dry}^{-1}$) than in the reference site (24.5 ± 3.3 ng g$_{dry}^{-1}$). Third, I contrasted Hg biomagnification in a temperate and tropical system. A significant directional increase in both methyl Hg (MeHg) and total Hg (THg) was found in both the Lake Erie East Marsh (both p=0.001) and Pantanal trophic levels (THg p=0.0002, MeHg p=0.001). Biomagnification factors, the magnitude of change in mercury burden between trophic levels, were similar in the top predator in each system (East Marsh, *Micropterus* 5.5; Pantanal, *Pygocentrus* 6.2) but the magnitude from omnivores to top predator was different (East Marsh 53.6 versus Pantanal 9.6). The rate of increase in Hg tissue levels as fish increase in size was highest in the top predator in each system and decreased with decreasing trophic level. Finally, I examined the role of selective predation on Hg dynamics through a literature synthesis. Hg impaired predators may favor easy to capture prey that, in turn, are Hg impaired. This exacerbates biomagnification and suggests a new aspect of optimal foraging theory. I outlined lab and field studies to examine this impact in predatory fish. Mechanisms involved in Hg magnification along food chains deserve more attention, particularly in tropical regions where the threat of chronic exposure to this neurotoxin may have the greatest implications for biodiversity.
This is for the two most important men in my life, my father, Ralph Simmers, and my husband, Dale Leady.
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I’d like to thank my family. My father, Ralph Simmers, passed on before I finished my degree. He is and always will be my role model for doing the right thing. My mother, Verna Simmers, has been through all my ups and downs along the way. My husband is my biggest fan. I love you more than words can say.

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Many grad students have come and gone during my own program. Marci Cole finished an M.S. on mercury in wetlands. We spent many hours twisting little wires in the basement. Michael Benedict was a tour guide on my first trip to Brazil. His assistance in the field was invaluable.

My committee has changed over the years. My current committee has helped me achieve a lifetime goal. I’d like to thank Dr. Tramer, who has been with me since the start, Dr. Fisher, Dr. Spongberg, and Dr. Williams. Lastly, I could not have done this without Dr. Gottgens. I’ve been a frustrating and difficult graduate student. You’ve been a patient and supportive advisor.
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List of Abbreviations

ANCOVA ................ Analysis of covariance
ANOVA ................ Analysis of variance

BASF ................ Badische Anilin- und Soda-Fabrik
BMF ................ Biomagnification factor (the magnitude of change in mercury burden between trophic levels)

cf. .................. Confer, “compare”
CRM .................. Certified reference materials
CRS .................. Constant Rate of Supply
CVAFS ............... Cold vapor atomic fluorescence spectroscopy

D.L .................. do Leverger

e.g ................ Exempli gratia, "for the sake of example"
et al ................ Et alii, “and others”

i.d .................. Inner diameter
ITCZ .................. Intertropical conversion zone

NIST ................ National Institute of Standards and Technology

SCUBA ................ Self-contained underwater breathing apparatus
SD .................. Standard deviation
Sp .................. Species
SRB .................. sulfur reducing bacteria
Sto ................ Santo

TL .................. Total length
USEPA .......................United States Environmental Protection Agency
USFDA .....................United States Food and Drug Administration
USGS ........................United States Geological Service

$z_{\text{max}}$ ........................Maximum depth
List of Symbols

± .................................. Plus or minus
° .................................. Degrees latitude or longitude

γ .................................. Gamma
δ^{15}N ............................ Delta-N-15 measure of the ratio between 15N:14N

%ME ............................ Percent of total mercury that is methylmercury
°C ............................... Degrees Celsius
^{137}Cs ......................... Cesium-137
^{210}Pb .......................... Lead-210
^{222}Rn .......................... Radon-222
^{226}Ra .......................... Radium 226
^{238}U ............................ Uranium-238
CH_{3}Hg ........................ Methylmercury
cm ............................. Centimeters
Hg .............................. Mercury
Hg^{0} ........................... Inorganic mercury
keV ............................. Kiloelectronvolt
Kg .............................. Kilogram
L ............................... Liter
m ............................... Meter
Me_{2}Hg ........................ Dimethyl mercury
MeHg ........................... Methylmercury
mg ............................. Milligram
min ............................. Minute
mm ............................. Millimeter
NaTEB .......................... Sodium tetraethyl borate
ng ............................. Nanogram
nm ............................. Nanometer
p ................................ P value
pCi ............................. Picocuries
pH .............................. Potential of hydrogen
ppm ........................... Parts per million
R^{2} ............................ R-squared
THg ......................... Total mercury
TP ......................... Total phosphorus
µg ......................... Microgram
y ......................... Year
Chapter 1

Introduction

Over the last several decades an incredible amount of work has been done on mercury in the environment. Mercury is highly toxic even in small doses. Its unique chemistry allows for a long residence time in the atmosphere and worldwide deposition (Fitzgerald et al. 2005). Studies range from environmental transport to effects in wildlife and humans (for review see Boening 2000). Time scales range from changes in chemical state in minutes (review of atmospheric chemistry in Schroeder and Munthe 1998) to months (Hg flux in the Arctic in Steffen et al. 1992) to hundreds of years in sediment cores (Lockhart et al. 2000). My work aims to augment our understanding of the transport and fate of mercury in the environment in areas where our knowledge base is incomplete. I examine mercury deposition in terms of century-long time scales using dated sediment cores, regional differences using sites in temperate and tropical aquatic systems, speciation of methyl and total mercury accumulation and magnification in food chains, and the potential of mercury’s impact on differential and selective predation.

Mercury is a naturally occurring element found in water, soil, rocks and volcanic dust. It is rare in the Earth's crust, having an average crustal abundance
mass of only 0.08 parts per million (ppm). Mercury deposits, however, are fairly concentrated. It is found either as a native metal (rare) or in cinnabar (most common).

### 1.1 Use of Mercury

Human use of mercury has been dated back to at least 1500BC in Egyptian tombs. The use of mercury in making amalgams dates back to at least 500BC. Mercury’s ability to form amalgams with gold and silver has had important applications in mining for those metals. Mercury was imported from mines in Spain to extract silver from Mexican and South American mines beginning in 1558. Later, mercury discovered in Huancavelica, Peru supplied the mines. More than 100,000 tons of mercury were mined over three centuries. Most mercury mines have shut down due to either depletion of the resource or the low global price of mercury.

The use of mercury in manufacturing is declining due to environmental regulations. Historical uses took advantage of mercury’s unique chemical properties. The hat trade used mercury in producing felt hats because it cut down on microbial slime. The phrase “mad as a hatter” was in use before Lewis Carroll's book *Alice's Adventures in Wonderland*. However, hatters and other mill workers suffered neurological damage including confused speech and distorted vision due to mercury poisoning. Methyl mercury was released into Minimata Bay in effluent from Chisso Chemical Company’s acetaldehyde facility where mercury was used as a catalyst. Pollution was so heavy at the mouth of the wastewater canal that a figure of 2 kilograms (kg) of mercury per ton of sediment was measured: a level that would be economically viable to mine. As of 1995, 2,252 victims had been officially recognized and 1,043 have died (Harada 1995).
The largest use of mercury in the late 20th century was in the production of chlorine and sodium hydroxide from salt water using a mercury cathode (Leopold 2002). In the United States (US), chlor-alkali plants have to report unaccounted for mercury losses to the United States Environmental Protection Agency (USEPA). In 2000 alone, approximately 65 tons were unaccounted for (USEPA 2003). Most production has now shifted to membrane technology that is mercury free and more energy efficient (Dufault et al. 2009).

Mercury has also been widely used in medicine. Pliny (23-79 AD) described the use of mercury in treating venereal diseases. Both internal and external applications were used for mercury in a variety of forms over the centuries. Today, concerns over health and environmental impact have reduced mercury’s use in medicine and medical devices. Thimerosal was used since the 1930s as a preservative in medical preparations including vaccines (USFDA 2012). Concerns over the exposure of a child’s developing nervous system to mercury caused a re-evaluation of its use. In the United States, vaccines for children contain no or only trace amounts of thimerosal (USFDA 2012). Mercurochrome was a once widely used topical antiseptic. It was discontinued in the US in 1998 but continues to be available in other countries (USFDA 2009).

1.2 Mercury in the Environment

Mercury cycles in the environment through compartments including water, sediment, air, and biota. Natural and anthropogenic activities release mercury into the atmosphere. Most atmospheric mercury (>95%) is in the elemental form (Hg\(^0\)). Natural sources releasing mercury to the atmosphere include volcanoes and the
degassing of the hydrosphere and lithosphere. Natural sources are responsible for approximately half of atmospheric mercury emissions (OECD 1994).

Globally, the reservoir of atmospheric mercury has increased by a factor of 2-5 post-industrialization (Engstrom and Swain 1997). In the US, the largest sources of mercury to the air are coal-fired power plants (50% of total manmade mercury emissions), industrial boilers (7%), burning of hazardous waste (4%), and electric arc furnaces in the steel industry (7%) (USEPA 2005). US anthropogenic mercury emissions are estimated to account for roughly 3 percent of the total global emissions (Branch 2008).

Mercury can be deposited from the atmosphere in either wet or dry deposition. Precalcaldu industrial atmospheric deposition rates have been estimated at 2-5µg m⁻² y⁻¹ (Swain et al. 1992). Modern deposition rates in areas not directly mercury impacted are around 15µg m⁻² y⁻¹ (Biester et al. 2007). Engstrom and Swain (1997) predicted that, based on the trend in their findings, global anthropogenic contributions may soon surpass regional anthropogenic contribution in Midwestern US lakes.

Atmospheric residence times vary based on the form of mercury. Atmospheric residence time of particulate mercury and mercury compounds is relatively short. These mercury species will be deposited near to their sources (Lindqvist and Rodhe 1985; Slemr et al. 1985). Residence times for elemental mercury range from 0.7-2.0 years and are sufficiently long to indicate the potential for global distribution (Slemr and Langer 1992).

Prior to the 1960’s, inorganic mercury was believed to be relatively inert in the environment. Then, it was demonstrated that inorganic mercury could be biotically and abiotically converted to MeHg (Wood et al. 1968). The exact methylation
mechanism used by bacteria is unknown but it may function as a microbial detoxification and excretion mechanism (Lindqvist and Schroeder 1989). Gilmour et al. (1992) suggested that anaerobic sulfur-reducing bacteria (SRB) produce MeHg as a byproduct of their natural sulfur chemistry under some conditions. MeHg is the most toxic and readily bioaccumulated form of the major species of mercury (Brossett 1987; Fitzgerald and Watras 1989).

1.3 Bioaccumulation and Biomagnification

The ability of mercury to bioaccumulate has intensified research interest. Bioaccumulation is the uptake and concentration of a toxic substance from the environment. Biomagnification is the increase in contaminant concentration in an organism in excess of bioaccumulation and is caused by the transfer of contaminant residues from lower to higher trophic levels.

MeHg readily bioaccumulates and biomagnifies in organisms. It is not easily metabolized or eliminated due to its highly lipophilic and very stable nature. MeHg is the only species of mercury to undergo biomagnification. Inorganic mercury (Hg⁰) and dimethyl mercury (Me₂Hg) do not biomagnify simply because they diffuse out of the cellular environment as freely as they enter it (Clarkson 1997). The high levels of mercury in long-lived species result from efficient uptake mechanisms from the environment and food organisms coupled with low elimination rates.

The proportion of MeHg relative to total mercury increases through the food web, being lowest in aquatic plants, intermediate in invertebrates and highest in fish, and piscivorous mammals and birds (CCME 2000; Keating et al. 1997). Almost all of the mercury found in biological systems has been absorbed in the form of MeHg
(Watras et al. 1998). MeHg is highly absorbable from the diet (95 to 100%) compared to inorganic mercury (5 to 10%) and can both bioaccumulate and biomagnify within aquatic food webs (CCME 2000; Wolfe et al. 1998).

In humans, two groups are most impacted by mercury exposure. The first group contains individuals who are sensitive due to age (children up to age 12 and women who may become pregnant). The second group contains individuals with high exposure risk including subsistence anglers, recreational fishermen, and indigenous populations. In humans, high dose effects of mercury include death, paresthesia (tingling), tremors, ataxia (lack of coordination), hearing and vision impairment, balance and speech disturbances, and motor difficulties. Children exposed in utero to high doses display cerebral palsy-like symptoms and delayed walking/talking. In utero exposure to lower doses caused delayed startle response, subtle neurological effects, deficits related to learning and information processing (Keating et al. 1997).

In wildlife, mercury exposure effects can include mortality (death), reduced fertility, slower growth and development and abnormal behavior that affect survival, depending on the level of exposure. In addition, research indicates that the endocrine system of fish, which plays an important role in fish development and reproduction, may be altered by the levels of MeHg found in the environment (Keating et al. 1997). As an example, in a lab study of zebra finches, chronic MeHg poisoning caused by ingestion of food containing 5 mg Kg$^{-1}$ MeHg led to reduced food intake, weight loss, progressive weakness in wings and legs, difficulty in flying, walking and standing, and an inability to coordinate muscle movement (Scheuhammer 1988).

Although acute neurological effects are usually not evident in wildlife, subtle behavioral alterations and reproductive impairment may be induced by chronic, low
level dietary MeHg exposure. Bouton et al. (1999) found that captive juvenile great egrets fed 0.5 mg Kg\(^{-1}\) MeHg in their diet demonstrated significantly different behavior compared to the control group. The dose chosen was comparable to actual dietary exposure levels of wild egrets in the Florida Everglades.

Linking biomagnification and the effect of mercury on behavior may be of significance in predator-prey interactions. Kania and O’Hara (1974) found after just 24 hours of exposure to 10 µg l\(^{-1}\) of mercury, mosquito fish were significantly more vulnerable to largemouth bass predation. Grayling embryos exposed to MeHg during development had impaired feeding efficiencies and reduced competitive abilities as adults (Fjeld et al. 1998). Golden shiners, fed diets that gave them a mean, whole-body total Hg concentration found in northern US lakes, demonstrated behaviors that would increase vulnerability to avian predators (Webber and Haines 2003).

**1.4 Research Objectives**

Even with the wealth of knowledge accumulated during decades of study, interesting questions remain in many areas of environmental mercury research including the reliability of using cores as records of deposition, tropical versus temperate ecosystem dynamics of mercury accumulation and magnification, the role of organic mercury in organisms, and the potential for mercury to impact predator and prey mercury body burdens and, therefore, mortality. My work attempts to address these questions in four specific objectives with an overall objective of increasing the understanding of the global mercury problem.

First, in the absence of long term data on the accumulation of mercury in ecosystems, lake sediments may provide an historical record of atmospheric
deposition. A core might contain a chronology of the mercury deposited to the sediments over time if mercury is not mobile in the sediments and if sediment layers have not been disturbed. If cores reflect the history of mercury deposition to a system (“inputs”), that chronology should correspond to historical sources of mercury to the system (globally and regionally). Cores would also correlate to “outputs” of mercury from an aquatic system such as tissue levels in fish taken from that lake. Lake Erie cores may serve as an excellent test case for this scenario due to the lake’s documented mercury pollution history and long term biological monitoring. Records of inputs to the system extend back over decades. “Outputs” from the system have also been monitored for decades. Mercury concentration in whole body homogenates of walleye (Sander vitreus vitreus formerly Stizostedion vitreum vitreum) from Lake Erie’s western basin have been analyzed each year since 1977. These data can be extended further using other sources. If cores reflect the history of mercury “input” and “output” to a system, then the mercury stratigraphy in the core should reflect the patterns found in historical databases and may allow both forecasting and hindcasting of mercury levels in fish.

Second, tropical systems have much less historical or current information on mercury dynamics compared to temperate systems. For example, only limited information is available on mercury use for the Pantanal, a large floodplain in central Brazil. If tropical system mercury dynamics are similar to temperate systems, then a comparison of mercury accumulation in a sediment core and in biota of an impacted site should reveal higher levels of mercury than those in a non-impacted control site. The cores would provide much needed historical information on previous mercury levels in the area and the onset of mercury contamination. A non-impacted site,
without a direct point source, documents the regional level of mercury impact. A survey of tissue levels in biota at both sites would allow me to compare tropical food chains to the better documented temperate food chains. If tropical systems follow the same patterns as temperate systems, then a mercury impacted site should have a higher rate of mercury deposition in the cores and higher tissue levels in biota than a non-impacted site in the same region.

Third, using samples collected in the Pantanal floodplain and in Lake Erie marshes, a comparison of total and organic mercury concentration in food webs is possible. MeHg is the most toxic and most readily biomagnified form of mercury. The process of mercury accumulation in fish has been studied extensively (for reviews see Boening 2000; Ullrich et al. 2001; Mousavi et al. 2011). However, the bulk of this work has focused on a limited number of species in a limited number of systems. The species of interest are primarily those of sport or commercial interest with direct impacts on human consumption. Trophic transfer at lower levels has been found to vary depending on physical and chemical characteristics of the lake, land use pattern in the watershed, etc. (Chen et al. 2005). Organisms representing different trophic levels will be analyzed for total and organic mercury concentration. In general, MeHg content increases with fish age and size. Although the same species are not present in each system, trophic levels such as primary producer or top carnivore may be comparable. This information can be used to improve the understanding of mercury biomagnification through comparison and contrast of “similar” food chains in dissimilar systems. If the process of mercury biomagnification is similar in Brazilian and Lake Erie wetlands, then a similar pattern of increase should be seen in mercury levels along the food chain.
Finally, the role of selective predation in mercury dynamics in the food web will be examined in a literature review and synthesis. I will review the current literature on the impact of mercury on predator and prey behavior and literature on selective predation. I will then link the two to show the potential impact of mercury on selective predation. Most models for mercury biomagnification utilize the average mercury body burden in prey to predict body burdens in the next trophic level. Average prey with average abilities to elude capture may not reflect reality. Among the earliest signs of dysfunction reported for humans and mammals exposed to MeHg are impaired vision, muscular weakness, and clumsiness (Keating et al. 1997). A predator may be selecting easy to catch prey over harder to catch prey. If predators themselves are mercury-impacted, the situation becomes even more likely. As an example, in 1965, in Niigata, Japan, “cat suicides” occurred because cats were being poisoned by mercury from dead fish on the beaches (Smith and Smith 1972). If those fish died of mercury poisoning, they would have higher body burdens than the average fish caught by researchers to document mercury levels. Higher levels of mercury in this easy to catch prey translated to higher rates of biomagnification in predators. If selective predation occurs based on mercury impacted predators and/or prey, then higher rates of biomagnification than predicted should be seen for average predators consuming average prey. Based on the literature synthesis, I will suggest lab and field studies to investigate the impact of selective predation on mercury biomagnification.

My research aims to contribute to the growing literature on mercury transport and fate by addressing these four research questions using a combination of field work in temperate and tropical aquatic systems, laboratory analyses of tissue and
sediment samples including the determination of sedimentary chronologies, and a
careful review and synthesis of available literature regarding the emerging issue of the
impact of selective predation on mercury body burdens in predators and prey.
Correspondence Between Lake Sedimentary Records and Long Term Databases for Mercury: A Lake Erie Test Case

Abstract

In the absence of long-term data on mercury accumulation, lake sediments may preserve a record of mercury input and its level in biological tissue. I tested the similarity of records of US industrial mercury consumption (“environmental input”) and tissue levels in walleye (*Stizostedion vitreum vitreum*) (“biological output”) with mercury stratigraphy in cores from the western basin of Lake Erie. Two cores, taken in 1995 and dated with $^{210}\text{Pb}$ and ancillary age markers, were analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) for total mercury. The 1995 core profiles showed mercury peaks in deposits dated to the late 1960s to early 1970s that corresponded to mercury peaks in surface sediments of a 1971 core from the same area. 1995 and 1971 cores were comparably enriched by a mean factor of 2.6±0.9SD. Total US industrial mercury consumption correlated with mercury accumulation rates in core A ($R^2=0.39$, $p<0.001$, $n=44$) but not in core B ($R^2=0.057$, $p=0.118$, $n=44$). Mercury accumulation rates correlated with fish tissue mercury concentrations in both
core A (R^2=0.52, p<0.001, n=44) and core B (R^2=0.51, p<0.001, n=44). Using a regression model for each core, I hindcasted average mercury levels of 25.5 (core A) and 8.9 (core B) ng Hg g^{-1} for pre-1900 fish tissues. These levels are much lower than 1993 levels of 100 ng Hg g^{-1}. The regression model was also used to hindcast to 1945 fish mercury levels. Museum fish analyzed in 1972 found 1945 tissue levels of 75 ng Hg g^{-1}. My regression model predicted a fish tissue level of 80 ng Hg g^{-1}. Caution should be used in assuming the relationship for sediment and fish tissue remains linear outside the range of data values but my model provides some restoration target for mercury levels in fish tissue pre-1900. Even in shallow systems (z_{max}< 10m), such as Lake Erie’s western basin, sediment cores preserved the documented record of mercury pollution and may be used to develop informed targets for restoration efforts.

2.1 Introduction

Lake sediment cores have been analyzed for mercury for many years as a way to understand mercury dynamics in a system in the past, establish baseline conditions and predict future trajectories. Records in cores are useful for long term trends that may not be as evident in short-term measurements. In a review of the utility of using lake sediment cores to document mercury deposition, Fitzgerald et al. (1998) found that the patterns in cores were “spatially and temporally coherent”. Timing of a rise in mercury accumulation coinciding with the start of the industrial period (pre-1850) was the same in almost every sediment core in lakes in the Midwestern US. The cores themselves ranged from less than 20 cm to over 90 cm long but all had a similar timing for the increase (Swain et al. 1992; Hurley et al. 1994; Engstrom and Swain
The magnitude of the rise in mercury increase was also very similar. Four studies of forty lakes in Canada and the US found modern concentrations elevated over background concentrations (pre-1900) by a ratio of 2.7±0.9 (Johnson et al. 1986; Rada et al. 1989; Swain et al. 1992). The pre-1900 concentrations were assumed to be the natural background rates of mercury in the system. The increase over this background rate was attributed to anthropogenic inputs resulting from local, regional and/or global increases.

An interesting set of papers based on cores in Clay Lake, Canada demonstrated the ability of cores to keep a mercury signal intact in the stratigraphy. This lake received inputs from a chlor-alkali plant that closed in 1970. A 1971 core showed a peak in mercury concentration at the surface (Armstrong and Hamilton 1973). In 1978, another core showed the peak a few centimeters deeper (Rudd et al. 1983). This was consistent with the contaminated sediments being buried under cleaner sediment. The latest core was in 1995 where the peak was several centimeters lower than previously (Fitzgerald et al. 1998). This clearly demonstrated cores retaining the signal of mercury contamination intact over time.

Similar to Clay Lake, Lake Erie also has a documented history of mercury pollution. Discovery of fish in Lake Erie with high mercury levels in their tissues led to a total sport and commercial fishing ban (Walters et al. 1974). The Great Lakes then became a focal point for mercury research in the early 1970s. The source of the majority of the mercury was traced to two chlor-alkali plants. The Dow Chemical Chlor-Alkali Plant in Sarnia, Ontario opened in 1949. A second chlor-alkali plant came online in 1965. These plants directly discharged mercury contaminated effluent
into the Detroit River leading into Lake Erie. In their 29 years of operation, these plants released about 390 tonnes of mercury (Gilbertson 2009).

Through the process of biomagnification, mercury deposited to water and sediments in lakes ends up in organisms. Hammerschmidt and Fitzgerald (2006) demonstrated the positive relationship between atmospheric deposition of mercury and state-wide average concentrations of methylmercury in largemouth bass in 25 states. Consumption of contaminated fish is the primary source of exposure for humans to mercury. Particularly at risk are fetuses exposed via the mother’s diet and young children with developing nervous systems (Grandjean et al. 1997). Currently, all 50 states have mercury in fish advisories (USEPA 2011). The USEPA chronic toxicity reference dose for humans is 0.001mg kg$^{-1}$ d$^{-1}$ or about four 227 gram freshwater fish meals per month in healthy adults (USEPA 2001).

Even chronic low doses of mercury have been shown to impact wildlife. Great white herons with elevated hepatic mercury had more diseases than low mercury counterparts (Spalding et al. 1994). In a study of captive great egret chicks, those fed low level mercury diets displayed decreased appetite and strength and altered maintenance behavior (Bouton et al. 1999). A multigenerational study on captive rats found significant effects of low doses of mercury on the subsequent generations’ reproduction (Lukacinova et al. 2012). Chronic exposure to low levels of mercury may produce magnified, long-term impacts in individual organisms, populations, communities and ecosystems.

The goal of this part of my dissertation was to correlate data from long term databases on mercury with mercury accumulation rates in cores in Lake Erie’s western basin. Sediment cores were used to establish a chronology of mercury
deposition over time. The chronology was then correlated to the known history of mercury pollution into the lake based on records of US industrial mercury consumption ("environmental input"), as well as the documented history of mercury levels in walleye (*Stizostedion vitreum vitreum*) ("biological output"). If significant, this correlation could be followed by a regression model that would allow me to "hindcast" past mercury levels in walleye.

The use of "hindcasting" is particularly valuable to set restoration goals. Mercury has always been present from natural sources to some extent in Lake Erie. An obvious goal is to reduce mercury in fish to below the 1 ppm USFDA action level. An ultimate goal would be to reduce mercury in fish to pre-industrial levels. Hindcasting may be used to establish such an informed target for restoration.

2.2 Methods

2.2.1 Site Description of Lake Erie

Lake Erie (42.2°N, 81.2°W) has a long, well-documented record with regards to its natural history and changes to the surrounding watershed. It is the shallowest, smallest and southernmost of the Great Lakes. The lake is divided into three basins with the western basin being shallowest. The lake is directly impacted by runoff from its densely populated, intensively farmed and highly industrialized watershed. The Detroit River is the major surface inflow of water for the lake. However, the Maumee River is the major source of suspended and dissolved solids (Rush 1982). The 1.7 million hectare Maumee River watershed is primarily agricultural and as a result produces a high sediment load. Walleye fishing has been important historically with commercial catches as high as 6,800,000 kg yr⁻¹ (OHC 2005). Commercial catches
dropped by the 1960s and were banned in 1970 due to high mercury levels (OHC 2005). Release of captive-reared walleye into the lake has increased sport fishing catches in the “Walleye Capital of the World” (OHC 2005). The lake, in particular its western basin, is tightly linked with watershed activities. Not only is the lake used for shipping, fishing, recreation and water supply, it also receives treated waste water effluent and cooling water from a coal-fired power plant.

### 2.2.2 Sediment coring in Lake Erie

In 1995, two sediment cores were obtained in the western basin of Lake Erie (core A- 41°52’73N 83° 09’45W and core B- 41° 45’55N 83° 06’26W) (Figure 2.1). A polycarbonate push core (inner diameter i.d. 7.5cm) was used by self-contained underwater breathing apparatus (SCUBA) divers in approximately 9.5m of water depth. Cores were extruded, sectioned at 2cm intervals, and stored frozen until analysis.

![Figure 2-1 Locations of sediment cores taken in 1995 in the western basin of Lake Erie. Core A- 41°52’73N 83° 09’45W and core B- 41° 45’55N 83° 06’26W. Core U42 4145.71’N 8259.2’W from Kemp et al. 1971.](image-url)
2.2.3 Dating of the 1995 Lake Erie Sediment Cores

Radioactive lead ($^{210}$Pb) is used widely to determine pollution chronologies in aquatic sediments. $^{210}$Pb is part of the uranium-238 ($^{238}$U) decay series where it follows radon-222 ($^{222}$Rn), an inert gas that emanates from the earth's crust into the atmosphere. Because of the long half-life of $^{238}$U (4.51 x 10$^9$ yr) and its widespread occurrence in the earth's crust, $^{222}$Rn emanation is assumed to occur at a constant rate over time. $^{222}$Rn decays in the atmosphere through its short-lived daughters to $^{210}$Pb, which is deposited on land and water by both wet precipitation and dry fallout processes. Once deposited in aquatic systems, this fallout ("unsupported") $^{210}$Pb is buried by subsequent sedimentation. The activity of $^{210}$Pb in each sediment layer declines with its age due to radioactive decay. Because of the relatively short half-life (22.3 yrs.) of $^{210}$Pb, this technique is restricted to sediments deposited within the last 100 years (Gottgens et al. 1999). The $^{210}$Pb activity in older sediment layers results from and is maintained ("supported") by continued decay of parent radionuclides contained in the soil. Subtracting the level of supported $^{210}$Pb from the total $^{210}$Pb activity yields the "unsupported" activity upon which age-depth relationships are based.

I used direct low-background, high-purity germanium $\gamma$-counting (14.5 x 40.0 mm well detector) following techniques described (Gäggeler et al. 1976; Appleby et al. 1986) and summarized earlier (Porcella 1996). The detector operates at a positive bias of 1,800 Volts and at a temperature near that of liquid nitrogen provided by a high vacuum cryostat-dewar system. Counts for regions of interest are obtained with a 4096-channel analyzer calibrated at 0.186 keV/channel. $\gamma$-Counting allows simultaneous assay for supported and unsupported $^{210}$Pb, as well as other
radionuclides (such as $^{137}$Cs), which may serve as ancillary age-markers. Additional specifics on the detector system, such as background suppression, energy calibration, and the computation of counting efficiencies may be found in Gottgens et al. (1999).

The samples were dried at 104°C for 24 hours, pulverized, and placed in low-density polypropylene vials. They were subsequently sealed with plastic cement and stored for a minimum of 21 days to equilibrate radon ($^{222}$Rn) with radium ($^{226}$Ra). Counting times per sample varied and were as long as 72 hours depending on the weight of the sample; small samples needed longer counting times to reduce error.

Sample spectra, including calculation of error bars, were analyzed following Gottgens et al. (1999). Isotope-activity error was estimated as the square root of the sum of the variances of the gross and background count rates.

Calculation of $^{210}$Pb dates followed the Constant Rate of Supply model (Appleby and Oldfield 1978). In this model, it is assumed that the incorporation of unsupported $^{210}$Pb to the sediment is produced at a constant rate even with a variable bulk sedimentation rate. In other words, if sedimentation rate increases, the unsupported $^{210}$Pb decreases (is diluted). This allowance for variable sedimentation is important in systems such as Lake Erie with variable sedimentation rates. The $^{210}$Pb profile produced will not follow a logarithmic decline with depth as would be expected if the initial concentration of $^{210}$Pb was always the same (Appleby and Oldfield 1983).

$^{137}$Cs activities served as independent marker horizon in the sedimentary profile. The first occurrence of this man-made nuclide in the profile generally coincides with the onset of widespread atmospheric testing of nuclear weapons (i.e. 1954). 1959-1960 and 1963-1964 are reported as periods of maximum fallout in the
northern hemisphere (Ritchie et al. 1973; Joshi 1989) and additional support for
\(^{210}\)Pb-derived age/depth relationships may come from matching peak-\(^{137}\)Cs activities
in the profile with these time periods.

Total phosphorus (TP) also served as an ancillary age marker. TP in sediment
core intervals was measured (APHA 1992). The rise in TP due to anthropogenic
input in the 1950s and 1960s and decline after control measures instituted since 1972
(Makarewicz and Bertram 1991) should be reflected in the cores. Reported water
column TP data from 1970-1985 were correlated with sedimentary TP data.

2.2.4 Total Mercury in 1995 Lake Erie Sediment Cores.

Sediment samples for mercury analysis were dried at room temperature.
Samples, mercury standards, and certified reference materials (CRM) were digested
with a 2:1 mixture of sulfuric acid and nitric acid for two minutes in 125 ml glass
bottles in a 95°C water bath (USEPA 1986) (Figure 2-2). Organic matter in the
cooled samples was oxidized by the addition of potassium permanganate and
potassium persulfate followed by incubation for two hours in a 95°C water bath. To
eliminate interference from the purple color left by the potassium permanganate,
hydroxylamine hydrochloride was added. Vigorous shaking of the bottles was
necessary to release evolved chlorine gas. In a closed air vessel, tin chloride was
added to reduce the mercury to its gaseous elemental form. Ultra-high-purity argon
carried the gaseous elemental mercury through a soda lime trap to purge water and
acid vapor which can interfere with detector readings. Mercury was then scrubbed
from the argon flow by a gold trap constructed of fine 24-karat gold mesh. After
eight minutes of adsorption, the gold trap was heated for 20 seconds with a nichrome
coil to release the mercury. The mercury was then carried through a cuvette in a Tekran CVAFS Mercury Detector 2500 where its fluorescence at 253.7nm was detected. A Hewlett Packard HP395 integrator recorded the peak height. A standard curve based on peak height was used to calculate mercury in ng. All chemicals used were ultra-high purity, trace metal grade (Fisher, Baker). Average detection limit for this method was <1 ng g⁻¹, computed as twice the standard deviation of 5 blanks (Cole 1997).

Samples for quality assurance and quality control were included. In a typical scenario, each run had 37 bottles. The Certified Reference Material (CRM) was Buffalo River sediment (NIST 2704, 60 ng Hg g⁻¹). Five reagent blanks were spaced throughout the run. They consisted of high purity water (reverse osmosis plus E-pure filtration) incubated as samples with all reagents added. Three samples were duplicated and spiked with a mid-range standard.

Figure 2-2 Total mercury method for sediments using tin chloride (SnCl₂) to release mercury into argon stream. Mercury absorbs on to a gold mesh. The gold mesh is heated to release the mercury. The mercury is detected by CVAFS at 253.7nm (Cole 1997).
2.2.5 Historical Lake Erie Core Data

In 1971, cores were obtained from Lake Erie and mercury profiles were established by depth in core by Kemp et al. (1974 and 1976). Dates for each slice in the core were established by pollen counts. The rise of ragweed pollen, *Ambrosia*, has been suggested as coincident with early colonial forest clearing and agriculture around 1850 (Fries 1962). The decline in Chestnut tree pollen, *Castanea dentata*, marks sediment deposits from around 1935 due to blight at that time (Anderson 1974). One 1971 core (U42) was located near my 1995 coring sites (41° 45’71N 82° 59’2W) (Kemp et al. 1974, 1976) (Figure 2.1).

2.2.6 Records From Long Term Databases

In Lake Erie, we are in the unique position of having relatively long, well documented databases for various parameters. Such databases are not the case for very many lake systems in the northern hemisphere and particularly not true of the southern hemisphere and the tropics. The mercury in Lake Erie came from environmental input – both natural and anthropogenic. Since the major anthropogenic input to Lake Erie was from two chlor-alkali plants, a database of purchases of mercury by the chlor-alkali industry was used to track “input” of mercury to the system. Likewise, organisms accumulate mercury from a variety of sources. A database representing levels of total mercury in walleye tissue or “output” should correspond to mercury accumulation rates in the system over the same time period. While other factors are certainly at work in any system, the overwhelming change in mercury levels due to anthropogenic pollution may overshadow other variables that would play roles in uncontaminated systems.
2.2.7 Historical Consumption of Mercury by the Chlor-Alkali Industry: “Mercury Input”

In 1970, two chemical plants, Dow Chemical Corporation in Sarnia, Ontario and Badische Anilin- und Soda-Fabrik (BASF) Wyandotte Chemical Corporation in Wyandotte, Michigan, were identified by government and independent reports as major contributors to mercury pollution to Lake Erie (Copeland 1970). These companies manufactured chlorine gas and caustic soda by an electrolytic process using a mercury cell. Mercury release was estimated at 22.7 kg day\(^{-1}\) from 1950-1970 for Dow and 4.5-9.1 kg day\(^{-1}\) from 1939-1970 for BASF (Walters et al. 1974). Both plants closed in 1970.

I assembled an approximate record of mercury input into the lake using information on the purchase of mercury by the chlor-alkali industry. The United States Geological Survey (USGS) Office of Minerals Information (now the Mineral Resources Program) tracks US consumption of mercury by all industry and by the chlor-alkali industry as a subset (1932-1994). These data reflect purchase of mercury on the open market. Specific data from the two closed chlor-alkali plants, implicated as major contributors to Lake Erie’s mercury problems in the 1970’s, were not made available and have been sealed (Copeland 1970).

2.2.8 Historical Mercury in Walleye Tissue: “Mercury Output”

I assembled an approximate record of mercury output from the lake using information on mercury in fish tissue. Mercury concentration in whole body homogenates of walleye (*Sander vitreus vitreus* formerly *Stizostedion vitreum vitreum*) from Lake Erie’s western basin aged 4+ and 5+ years from the Department
of Fisheries and Oceans have been analyzed each year since 1977. Data reported by several agencies (Ontario Ministry of the Environment, Ontario Ministry of Natural Resources, Ohio Environmental Protection Agency, Michigan Department of Natural Resources, Michigan Department of Agriculture, Michigan Office of Public Health, United States Food and Drug Administration and United States Fish and Wildlife Service) for walleye from the western basin of Lake Erie but of unknown sample type were used to extend the data set back to 1968 (GLWQB 1970).

Walleye are large predatory fish native to most of Canada and the northern US (Hubbs et al. 2004). In the Great Lakes, walleye are one of the most economically important fish pursued both commercially and by sport anglers (Locke et al. 2005). Because of potentially high body burdens of mercury and high consumption rates by humans, walleye are of great interest to government agencies (USEPA 2011).

2.3 Results and Discussion

2.3.1 Chronology of 1995 Sediment Cores

Two cores were retrieved from western Lake Erie in 1995. Core A was 55 cm long while core B was 52 cm long. Unsupported \(^{210}\)Pb activities decreased with sediment depth and approached background levels in both cores near 40 and 47 cm depth (Figure 2.3). Using those activities, the Constant Rate of Supply (CRS) dating model was applied to calculate dates for depths in the cores. CRS is commonly applied in studies that reconstruct pollution histories, particularly when sedimentation rates have varied over time. Additional support for the chronology came from \(^{137}\)Cs activity in the core. A peak in \(^{137}\)Cs appeared in layers dated to the 1956 and 1960 which coincided with the period of maximum fallout from atmospheric bomb testing.
The total phosphorus (TP) accumulation rate profiles also supported the $^{210}$Pb core chronology. Both cores showed TP peaks dated to the late 1960s and early 1970s (Figure 2.4). This was consistent with the increasing eutrophication of Lake Erie followed by a decrease after pollution control legislation (Markarewicz and Bertram 1991). The correlation between TP accumulation rate (g m$^{-2}$ yr$^{-1}$) and TP in the water column in Lake Erie (µg L$^{-1}$) (data from Makarewicz and Bertram 1991) was significant for both core A ($r=0.78$, $p<0.01$) and core B ($r=0.70$, $p<0.01$). Regression analysis showed that 57% and 49% of the variability in TP accumulation rate could be explained by water column TP in cores A and B, respectively (Figure 2-5).
Figure 2-4. Total Phosphorus (TP) accumulation rate in sediments (g m\(^{-2}\) yr\(^{-1}\)) in Core A (left panel) and Core B (right panel) versus year of deposition for 1995 cores.

Figure 2-5. Total phosphorus accumulation rates in sediments versus total phosphorus in the water column in Core A (left panel) and Core B (right panel). The source of Lake Erie water column data (1970-1985): (Makarewicz and Bertram, 1991).
2.3.2 Total Mercury in 1995 Cores

Quality control for mercury in sediments fell within acceptable ranges. Spike recoveries were 94.1±7.2% of the expected value. Analysis of the Certified Reference Material (CRM), Buffalo River sediment (NIST 2704, 60 ng g\(^{-1}\)) was 99.8±1.9% of the certified value. Average detection limit for this method was <1 ng g\(^{-1}\).

The 1995 cores showed a pattern consistent with the known history of mercury pollution in Lake Erie. Mercury concentrations were relatively low in the circa 1900 pre-industrial period (Figure 2.6). They rose to a peak in layers dated to the late 1960s to early 1970s during maximal industrial mercury use and subsequent environmental contamination. Mercury concentrations in core A increased beginning in 1964 with a sharp peak at 14.5cm, a layer dated to 1970. This pattern was expected if the 1995 cores did preserve the 1971 core profile. Core B had a plateau of maximum mercury concentrations from 1958 to 1969. This plateau might reflect some smearing and reworking of the core signals in core B, consistent with the patterns seen for \(^{137}\)Cs (Figure 2.3) and TP (Figure 2.4).

Mercury levels in both cores dropped sharply with the closing of the chlor-alkali plants and continued dropping to approximately 350-400 ng g\(^{-1}\) in 1995 when the cores were taken. Marvin et al. (2004) found similar sediment mercury levels in the western basin of Lake Erie at 402 ng g\(^{-1}\) for 1995-1997.

Lake Erie has a long, well documented history of changing chemical and physical parameters. It follows that the sedimentation rate in this lake has varied over time. The CRS model is useful in such lakes. Although peak mercury levels were different between the 1995 cores, integrated accumulation rates, found by multiplying bulk density (g cm\(^{-3}\)) by total mercury concentration (ng g\(^{-1}\)) for each core slice from
1952 to 1970 and integrating over depth (cm), were similar (core A: 3602 ng Hg cm\(^{-2}\); core B: 3205 ng Hg cm\(^{-2}\)). Core B does show some evidence of reworking as was also noted in the \(^{137}\)Cs and TP profiles as evidenced by a broader peak.

Figure 2-6. Total mercury concentration versus depth in 1995 cores A (left) and B (right) and 1971 core U42 (middle). Cores are aligned with 1970 and 1850 dates in all three cores. Year of deposition determined by \(^{210}\)Pb analysis for 1995 cores and pollen stratigraphy for 1971 core (data from Kemp et al. 1974, 1976).

My data support the assertion by Fitzgerald et al. (1998) and many others that the patterns in cores they examined were “spatially and temporally coherent”. In almost every core that had several lines of support for the dating chronology, timing of a rise in mercury accumulation coincided with the start of the industrial period (pre-1850). The cores themselves ranged from less than 20cm to over 90 cm but all had a similar timing for the increase (Swain et al. 1992; Hurley et al. 1994; Engstrom
and Swain 1997). The magnitude of the rise in mercury increase was also very similar (Table 2.1).

2.3.3 Comparison of 1995 and 1971 cores

Accumulation rates of the 1995 (core A and B) and 1971 (U42) cores could not be compared directly due to differences in dating methods. Sediment mercury concentrations for layers dated to 1971 in core A and core B were 24% and 59% lower than U42 surface layers. Lower sediment mercury concentrations in core B for the 1971 dated sediments were expected due to the possible smearing and reworking discussed earlier.

Enrichment factors based on concentration were used to compare patterns among the 1995 and 1971 cores. Accumulation rates could not be calculated for the 1971 core that was dated by pollen stratigraphy (Kemp et al. 1974). Enrichment factors were calculated by dividing the 1971 mercury concentration by circa 1900 values in all three cores. The enrichment factor for the 1971 core was 2.8. The 1995 cores had factors of 2.6 (core A) and 3.1 (core B). All 3 cores were enriched by a mean factor of 2.6±0.9SD. Accumulation rates can be used to calculate enrichment factors for the 1995 cores in comparison to other modern cores. Lake Erie’s enrichment factor of 4.0 falls in line with other enrichment factors calculated for Lake Superior (4.0) and Lake Michigan (6.9) and mercury impacted sites such as south Florida (4.9) or Finland (4.4) (Table 2.1).

Lake Erie has very high pre-industrial rates of mercury accumulation (Table 2.1). Lake Erie’s 273 μg m⁻² yr⁻¹ is more than 20 times South Florida’s 11 μg m⁻² yr⁻¹ (Rood et al. 1995). In comparison to Lake Superior (2.7 μg m⁻² yr⁻¹) or Lake
Michigan (3.1 µg m⁻² yr⁻¹), Lake Erie is 100 times higher. There are no other dated Lake Erie cores for comparison of pre-industrial mercury accumulation rates (Drevnick et al. 2012). Compared to other locations, pre-1850 Lake Erie was already heavily impacted by agriculture. Historical accounts detail the settlement and drainage of the Great Black Swamp (Platt 1987). By the 1880s, the area had been extensively tiled and resembled modern day agricultural fields (Platt 1987). Mercury chloride was a common seed treatment around the turn of the century (Morton and Staub 2008). Agricultural runoff, including sediments and chemicals, likely contributed to this historical mercury load in Lake Erie sediments. The Detroit River and the Maumee River are major sources of sediment to the western basin (1.8 million tons year⁻¹ and 1.2 million tons year⁻¹, respectively) (Lick 1982) and likely contributed mercury.

Historically high mercury loads may also be due to coal mining and coal-burning industries surrounding Lake Erie. Pennsylvania, Illinois and Ohio were major sources of coal in the early days of US coal mining beginning in the mid-1850s (Chandler 1972). Coal mined in the US has a mercury concentration of 0.17±0.17 µg g⁻¹ (Tewalt et al. 2001). Historically, coal was the main source of energy for transportation and industry from the 1850s until the 1950s (Schurr et al. 1960). Coal remained a major fuel source for electricity generation due to its low cost and relative abundance. The USEPA cited mercury emissions from electric utilities as the largest remaining anthropogenic source of mercury released to the air (Keating et al. 1997). Emissions from coal-fired utilities accounted for 13 to 26 percent of the total (natural plus anthropogenic) airborne emissions of mercury in the United States (Keating et al. 1997). Coal burning industries included steel plants and steam-powered facilities
including locomotive engines. In the late 1800’s, US coal began to be used to produce coke used in steel production (American Coal Foundation 2005). As an indicator of the impact of coal-burning engines, Lake Erie’s shores had railways circling the lake as far back as 1850 (“Railways Round” 1852). All early locomotives that burned wood were quickly converted to coal after 1830 (American Coal Foundation 2005) generating additional mercury contamination.

At the height of the mercury pollution problem in Lake Erie in the 1970s, the enrichment factor was 12 for western Lake Erie or three times its 1990s level of enrichment. Calculation of 1970: Pre-1850 enrichment factors for Lake Michigan (11.22) showed similar level of impact of industrial mercury use and loss in the Great Lakes area (Drevnick et al. 2012). Lake Superior had a much lower 1970: Pre-1850 enrichment factor calculated at 4.1 (Drevnick et al. 2012). This is most likely due to lower industrial and agricultural activity in the watershed (Minnesota Historical Society 2013).

2.3.4 Relationship of Mercury Accumulation Rates in Sediment to Historical Databases

2.3.4.1 Historical Consumption of Mercury by the Chlor-Alkali Industry:

“Mercury Input”

“Input” of anthropogenic mercury to Lake Erie was primarily from two chemical plants, Dow Chemical Corporation in Sarnia, Ontario and BASF Wyandotte Chemical Corporation in Wyandotte, Michigan, as previously indicated.

I compared mercury accumulation rates in sediment cores with purchases of mercury on the open market by the chlor-alkali industry (Figure 2.7). Mercury input
(Hg consumption by chlor-alkali industry) correlated with mercury accumulation rates in core A ($R^2=0.39$, $p<0.001$, $n=44$) but not in core B ($R^2=0.057$, $p=0.1177$, $n=44$) (Figure 2.8). In core A, mercury accumulation rates in the western basin of Lake Erie reflect an overall trend of purchases of mercury on the open market by the chlor-alkali industry. A lack of closer correspondence was likely due to the general purchase data not reflecting actual use by the two plants around Lake Erie and, more importantly, the loss at two specific chlor-alkali plants in Sarnia, Ontario. Other sources of mercury to Lake Erie also contributed to mercury in sediments. Additional local sources included pollution for other industries, household waste, and medical waste. Both regional and global sources contribute to atmospheric deposition. The change in mercury loading due to the chlor-alkali plants seemed to overwhelm all other sources and show up clearly in the cores. Cores taken in locations with large scale changes in mercury pollution would also be expected to demonstrate this chronology. Cores from locations with several sources of mercury that overlap and equally contribute to sediments may not show such a clear signal.
Table 2.1. Mean (and range) of modern and pre-industrial total mercury accumulation rates and ratios for selected regions arranged by descending Hg flux ratios. Ratios are computed by averaging all individual cores from each region. Modern and pre-industrial mercury accumulation rates generally apply to post-1980 and pre-1850 time periods, respectively, unless otherwise noted.

<table>
<thead>
<tr>
<th>Location</th>
<th>Mercury flux ratio (modern/pre-industrial)</th>
<th>Number of core sites</th>
<th>Modern mercury flux ($\mu$g m$^{-2}$ yr$^{-1}$)</th>
<th>Pre-industrial mercury flux ($\mu$g m$^{-2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Erie (~1970)</td>
<td>12 (10-13)***</td>
<td>2</td>
<td>3006 (3952-2059)***</td>
<td>273** (153-395)</td>
<td>This study</td>
</tr>
<tr>
<td>South Florida</td>
<td>4.9 (1.6-19.1)</td>
<td>18</td>
<td>53 (23-141)</td>
<td>11** (8-14)</td>
<td>Rood et al. (1995)</td>
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<tr>
<td>Finland</td>
<td>4.4 (1.2-8.9)</td>
<td>9</td>
<td>26.5 (2.3-49.5)</td>
<td>7.8 (1.9-27.0)</td>
<td>Verta et al. (1989)</td>
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<tr>
<td>Lake Erie (1990s)</td>
<td>4.0 (2.7-5.4)</td>
<td>2</td>
<td>937.4 (824-1051)</td>
<td>273** (153-395)</td>
<td>This study</td>
</tr>
<tr>
<td>Lake Superior</td>
<td>4.0</td>
<td>9</td>
<td>10.8</td>
<td>2.7</td>
<td>Drevnick et al. (2012)</td>
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<td>7</td>
<td>23 (16-32)</td>
<td>6.4 (4.5-9.0)</td>
<td>Engstrom et al. (1994)</td>
</tr>
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<td>1</td>
<td>21.4</td>
<td>3.1</td>
<td>Drevnick et al. (2012)</td>
</tr>
<tr>
<td>Sweden</td>
<td>3.0 (1.2-7.5)</td>
<td>11</td>
<td>12.5 (6.7-20.7)</td>
<td>5.8 (1.9-17.2)</td>
<td>Johansson (1985)</td>
</tr>
<tr>
<td>Southeastern Alaska</td>
<td>2.0 (1.8-2.1)</td>
<td>3</td>
<td>16.5 (11.5-26.0)</td>
<td>8.3 (5.5-12.7)</td>
<td>Engstrom and Swain (1997)</td>
</tr>
</tbody>
</table>

*** circa 1970 rates, ** pre-1900 rates
Figure 2-7 Comparison of year versus sedimentary record (1995 cores of the western basin of Lake Erie) in panels A (core A) and B (core B), environmental input (consumption by the US chlor-alkali industry) in panel C, and environmental output (walleye tissue concentration) in panel D.
2.3.4.2 Historical Records of Mercury in Walleye Tissue: “Mercury Output”

The effect of mercury in the sediments on biota was examined as “Output”. In particular, I examined mercury concentration in whole body homogenates of Walleye (*Sander vitreus vitreus* formerly *Stizostedion vitreum vitreum*) from Lake Erie’s western basin against mercury accumulation rates in the 1995 cores. Total mercury
accumulation rates correlated with fish tissue mercury concentrations in both core A ($R^2=0.52$, $p<0.001$, n=44) and core B ($R^2=0.51$, $p<0.001$, n=44) (Figure 2.9). Large anthropogenic inputs have been correlated with increased mercury levels in fish in many locations (Boening 2000). Large decreases in anthropogenic input, as is the case for Lake Erie, should also be reflected in fish tissue levels. Although the pathway from mercury in sediments to the tissue of walleye, a top predator, is multi-compartmental and influenced by many factors, clearly large changes in mercury accumulation in sediment are linked to large changes in mercury in fish.

Changes to the biology and chemistry of Lake Erie from pre-industrial times to recent day have been marked. Some of those alterations are known to influence bioaccumulation of mercury in fish. For example, high zooplankton diversity was found to reduce mercury biomagnification in northeastern US lakes sampled (Chen and Folt 2005). Smallmouth bass were found to have higher mercury levels despite declining sediment concentrations in Lake Erie, perhaps attributable to consumption of non-native round gobies (Hogan et al. 2007). More acidic lakes in Wisconsin were found to have higher mercury concentrations in walleye than less acidic lakes (Wiener et al. 1990). In spite of these confounding factors, my broad-scale comparison between the history of sedimentary signals of mercury and tissue levels of this contaminant is walleye still reveals statistically significant correlation. If the objective is to discern finer time scale correlations, paleolimnological data may not be appropriate.
Figure 2-9 Correlation of walleye tissue Hg (µg g⁻¹) from three historical databases and mercury accumulation rates in Lake Erie sediment from 1995 cores. Core A in top panel, core B in bottom panel. Source of 3 tissue data sets: ♦= OMNR 1994, ■ and ▲= GLWQB 1970.

\[ R^2 = 0.519 \]
\[ p < 0.001 \]

\[ R^2 = 0.511 \]
\[ p < 0.001 \]
Lake Erie has an unusually well-documented history of fish tissue data extending over decades of sampling. For most areas, such documentation is not available. Efforts to reduce anthropogenic mercury use and loss are aimed at reducing mercury in the environment and in wildlife and their human consumers. Informed goals for fish tissue levels for restoration are based on bringing levels below the 1 mg L\(^{-1}\) (1 ppm) United States Food and Drug Administration action level. Restoration to undetectable mercury levels is unrealistic if the natural system has always been impacted by some level of mercury. Mercury is a naturally-occurring element that will always have some level of impact on an ecosystem. Thus, restoration to pre-industrial (pre-1850) levels would be more realistic. However, I would need to know what mercury levels in fish tissue were at that time and, in Lake Erie, fish tissue databases extend only back to 1968.

The regression model for mercury accumulation rates in sediment and walleye tissue was used to “hindcast” average mercury levels for pre-1900 fish tissues. In core A, the 1897 mercury accumulation rate in sediments was 341.4 µg Hg m\(^{-2}\) yr\(^{-1}\). Applying the regression equation for core A, a circa 1900 Hg fish tissue level of 25.5 ng Hg g\(^{-1}\) was calculated. In core B, the 1899 sediment mercury accumulation rate was 230.3 µg Hg m\(^{-2}\) yr\(^{-1}\). Applying the regression equation for core B, a circa 1900 Hg fish tissue level of 8.9 ng Hg g\(^{-1}\) was calculated. As expected, the pre-industrial mercury levels in fish tissue were extremely low (average 17.2 ng Hg g\(^{-1}\)) compared to the 1993 levels for whole walleye from the same data set at 100 ng Hg g\(^{-1}\).

In the early 1970’s, museum fish were analyzed to attempt quantifying historical mercury levels in Lake Erie fish (Evans et al. 1972). They found an average of 75 ng Hg g\(^{-1}\) prior to 1945 in various fish. Using the same regression
equation, my model predicted 1945 levels in fish tissue to be 80 ng Hg g\(^{-1}\) (core A=126.9, core B= 33). The correspondence is surprisingly close based on the simplicity of the regression model.

Hindcasting is used in meteorology and oceanography to validate forecasting models. Data are put into the model to check if the corresponding known changes would have been predicted. It has been used recently for testing models of near-surface dynamics in the Adriatic Sea (Sikiric et al. 2012), spring drought predictions in Portugal (Santos et al. 2012), and phylogenetic distributions of Brazilian trees (Collevatti et al. 2012). Hindcasting in pre-industrial Lake Erie is probably more reliable than forecasting in Lake Erie. Lake Erie in the past was more stable than the current Lake Erie influenced by a wide variety of pollutants and invaders. The invasion of zebra mussels and round gobies was indicated as the agent behind higher body burdens of mercury in Lake Erie walleye than in any of the other Great Lakes (Hogan et al. 2007). Round gobies consuming zebra mussels bring contaminants that had been limited to benthic-based food web into the pelagic-based food web of walleye (Hogan et al. 2007). Regardless of the time frame, caution should be used in assuming that the regression relationship for sediment and fish tissue remains linear outside the range of my data.

Environmental monitoring and restoration plans for any particular region should be tailored by the history of that region. Mercury is a naturally occurring element so it is expected that rocks, sediments, water, and soils naturally contain small but varying amounts of mercury. Concentrations of naturally occurring mercury in soils range from 0.003 to 4.6 mg kg\(^{-1}\) (Steinnes 1997). Restoration targets should take into account the presence of naturally occurring mercury. Measuring
current mercury levels in the local environment will contain both anthropogenic and naturally occurring mercury in some ratio. Quantifying past naturally-occurring levels might be accomplished using paleolimnological analysis. In areas of the world lacking historical databases, paleolimnological analysis can provide informed targets for restoration. Analysis of long-term trends using sedimentary records may provide important information for the understanding and management of mercury contamination in lacustrine systems.

2.4 Summary and Conclusions

The goal of this part of my dissertation was to correlate data from long term databases on mercury with mercury accumulation rates in cores in Lake Erie’s western basin. Lake Erie is an ideal test case for the utility of cores because it has a well-documented history of mercury pollution and long databases reflecting “mercury input” (historical consumption of mercury by the chlor-alkali industry) and “mercury output” (historical mercury in walleye tissue). Significant correlations were found for both “mercury input” and “mercury output” with mercury accumulation rates in sediments. My work supports the use of sediment cores as accurate historical records of long term trends. This technique can be used in systems that are not as well documented to set informed targets for mercury restoration goals. Hindcasting may be used to predict past fish mercury levels. My simple regression model found similar tissue levels to museum fish dated to 1945. My regression model was then used to predict pre-1900 mercury tissue levels in walleye. Although caution should be used in assuming a linear relationship outside the range of data values, my model can
be used to set informed mercury restoration goals for areas lacking historical records of mercury pollution.
Chapter 3

Mercury Accumulation in Sediment Cores and Along Food Chains in Two Regions of the Brazilian Pantanal


Abstract

The Pantanal is a 140,000 km² floodplain wetland stretching across western Brazil and parts of Bolivia and Paraguay. Gold mining with mercury (Hg) amalgamation has thrived since 1980 along its northern rim. We quantified Hg accumulation in sediment cores (N=5) and food chains in this general region of the northern Pantanal and in a reference region, 200 km deeper into the wetland (Acurizal). Cores were dated with $^{210}$Pb and $^{137}$Cs using direct gamma-assay. Total Hg was analyzed by cold-vapor atomic fluorescence using a gold-mesh pre-concentration trap. Average pre-1940 Hg accumulation in cores was not significantly different (N=5, p=0.14) between both regions and comparable with rates calculated for global reference sites. Post gold-rush Hg (post-1980) deposition averaged $55 \pm 11.3 \mu g \ m^{-2} \ yr^{-1}$ in the northern impacted region and was more than 1.5 times higher than the post-1980 rate.
in Acurizal, implying a regional Hg effect of gold mining. Post-1980 Hg accumulation in Acurizal, in turn, was 2.1 times the rate reported for a global reference during that time period, suggesting an additional basin-wide effect over such reference sites. By combining our core data with assessments of the size of the impacted area and the amount of Hg released to the region since 1980, we estimated that only 2-8% of this Hg was recovered as a sedimentary signal. The remainder of the Hg was lost to the atmosphere, downstream areas, or stored in biota. Hg concentrations in surface sediments in the northern Pantanal (45.5 ± 5.5 ng g\text{dry}\textsuperscript{-1}) were significantly higher than those in our reference region (29.1 ± 0.7 ng g\text{dry}\textsuperscript{-1}). Hg levels in primary producers were also elevated in the northern Pantanal. *Eichhornia crassipes* roots contained 2.7-3.0 times more mercury than shoots in both regions and *Salvinia auriculata*, suggested as a biological monitor for Hg pollution, contained almost four times more mercury in the northern Pantanal (90.7 ± 9.1 ng g\text{dry}\textsuperscript{-1}) than in Acurizal (24.5 ± 3.3 ng g\text{dry}\textsuperscript{-1}). Plant grazers and scavengers, such as apple snails (*Pomacea* sp.) and adult water beetles (Fam. Hydrophilidae), were low in Hg, confirming previous data showing that the channeling of mercury from lower to higher trophic levels along herbivorous links was inefficient compared to transfer along carnivorous links. Collections of 12-16 individuals of four species of Characidae (*Aphyocharax* sp., *Tetragonopterus* sp., *Serrasalmus spiropleura* and *Pygocentris nattereri*) in both regions showed elevated Hg body burdens in both piranhas *S. spiropleura* and *P. nattereri* from the northern Pantanal (149.9 ± 84.2 and 302.2 ± 159.1 ng g\text{dry}\textsuperscript{-1}, respectively). Fish length for each species was not statistically different between regions. *P. nattereri* length correlated significantly (p<0.001) with Hg content in both regions, but the slope of the regression in the
northern Pantanal was 2.6 times the slope for the Acurizal collection, indicating an elevated rate of biomagnification in the Hg-impacted region. Signals of Hg use in mining can be quantified in sediment core chronologies and biological tissues, although species at different trophic levels show dissimilar impacts. Mechanisms involved in Hg magnification along food chains deserve more attention, particularly in tropical regions where the threat of chronic exposure to this neurotoxin may have the greatest implications for biodiversity.

3.1 Introduction

Mercury is a potent neurotoxin that readily bioconcentrates and biomagnifies. In the United States, sixty percent of the fish consumption advisories issued are for mercury contamination (Keating et al. 1997). Globally, the major source of mercury to freshwater systems is atmospheric deposition from natural and anthropogenic sources (Swain et al. 1992) but discharges from industry, mining activities, and direct watershed runoff may increase regional loadings (Gill and Bruland 1990; Lacerda et al. 1991a).

The vast majority of ecological studies on patterns of mercury accumulation are from the temperate zone. Mercury concentrations in sediment and biological samples have been documented in only a few tropical aquatic ecosystems (Cuvina-Aralar 1990; Lacerda et al. 1991b; Filho and Maddock 1997; Olivero and Solano 1998; Guimaraes et al. 1998; Mauro et al. 1999), and long-term trends in mercury accumulation in the tropics are essentially unknown. In the tropical environment, with potentially high rates of methylation (Mauro et al. 1999) and poorly-controlled mercury use and discharges, the threat of chronic mercury toxicity for longer-lived
organisms at higher trophic levels may be particularly severe. In addition, the implications of chronic exposure to mercury on biocomplexity in the tropics have not been evaluated.

We selected the Pantanal, one of the world's largest tropical wetland systems, to measure long-term trends in mercury accumulation and to quantify patterns of mercury transfer in food webs. Covering an area of some 140,000 km$^2$ in the upstream basin of the Paraguay River, the Pantanal stretches across western Brazil and parts of Bolivia and Paraguay. Plant and animal life in this savanna type wetland are strongly influenced by distinct seasonal flooding with maximum water level fluctuations of five meters between the dry and rainy seasons. Periods of severe flooding are followed by extreme droughts with only a small portion of the wetland remaining inundated year-round. The Pantanal is famous for the abundance and diversity of its fauna. Hyacinth macaws, jaguars, giant river otters and Victoria lilies prosper in this floodplain.

Deforestation, expanding agriculture, illegal hunting and fishing, drainage activities associated with a planned waterway project, and mercury contamination associated with gold mining threaten the Pantanal's remarkable diversity (Alho et al. 1988). After an initial gold rush several centuries ago, gold mining returned to the northern edge of the Pantanal near Poconé in the early 1980s. The Rio Bento Gomes, in the Poconé region, receives drainage from mining and ore dressing sites (Filho and Maddock 1997) and an estimated 15-20 tons of mercury was released into the local environment between 1980 and 1990 (Lacerda et al. 1991a). In all of Brazil, gold refining utilizes more mercury (168 tons year$^{-1}$) than the industrial sector (105 tons year$^{-1}$) (Ferreira and Appel 1992). These mines in the northern Pantanal region have
remained active in the 1990s.

Trends in mercury deposition over decades to centuries have been successfully inferred from natural archives such as sediment cores (summarized in EPRI 1996). Mercury accumulation rates over time can now be calculated from sediment cores analyzed stratigraphically for mercury and dated by \(^{210}\text{Pb}\) and other radionuclides such as \(^{137}\text{Cs}\). As a measure of environmental input, results presented as such rates of accumulation are superior to those presented in units of concentration. The latter, expressed as a relative measure of sediment composition (mg g\(^{-1}\)), is the conventional expression of sediment stratigraphy. Such data, however, are vulnerable to variation in sedimentation of other components. These variations may result in the dilution of the target analyte and underestimation of its environmental input. Accumulation is normalized over time, thus avoiding the problem of covariance among different sedimentary components.

Food web transfer is important for the accumulation of mercury and the highest levels occur in the longer-lived species in upper trophic levels (Cabana et al. 1994). The majority of mercury invades aquatic systems in inorganic form. Methylmercury, however, is the most toxic and bioaccumulated form of the different mercury species and predators, such as some fish, contain primarily methyl-mercury. In spite of the acute and chronic impact of mercury contamination, there is an incomplete understanding of the transfer of mercury between trophic levels (Hill et al. 1996), particularly in tropical regions with less information on the ecology and natural history of species (Cleckner et al. 1998; Por 1995). Quantifying mercury dynamics in lower and intermediate trophic levels seems particularly important to clarify the efficiency of mercury biomagnification.
In this work, we compare records of mercury accumulation in sediment cores and mercury dynamics in food webs in the region of gold mining in the northern Pantanal to a reference area 200 km deeper into this floodplain. This is the first study to report detailed radionuclide-dated mercury accumulation profiles for the Pantanal and to document mercury levels in a variety of organisms linked in *in-situ* food webs. We test the hypothesis that mercury accumulation rates are elevated in northern Pantanal sediments deposited since the return of gold mining to that region in 1980. In addition, we predict that tissue concentrations in biota will be higher in the northern Pantanal than levels in the same taxa at the reference sites.

Figure 3-1. Map of the Pantanal with the five core locations indicated.
3.2 Methods

3.2.1 Site Description

We sampled in three sites in the region of gold mining and in two reference sites deeper into the floodplain (Figure 3-1) and selected wetland locations with minimum disturbance and with maximum water depth. Sites within 25 km of the Poconé mining region (northern Pantanal) included a marsh near Santo Antonio do Leverger (15°51’30” S / 56°05’30” W), a floodplain depression adjacent to the Rio Bento Gomes (16°19’00” S / 56°32’00” W), and a shallow lake (Baia Piuval, Fazenda Ipiranga) on the Rio Bento Gomes (16°22’30” S / 56°34’00” W) approximately 20 km south of Poconé. The reference marshes were located about 200 km into the floodplain near Acurizal (Acurizal 1: 17°50’11” S / 57°32’21” W; Acurizal 2: 17°49’59” S / 57°32’54” W), in an area owned and managed by the Ecotropica Foundation, Cuiaba, Brazil. Water depth at the time of sampling varied from 36 cm (Sto. Antonio and Bento Gomes) to 125 cm (Acurizal 2). Vegetation at all sites was dominated by floating aquatic species (including *Eichhornia azurea*, *E. crassipes*, *Salvinia auriculata*, *Azolla* sp., and *Pistia stratiotes*), common in neotropical systems with highly-fluctuating water levels.

3.2.2 Sample Collection

At each site, we took a sediment core using a thin-walled polycarbonate tube (i.d. 7.5 cm) and carefully selected biological samples to represent different trophic levels along a food chain. We focused on selecting the same species, number of individuals, and size class in each sample location. Observations of the cores were made in the field to detect changes in sediment color or texture. Cores were carefully
extruded in-situ in 1 or 2 cm sections, stored in plastic bags and frozen. Cores were shorter (average length 23.3±11.4 cm) than might be expected for temperate zone cores due to the low rate of accumulation of organic material in the tropics. Plants and fish were identified to genus or species and frozen. All samples were handled using clean field techniques. *Aphyocharax* sp. was analyzed whole. The larger fish species (*Tetragonopterus* sp., *Serrasalmus* spiropleura and *Pygocentris* nattereri) were analyzed as filets. We compared whole body mercury concentrations directly to filet mercury concentrations following Goldstein et al. (1996) who demonstrated a consistent 1 to 1 ratio between whole body and filet mercury content in Minnesota fish species. Standard lengths (i.e., length from nose to tail base) were not significantly different between sites for the fish *Aphyocharax* sp., *Tetragonopterus* sp., *Serrasalmus* spiropleura and *Pygocentris* nattereri.

3.2.3 Dating of sediment cores

Radioactive lead (210Pb) is used widely to determine pollution chronologies in aquatic sediments. 210Pb is part of the uranium-238 (238U) decay series where it follows radon-222 (222Rn), an inert gas that emanates from the earth's crust into the atmosphere. Because of the long half-life of 238U (4.51x10^9 yr) and its widespread occurrence in the earth's crust, 222Rn emanation is assumed to occur at a constant rate over time. 222Rn decays in the atmosphere through its short-lived daughters to 210Pb, which is deposited on land and water by both wet precipitation and dry fallout processes. Once deposited in aquatic systems, 210Pb is buried by subsequent sedimentation. The activity of 210Pb in each sediment layer declines with its age due to radioactive decay. Because of the relatively short half-life (22.3 yrs.) of 210Pb, this
technique is restricted to sediments deposited within the last 100 years (Gottgens et al. 1999). The $^{210}\text{Pb}$ activity in older sediment layers results from and is maintained ("supported") by continued decay of parent radionuclides contained in the soil. Subtracting the level of supported $^{210}\text{Pb}$ from the total $^{210}\text{Pb}$ activity yields the "unsupported" activity upon which age-depth relationships are based.

We used direct low-background, high-purity germanium $\gamma$-counting (14.5 x 40.0 mm well detector) following techniques described earlier (Gäggeler et al. 1976; Appleby et al. 1986) and summarized (EPRI 1996). The detector operates at a positive bias of 1800 Volts and at a temperature near that of liquid nitrogen provided by a high vacuum cryostat-dewar system. Counts for regions of interest are obtained with a 4096-channel analyzer calibrated at 0.186 keV/channel. $\gamma$-Counting allows simultaneous assay for supported and unsupported $^{210}\text{Pb}$, as well as other radionuclides (such as $^{137}\text{Cs}$), which may serve as ancillary age-markers. Additional specifics on the detector system, such as background suppression, energy calibration, and the computation of counting efficiencies may be found in Gottgens et al. (1999).

The samples were dried at 104°C for 24 hours, pulverized, and placed in low-density polypropylene vials. They were subsequently sealed with plastic cement and stored for a minimum of 21 days to equilibrate radon ($^{222}\text{Rn}$) with radium ($^{226}\text{Ra}$). Counting times per sample varied and were as long as 72 hours depending on the weight of the sample; small samples needed longer counting times to reduce error. Sample spectra were analyzed following Gottgens et al. (1999). Calculation of $^{210}\text{Pb}$ dates followed the Constant Rate of Supply model (Appleby and Oldfield 1978).

$^{137}\text{Cs}$ activities served as independent marker horizon in the sedimentary profile. The first occurrence of this man-made nuclide in the profile generally
coincides with the onset of widespread atmospheric testing of nuclear weapons (i.e. 1954). 1959-1960 and 1963-1964 are reported as periods of maximum fallout in the northern hemisphere (Ritchie et al. 1973; Joshi 1989) and additional support for \(^{210}\text{Pb}\)-derived age/depth relationships may come from matching peak-\(^{137}\text{Cs}\) activities in the profile with these time periods.

3.2.4 Mercury analysis

Mercury was analyzed using cold-vapor atomic fluorescence spectroscopy (CVAFS) at 253.7 nm (USEPA 1995) on a Tekran® Detector (model 2500). Sediment and plant material were air-dried at room temperature and pulverized. Fish and other tissues were first analyzed wet and later converted to a dry-weight basis by analyzing separate tissue samples for moisture content. Results were expressed both on a wet- and dry-weight basis. Samples were digested with mixed warm acids for 2 hours. Following reduction with \(\text{SnCl}_2\), \(\text{Hg}^{\text{II}}\) was purged with ultra high-purity argon gas (125 ml min\(^{-1}\) flow rate), scrubbed through a soda-lime trap, adsorbed onto a pure gold-mesh trap, and thermally desorbed using a heated Nichrome coil. Determination of total mercury concentrations in samples, standards, spikes, replicates and certified reference materials used peak height on a Hewlett-Packard® Integrator (model 395). Detection limit, computed as twice the standard deviation of five method blanks, was <1 ng g\(^{-1}\) after correction for moisture content.

3.3 Results and Discussion

3.3.1 Sedimentary records of mercury deposition

Unsupported \(^{210}\text{Pb}\) activities decreased with sediment depth and approached
background levels of supported $^{210}\text{Pb}$ in three of the five cores (Figure 3-2). Gamma-assay demonstrated that the lengths of both cores recovered from Acurizal were insufficient to reach background levels of $^{210}\text{Pb}$. Therefore, unsupported $^{210}\text{Pb}$ activities had to be estimated for the lower 3 cm (Acurizal 1) and 4 cm (Acurizal 2). Sensitivity analysis revealed that halving and doubling of unsupported $^{210}\text{Pb}$ activities in those lower sections resulted for core Acurizal 1 in a mean age range of $\pm 0.5$ years sediments dated to 1980, $\pm 1.3$ years for 1960 deposits, and $\pm 4.7$ years for 70-year old deposits. The same analysis for core Acurizal 2 produced mean age ranges of $\pm 0.8$ years, $\pm 2.9$ years and $\pm 9.3$ years for 1980, 1960 and 1930 deposits, respectively. We concluded that the dated profiles for both cores were robust enough to calculate average mercury accumulation rates for 20-year intervals. We opted for a coarse dating resolution separating post-1980 deposits from 1960-1980, 1940-1960, and pre-1940 sediments. Large dating uncertainty in the bottom of the cores made $^{210}\text{Pb}$ dates unreliable for sediments older than 80 years.

We used the Constant Rate of Supply (CRS) dating model, which assumes a constant flux of $^{210}\text{Pb}$ to the sediments regardless of variations in the rate of sediment accumulation. This model is commonly applied in studies that reconstruct pollution histories, particularly when sedimentation rates have varied over time. Its use in our work was supported by three conditions (cf. Appleby and Oldfield 1983). First, the unsupported $^{210}\text{Pb}$ profiles were non-linear and non-monotonic indicating varying sedimentation rates (Figure 3-2). Second, cumulative $^{210}\text{Pb}$ residuals were similar within each of our two regions (Table 3.1) despite the differing sediment accumulation rates. Finally, the cumulative $^{210}\text{Pb}$ residuals in our five cores ranged from 20.5 to 29.0 pCi cm$^{-2}$, corresponding to $^{210}\text{Pb}$ fallout rates of 0.64 to 0.90 pCi
cm$^{-2}$ yr$^{-1}$. These rates were well within the range of fallout rates of 0.19 to 0.93 pCi cm$^{-2}$ yr$^{-1}$, reported for a large number of geographically-distinct sites (Appleby and Oldfield 1983).

$^{137}$Cs profiles were not as striking as those found in cores from the northern hemisphere (Figure 3-2). The onset of $^{137}$Cs activity (> our detection limit of 0.30 pCi g$^{-1}$) corresponded with $^{210}$Pb derived date of 1952 ± 1.8 (SD) in the northern Pantanal cores. Detectable $^{137}$Cs occurred in deposits laid down since 1967 ± 5.7 SD in the Acurizal cores. Krishnaswami and Lal (1978) suggested that inter-hemispheric mixing rates may be slower than intra-hemispheric rates and demonstrated this effect with strontium. Atmospheric bomb testing, the source for $^{137}$Cs, was conducted primarily in the northern hemisphere. Thus, it may be expected to find weak or delayed $^{137}$Cs signals in southern hemisphere cores. The difference in magnitude of the $^{137}$Cs signals in the northern Pantanal versus Acurizal may be due to the intertropical conversion zone (ICTZ) delivering some $^{137}$Cs through atmospheric circulation to the more Northern sites but not reaching far enough South to the Acurizak region (Saha 1970).
Figure 3-2. Unsupported $^{210}\text{Pb}$ (lines) and $^{137}\text{Cs}$ (bars) activities for two regions of the Pantanal - Acurizal (Acurizal 1 and 2) and the northern Pantanal (Ipiranga, Bento Gomes and Sto. Antonio D.L.). Selected $^{210}\text{Pb}$-derived sediment ages are indicated. Counting errors are $\pm$ 1SD. $^{137}\text{Cs}$ activity was measured concurrently with $^{210}\text{Pb}$ but only values exceeding instrument detection (0.30 pCi g$^{-1}$) are given. Dotted lines in Acurizal 1 and Acurizal 2 cores represent down-core estimated values (see text for details).
Table 3.1. Summary of radionuclide data for cores from two regions of the Brazilian Pantanal. Cores from the northern Pantanal are Bento Gomes, Santo Antonio D.L., and Ipiranga.

<table>
<thead>
<tr>
<th>Coring Site</th>
<th>Cumulative Residual $^{210}$Pb (pCi cm$^{-2}$)</th>
<th>Calculated $^{210}$Pb flux (pCi cm$^{-2}$ yr$^{-1}$)</th>
<th>$^{210}$Pb derived age for $^{137}$Cs onset*</th>
<th>$^{210}$Pb derived age for $^{137}$Cs peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bento Gomes</td>
<td>24.1</td>
<td>0.75</td>
<td>1951</td>
<td>1973</td>
</tr>
<tr>
<td>Sto. Antonio</td>
<td>29.0</td>
<td>0.90</td>
<td>1954</td>
<td>1970</td>
</tr>
<tr>
<td>Ipiranga</td>
<td>22.9</td>
<td>0.71</td>
<td>1954</td>
<td>1979</td>
</tr>
<tr>
<td>Acurizal 1</td>
<td>20.7</td>
<td>0.65</td>
<td>1963</td>
<td>1963</td>
</tr>
<tr>
<td>Acurizal 2</td>
<td>20.5</td>
<td>0.64</td>
<td>1971</td>
<td>1971</td>
</tr>
</tbody>
</table>

* Onset defined as oldest section with $^{137}$Cs activity exceeding instrument detection (0.3 pCi g$^{-1}$)

Figure 3-3. Average total mercury accumulation rates for selected time intervals for two regions of the Pantanal. Rates for the northern Pantanal are averaged for three cores. Acurizal rates represent average of two cores. Error bars represent +1 SD.
Average pre-1940 mercury accumulation in cores from Acurizal and the
northern Pantanal were not significantly different (14 ± 3.3 and 18 ± 4.2 μg Hg m\(^{-2}\) yr\(^{-1}\), respectively, p=0.14) (Figure 3-3). They were comparable to the rates of 12.3 ± 5.0 μg Hg m\(^{-2}\) yr\(^{-1}\) calculated for the 1900-1940 time period in cores from southeastern Alaska as a global reference (Engstrom and Swain 1997). Mercury accumulation rates during 1940-1960 and 1960-1980 were also not significantly different between our two regions (p=0.46 and p=0.17, respectively). After the onset of gold mining in the early 1980s, however, northern Pantanal mercury deposition averaged 55 ± 11.3 μg m\(^{-2}\) yr\(^{-1}\), which was more than 1.5 times higher than accumulation rates during the same time period in Acurizal sites (Figure 3-3). This difference between the two regions was statistically significant at a p-value of 0.072. I consider p-values less than 0.10 realistic in assigning statistical significance in coring studies where the number of samples (e.g., cores) is characteristically low. Modern mercury fluxes in the northern Pantanal were higher than those from systems in north temperate regions and comparable to rates found in subtropical South Florida (Table 3.2). Pre-1940 mercury accumulation in both Pantanal regions was higher than pre-industrial rates in the northern hemisphere, although flux ratios were intermediate averaging 3.2 ± 1.6 in the northern Pantanal and 2.7 ± 0.9 in Acurizal (Table 3.2).
Table 3.2. Mean (and range) of modern and pre-industrial total mercury accumulation rates and ratios for selected regions arranged by descending Hg flux ratios. Ratios are computed by averaging all individual cores from each region. Modern and pre-industrial mercury accumulation rates generally apply to post-1980 and pre-1850 time periods, respectively, unless otherwise noted.

<table>
<thead>
<tr>
<th>Location</th>
<th>Mercury flux ratio (modern/pre-industrial)</th>
<th>Number of core sites</th>
<th>Modern mercury flux (µg m(^{-2}) yr(^{-1}))</th>
<th>Pre-industrial mercury flux (µg m(^{-2}) yr(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Florida</td>
<td>4.9 (1.6-19.1)</td>
<td>18</td>
<td>53 (23-141)</td>
<td>11** (8-14)</td>
<td>Rood et al. (1995)</td>
</tr>
<tr>
<td>Finland</td>
<td>4.4 (1.2-8.9)</td>
<td>9</td>
<td>26.5 (2.3-49.5)</td>
<td>7.8 (1.9-27.0)</td>
<td>Verta et al. (1989)</td>
</tr>
<tr>
<td>Minnesota-Wisconsin</td>
<td>3.7 (3.2-4.9)</td>
<td>7</td>
<td>23 (16-32)</td>
<td>6.4 (4.5-9.0)</td>
<td>Engstrom et al. (1994)</td>
</tr>
<tr>
<td>North Pantanal (Brazil)</td>
<td>3.2 (2.5-5.1)</td>
<td>3</td>
<td>54.9 (45.6-70.8)</td>
<td>18.2* (14.0-22.3)</td>
<td>This study</td>
</tr>
<tr>
<td>Sweden</td>
<td>3.0 (1.2-7.5)</td>
<td>11</td>
<td>12.5 (6.7-20.7)</td>
<td>5.8 (1.9-17.2)</td>
<td>Johansson (1985)</td>
</tr>
<tr>
<td>West Canada</td>
<td>2.7 (1.1-7.1)</td>
<td>9</td>
<td>12.1 (3.8-28.4)</td>
<td>5.6 (0.7-14.5)</td>
<td>Lockhart et al. (1995)</td>
</tr>
<tr>
<td>Acurizal (Brazil)</td>
<td>2.7 (2.0-3.3)</td>
<td>2</td>
<td>35.4 (33.1-37.7)</td>
<td>13.8* (11.5-16.2)</td>
<td>This study</td>
</tr>
<tr>
<td>South Ontario</td>
<td>2.2 (1.5-3.2)</td>
<td>5</td>
<td>22 (10-44)</td>
<td>10** (4.8-13.6)</td>
<td>Johnson et al. 1986</td>
</tr>
<tr>
<td>Southeastern Alaska</td>
<td>2.0 (1.8-2.1)</td>
<td>3</td>
<td>16.5 (11.5-26.0)</td>
<td>8.3 (5.5-12.7)</td>
<td>Engstrom and Swain (1997)</td>
</tr>
</tbody>
</table>

** pre-1900 rates;  * pre-1940 rates
Elevated accumulation rates of mercury in post-1980 deposits in the northern Pantanal (relative to rates for the same time interval at our reference sites) suggested a regional effect of gold mining. Furthermore, increased rates in both our Pantanal regions over global reference sites, such as southeastern Alaska, pointed to a basin-wide effect of mercury emissions. Cores from both regions in the Pantanal showed comparable mercury chronologies until the onset of mining. At that time, a significant regional signal was added to the northern cores. I estimated the magnitude of that regional signal at 19.5 μg Hg m⁻² yr⁻¹, i.e., the difference between average post-1980 rates for both regions. This amounted to more than 70 kg yr⁻¹ of mercury, if I estimated the size of the mercury impacted region at roughly 3,600 km² (60 x 60 km). Lacerda et al. (1991a,b) estimated that 15,000-20,000 kg of mercury were released into the local environment between 1980 and 1990. Using this average of 1,750 kg yr⁻¹ of mercury, our regional sedimentary signal only accounted for 4% of the mercury lost to the environment with the remainder lost to the atmosphere and downstream areas, or temporarily incorporated in biota. Halving (1,800 km²) and doubling (7,200 km²) of our estimate of the impacted region yielded similarly-low estimates of the regional sedimentary signal of 2 and 8% of the total released mercury. These may be realistic estimates, although our data are based on only five cores and a very rough estimate of the size of the impacted region and the amount of released mercury.

3.3.2 Mercury levels in surface sediments and biota

Surface sediments were defined as the top 5 cm of deposits in the sediment cores. Total mercury concentrations in these sediments averaged 45.5 ± 5.5 ng Hg g⁻¹ dry in the
northern Pantanal (Table 3.3). These levels were lower than the 62-80 ng Hg g\textsubscript{dry}\textsuperscript{-1} found by Lacerda \textit{et al.} (1991b) closer to gold mines near Poconé or the 71-116 ng Hg g\textsubscript{dry}\textsuperscript{-1} found at Baia Piuval by Guimaraes \textit{et al.} (1998). Surface sediments at Acurizal averaged 29.1 ± 0.7 ng Hg g\textsubscript{dry}\textsuperscript{-1} and were significantly lower (p<0.05) than those in the northern Pantanal. Although our impacted northern region was significantly higher in mercury in surface sediments than Acurizal, both our regions were in the low range of mercury concentrations documented for surface sediments in northern hemisphere wetland systems, including Lake Erie wetlands (64.3 ng Hg g\textsubscript{dry}\textsuperscript{-1}, N=5; Cole 1997), the Okefenokee Swamp (68.3 ng Hg g\textsubscript{dry}\textsuperscript{-1}, N=3; Leady, unpublished data), and the Everglades (120 ng Hg g\textsubscript{dry}\textsuperscript{-1}, N=45; Rood \textit{et al.} 1995).

Mercury levels in biological samples from both regions in the Pantanal are given in Table 3.3. I report both wet and dry weight concentrations for animal tissues. Mercury levels per gram wet weight are commonly documented in the literature and our wet weights provide a measure for comparison. Mercury concentrations per dry gram, on the other hand, are a more appropriate measure when comparing trace levels in biological tissues with different moisture content along food chains.
Table 3.3. Comparison of average mercury content (ng g\(^{-1}\)) of biological tissues and sediment samples from two regions in the Pantanal. Left columns contain wet weight values; right columns contain dry weight levels after hygroscopic correction. Values in parentheses represent one standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>Wet weight Total Hg (ng g(^{\text{wet}}))</th>
<th>Dry weight Total Hg (ng g(^{\text{dry}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Northern Pantanal</td>
<td>Acurizal</td>
</tr>
<tr>
<td>Pygocentris nattereri</td>
<td>67.7 (31.6)</td>
<td>37.0 (26.6)</td>
</tr>
<tr>
<td>Serrasalmus spiropleura</td>
<td>44.8 (24.5)</td>
<td>33.4 (18.0)</td>
</tr>
<tr>
<td>Tetragonopterus sp.</td>
<td>7.0 (3.1)</td>
<td>20.9 (3.7)</td>
</tr>
<tr>
<td>Aphyocharax sp.</td>
<td>13.4 (3.1)</td>
<td>14.7 (9.3)</td>
</tr>
<tr>
<td>Pomacea sp.</td>
<td>0.5 (0.3)</td>
<td>0.4 (0.2)</td>
</tr>
<tr>
<td>Hydrophilidae</td>
<td>0.7 (0.6)</td>
<td>1.7 (1.1)</td>
</tr>
<tr>
<td>Salvinia auriculata</td>
<td>90.7 (9.1)</td>
<td>24.5 (3.3)</td>
</tr>
<tr>
<td>Eichhornia crassipes- roots</td>
<td>102.0 (33.2)</td>
<td>64.1 (29.6)</td>
</tr>
<tr>
<td>Eichhornia crassipes-shoots</td>
<td>34.0 (9.8)</td>
<td>23.5 (4.5)</td>
</tr>
<tr>
<td>Periphyton</td>
<td>41.6 (1.7)</td>
<td>46.6 (5.7)</td>
</tr>
<tr>
<td>Surface sediment (top 5cm)</td>
<td>45.5 (5.5)</td>
<td>29.1 (0.7)</td>
</tr>
</tbody>
</table>

Periphyton are major primary producers in freshwater systems and form an important trophic link between producers and herbivorous grazers. In addition, periphytic communities play a significant role in the methylation of mercury, as demonstrated by Cleckner et al. (1999) in the Florida Everglades. In other words, periphyton contribute to the conversion of inorganic mercury to the more toxic and bioaccumulated organic forms. Total mercury concentrations in periphyton were not significantly different between our two regions and levels were comparable to periphyton in contaminated sites in Tennessee (5-50 ng Hg g\(^{\text{dry}}\)) (Hill et al. 1996).

Mercury levels in Salvinia auriculata were significantly different between the two regions (p=0.006). This floating fern contained almost 4 times more mercury in the northern Pantanal than in Acurizal (Table 3.3). The Salvinia samples probably represent
the best population estimate of any of our biological samples. They were analyzed as a series of subsamples of a homogenate of a large number of whole plants from each region. Aula et al. (1995) proposed *S. auriculata* as a biological monitor for mercury pollution in their work in the Tucurui reservoir in the Amazon basin. They found levels of 25-225 ng Hg g$_{\text{dry}}^{-1}$ in *S. auriculata* depending on season and exposure of leaves to air or water. A Russian reservoir study found the highest levels of mercury among the macrophytes in the related species *Salvinia natans* (Kipriyanova 1997). High levels of mercury in *Salvinia* spp. may be related to the high surface area to volume ratio of this primitive plant, which maximizes exposure to mercury in the environment. Data summarized by Moore et al. (1995) on a collection of wetland plants from Canada show the same trend with highest mercury levels occurring in small plants with low vascular complexity and high surface to volume ratios.

*Eichhornia crassipes* can readily absorb and retain mercury (Lenka et al. 1990). Roots in the northern Pantanal averaged 102.0 ± 33.2 ng Hg g$_{\text{dry}}^{-1}$ (Table 3.3), 1.6 times higher than Acurizal but not significantly different between both regions (N=8, p=0.07). Shoots in the northern Pantanal averaged 34.0 ± 9.8 ng Hg g$_{\text{dry}}^{-1}$ (Table 3.3), 1.4 times higher than Acurizal but again not significantly different (N=8, p=0.06). Olivero and Solano (1998) found an average of 225 ± 21 ng Hg g$_{\text{dry}}^{-1}$ in roots of *Eichhornia crassipes* from a gold mining area in Columbia. Our stem and leaf mercury levels fell in the low end of the range of 30-140 ng Hg g$_{\text{dry}}^{-1}$ reported for the emergent macrophyte *Pontederia lanceolata* in the northern Pantanal (Lacerda et al. 1991b). Shoots and leaves of aquatic vegetation in uncontaminated areas in north temperate zones contained less than 100 ng Hg g$_{\text{dry}}^{-1}$ and usually less than 10 ng Hg g$_{\text{dry}}^{-1}$ (Cocking et al. 1991; Siegel et al. 1985).
Mercury levels in water hyacinth leaves from our sites in the Pantanal fell well below this value of contamination.

At both sites, mercury concentrations in *Eichhornia* roots were 2.7-3.0 times those in shoots. This matched our previous findings in the Okefenokee Swamp, where I found a trend for mercury to increase in concentration from leaves to stem to roots. For example, *Xyris smalliana* had root concentrations of 91.8 ng Hg g<sub>dry</sub>⁻¹ and shoot concentrations of 26.0 ng Hg g<sub>dry</sub>⁻¹ (unpublished data). Kipriyanova (1997) found a similar trend in a Russian reservoir with concentrations of almost all trace metals, including mercury, higher in roots and root stock than in macrophyte tissue above the sediment surface. Aula et al. (1995) also found submerged roots and leaves of *Salvinia auriculata* to be significantly higher in mercury than floating leaves. Factors that may contribute to such concentration differences among plant tissues include the increased levels of mercury in sediments (relative to water and air) and the possibility that aerial plant parts may rid themselves of mercury as vapor by reducing ionic Hg to elemental Hg (Siegel et al. 1987). In addition, plant roots are generally older than stems and leaves and have had more time to accumulate mercury.

Aquatic insects represent a major component of the diet of many fish species. As such, they constitute an important pathway for the channeling of mercury along a food chain (Hall et al. 1997). Adult water scavenger beetles (Order Coleoptera, Family Hydrophilidae) were collected on macrophytes from both study regions. As adults, these beetles are scavengers on dead vegetation. Their mercury concentrations were among the lowest in this study and were not significantly different between our regions (Table 3.3). Mercury levels in apple snails (*Pomacea bridgesi*, formerly *Ampullarius australis*) were
also low in our samples (N=10, 0.4-0.5 ng Hg g\text{wet}^{-1}) and not significantly different between regions (Table 3.3). *Pomacea* spp. are primary consumers feeding on periphyton and aquatic macrophytes. The snails in our collection averaged 11.5 ± 1.7 mm in diameter and were not different in size between our two regions (p=0.46). 

Lacerda *et al.* (1991a) reported mercury levels in *Pomacea bridgesi* below their detection limit (e.g., 40 ng Hg g\text{wet}^{-1}) at a site approximately 15 km downstream from a gold mine in Poconé. Their snails ranged in size and were larger than our individuals making a direct comparison between the two collections problematic. In fact, they noted a significant positive relationship between shell size and mercury content in their snail collection (Lacerda *et al.* 1991a). Eisenmann *et al.* (1997) found an average of 63 ng Hg g\text{wet}^{-1} in south Florida apple snails (*Pomacea paludosa*) with a mean shell diameter of 36 mm. Again, these larger and likely older snails may not be directly comparable to our smaller individuals. Both the beetles and the snails consume predominantly plant matter and it is interesting to note that mercury levels in these primary consumers in our samples are considerably lower than in their potential food source (e.g., periphyton and macrophyte tissue). The channeling of mercury from lower to higher trophic levels along herbivorous links in food chains may be relatively inefficient compared to transfer along carnivorous links, a phenomenon previously noted in Lake Erie wetlands (Cole 1997) and in the Florida Everglades (Roelke *et al.* 1991). Both the high water content of plant material consumed by herbivores, which in effect dilutes the mercury intake, and the low percentage of organic mercury in plant material (Moore *et al.* 1995) may play a role in this inefficient transfer.
In both regions, we made collections of four different species from the Characidae, a large family of about 300 species found mostly in South America. *Aphyocharax* sp. is a small planktivorous characid fish with a standard length of 2.5 ± 0.1 cm in our samples. This length was not different between our two sampling regions (N=12, p=0.33). Its mercury content was similar between the northern Pantanal and Acurizal (N=12, p=0.37). *Tetragonopterus* sp. consumes a variety of small aquatic invertebrates, as well as small fish. Contrary to our prediction, mercury levels in *Tetragonopterus* were significantly higher (p=0.00003) in our reference region than in the northern Pantanal. Fish length was similar between both regions (standard length 7.8 ± 0.4 cm, N=12, p=0.14) and we have no basis to believe that we collected a different species of *Tetragonopterus* from each region.

*Serrasalmus spiropleura*, a predatory piranha, was also sampled at both regions. Although this piranha has a reputation of fin-biting, its diet is more varied and feeding strategy more opportunistic than our other large predator *Pygocentris nattereri* (Sazima and Machado 1990). Mercury content of 12 filets (Table 3.3) and standard fish lengths (10.6 ± 2.1 cm) were not significantly different between regions (p=0.19, p=0.43, respectively). *P. nattereri* was the largest predatory piranha sampled (standard length 13.7 ± 2.4 cm). The mercury content of filets was significantly higher in the northern Pantanal region (N=16, p= 0.04). The standard length of our *P. nattereri* collections was not significantly different between regions (N=16, p=0.37). Our results compare well with Lacerda *et al.* (1991a) who reported 60 ± 10 ng Hg g<sub>wet</sub>⁻¹ in this species in the Bento Gomes river some 20 km downstream from gold mines in Poconé. Lacerda *et al.* (1994) found 300 ± 360 ng Hg g<sub>wet</sub>⁻¹ in this species in the Carajas mining region in the
southeastern Amazon, i.e., 4.4 times the amount in our *Pygocentris* from the northern Pantanal.

We correlated standard fish length with mercury levels for *P. nattereri* from the two regions (Figure 3-4). Both correlations were significant (longer fish contain more mercury), but the slope of the regression line for the northern Pantanal was 2.6 times the slope for the Acurizal collection. This difference in slope was statistically significant (p=0.05). It indicated that, as these piranhas get larger, *P. nattereri* gained 2.6 times more mercury per cm of growth near the mining region than in Acurizal. This implied an elevated rate of biomagnification in the northern Pantanal compared with our reference region.

![Figure 3-4. Regressions of standard length (cm) and mercury content (ng g\(^{-1}\) dry) of filets of *Pygocentris nattereri* from two regions of the Pantanal: Acurizal (closed circles) and the northern Pantanal (open circles).](image)

Interestingly, we found nearly the same ratio for *S. spiropleura*, although the correlation between fish length and mercury content was not significant at 0.05 level for our Acurizal collection. Unfortunately, these piranhas were very difficult to age and an
alternative explanation for these results may be that *P. nattereri* in the northern Pantanal grew more slowly than near Acurizal. Although the age/size relationship is complicated, in general larger fish of the same species are older and have had a longer time to accumulate mercury.

In summary, we documented for the first time radionuclide-dated mercury accumulation profiles from a mercury-impacted and a reference region in the Pantanal. We uncovered a regional effect of mercury released from gold mining in cores from the northern Pantanal. We also showed a basin-wide effect of elevated mercury accumulation in all our cores relative to global reference sites. In addition, we documented mercury levels in a variety of organisms linked in *in-situ* food webs and we focused on comparing the same taxa, number of individuals, and size classes between both regions. Plant tissues contained more mercury in the impacted northern Pantanal than in our reference region. Herbivores contained little mercury in both regions, while larger carnivorous piranha species showed elevated mercury body burdens in the northern Pantanal. This confirmed previous work which showed that the channeling of mercury from lower to higher trophic levels along herbivorous links is inefficient compared to transfer along carnivorous links. Our data also suggested that the rate of mercury magnification in upper trophic-level carnivorous fish was significantly higher in the northern Pantanal than in the reference region. Magnification of mercury along food chains and its chronic and toxic impact on biota may threaten biodiversity and human health. Understanding mercury dynamics in the Pantanal, with its remarkable biodiversity and with a human population that traditionally relies on a high per capita fish
consumption, is therefore particularly important. Our work intended to contribute to this understanding.

3.4 References


Chapter 4

Organic Mercury Biomagnification in Food Webs in the Wetlands of the Northern Pantanal, Brazil and Western Basin of Lake Erie

Abstract
Understanding the dynamics of mercury biomagnification depends on knowledge of both the natural history of each species and the history of mercury contamination in the region. Here, I compare and contrast mercury dynamics in temperate and tropical systems. If the process of mercury biomagnification is similar in Brazilian and Lake Erie wetlands, then a similar pattern of increase should be seen in mercury levels along a food chain. I examined MeHg biomagnification in two locations (East Marsh, Lake Erie, USA and Baia Piuval, Pantanal, Brazil) as examples of temperate and tropical systems with a history of mercury pollution. In each location four trophic levels were analyzed for MeHg and THg on a wet and dry weight basis. Using the Jonckheere-Terpstra test, a significant directional increase in both methyl and total mercury with increasing trophic level was found in both the Lake Erie East Marsh (both p=0.001) and Pantanal trophic levels (THg p=0.0002, MeHg p=0.001). The pattern of biomagnification in East Marsh
was more pronounced than that in the Pantanal. Differences between temperate and tropical systems may be attributed to changes in feeding habits during the year and/or differences in the relative growth rate/age of the fish examined. Biomagnification factors, the magnitude of change in mercury burden between trophic levels, were similar in the top predator in each system (East Marsh, *Micropterus* 5.5; Pantanal, *Pygocentrus* 6.2) but the magnitude from omnivores to top predator was different (East Marsh 53.6 versus Pantanal 9.6). In both the Pantanal and East Marsh, significant positive relationships existed between MeHg concentration in tissue and length of fishes in all but one species, *Tetragonopterus*. The rate of increase in MeHg per cm growth was highest in top predators (*Micropterus* 37.4 ng MeHg g\(^{-1}\) dry cm\(^{-1}\) and *Pygocentrus* 17.9 ng MeHg g\(^{-1}\) dry cm\(^{-1}\)) and decreased with decreasing trophic level. East Marsh (24.9±14.7 ng MeHg g\(^{-1}\) dry cm\(^{-1}\)) had twice the average rate of MeHg increase in fish tissues as the Pantanal (12.3±7.9 ng MeHg g\(^{-1}\) dry cm\(^{-1}\)), likely due to the much higher rate of mercury contamination in the Lake Erie region. Results indicate the need for further natural history information in tropical species. My results supported the prediction of increasing tissue levels of MeHg during the lifetime of a fish as it increases in size and the existence of differences in rates of biomagnification among species of fish and between temperate and tropical systems. The paucity of data on this makes understanding mercury dynamics (for use in setting fish consumption advisories, for example) very difficult.
4.1 Introduction

Mercury in the environment is the result of both natural and anthropogenic processes. Anthropogenic contamination has increased 2-5 times since the industrial revolution in many areas (Engstrom and Swain 1997). Significant anthropogenic mercury sources are the use and loss of mercury in manufacturing (including chlor-alkali plants) and the burning of fossil fuels (including coal for electric power generation) (Keating et al. 1997).

Total mercury in environmental samples is composed of both inorganic and organic forms. Organomercurial compounds, especially methylmercury (CH$_3$Hg or MeHg), are found in lower concentrations in the environment but are more toxic and more readily bioaccumulated (Brossett 1987; Fitzgerald and Watras 1989). Inorganic mercury can be methylated into methyl mercury (MeHg), one form of organic mercury. Methylation is primarily by anaerobic microorganisms such as sulphate-reducing bacteria (Gilmour et al. 1992). Methylation occurs in sediments (King et al. 2000), water (Eckley and Hintlemann 2006) and periphyton (Mauro et al. 2002). MeHg is absorbed more readily and excreted more slowly than other forms of mercury (Young et al. 2001). MeHg in an organism is the result of both bioaccumulation (direct uptake from the environment through gills for example) and biomagnification (accumulation of MeHg from food) (Baeyans et al. 2003). Uptake through the gills is relatively small compared to dietary uptake (Hall et al. 1997).

The percentage of organic mercury in the total mercury burden varies by trophic level and organism. Mercury in sediments is primarily inorganic. In plants, methyl mercury comprises 0 to 23% of the total mercury concentration (Cappon 1987). Usually
less than 60% of the mercury in invertebrates is organic (Wren et al. 1995). In fish, 85-98% of the mercury is organic (Grieb et al. 1990; Bloom 1992).

The process of total and methyl mercury accumulation in fish and other organisms has been studied in limited species primarily in the temperate zone (for reviews see Boening 2000; Ullrich et al. 2001). The species of interest are primarily those of sport or commercial utility with direct impacts on human consumption. Far less information is available for organisms at the base of food chains. The extent of trophic transfer depends on physical features such as characteristics of the watershed and water body, and the history of natural and anthropogenic mercury contamination of the region (Chen and Folt 2005). In a specific organism, accumulation and trophic transfer will depend on characteristics of the water body it inhabits and the age, size, and trophic position of the organism.

In the Pantanal wetland of Brazil, a history of use and release of mercury in the mining of gold has raised concerns due to its impact on both humans and wildlife (Alho et al. 1988; Lacerda et al. 1991a,b). Research has documented the history of mercury deposition using sediment cores and sampling of various organisms (Leady and Gottgens 2001; Hylander et al. 2003; Lacerda et al. 2011; Vieira et al. 2011). Research has focused on general classes or types of organisms due to the lack of detailed natural history information (Lacerda et al. 1991a). Isotope studies have found an average shift of 0.7 trophic levels within a species due to the alternation of abundant and variable food during flooding with increasing carnivory and starvation during the dry season (Wantzen et al. 2002). It is only in the last decade that fish consumption advisories have been
considered in Brazil. The threat of mercury toxicity had to be balanced with the basic need for calories and the benefits of eating fish (Boischio and Henshel 2000).

High mercury levels were discovered in Lake Erie fish in 1970. One of the main sources of mercury contamination in this case were chlor alkali plants along the Detroit River. Various organisms (primarily sport and commercial fish) have been examined to help determine human health consumption advisories. Patterns of total mercury accumulation have been quantified along two food chains in five coastal marshes of western Lake Erie (Cole 1997). Herbivory was suggested as less effective at channeling total mercury to higher trophic levels than chains with numerous detrivore links.

Food chain length and composition have proven vital to understanding mercury biomagnification (Cabana et al. 1994). A simple food chain model might consist of benthic invertebrates, prey fish, and piscivorous fish. Benthic organisms are exposed to sediment-associated contaminants by a variety of routes. Direct contact with sediments and sediment pore water, ingestion of particles incidentally or as food and filtration of the pore water are potential routes (Saouter et al. 1991). Fish are exposed to mercury primarily through ingestion and from uptake through the gills during respiration (Hall et al. 1997).

The purpose of this part of my dissertation was to compare and contrast mercury biomagnification in tropical and temperate wetland organisms from locations with histories of regional mercury pollution. I hypothesized that, if the process of mercury biomagnification is similar in Brazilian and Lake Erie wetlands, then a similar pattern of increase should be seen in mercury levels along both food chains. Analogously, I should also find similar patterns of enrichment of MeHg in comparable levels in both food
chains. Very little is documented on the levels of MeHg in the Pantanal or on the specifics governing biomagnification in that system. Fish are extremely important to the economic and physical health of the people of the Pantanal. A clearer understanding of the levels and process involved in biomagnifying mercury will assist in determining safe and reasonable fish consumption advisories (Boischio and Henshel 2000).

4.2 Materials and Methods

4.2.1 Site descriptions

4.2.1.1 Lake Erie marsh

The East Marsh in Magee Marsh Wildlife area was sampled as part of a larger project on mercury in wetlands (Cole 1997) (Figure 4-1). This diked marsh is shallow with open water pools and canals. The impoundments are managed for water levels to promote plant germination, wildlife habitat, and migration stopovers for waterfowl. It is dominated by cattail (Typha sp.), bulrush (Scirpus spp.), water lily (Nymphaea sp.), and pond weeds (Potomogeton sp.) (Bolesenga and Herdendorf 1993). The sediments are approximately 0.5-1.0 m deep over clay and contain decomposing organic matter (Bolesenga and Herdendorf 1993). The marsh is located approximately 30 km east of Toledo, Ohio on the southwestern shore of Lake Erie (41° 36′51″ N/ 083° 09′50″ W) (Figure 4-1).

Collection methods appropriate to the organism were used. Palaemonetes kadiakensis were collected by dip net. Fundulus notatus were collected by seining. Micropterus salmoides and Lepomis gibbosus were collected by electrofishing. All samples were handled using clean field techniques. Stainless steel tools and acid washed
sample bottles were used to minimize mercury contamination. Collected organisms were identified to genus or species and frozen. *Micropterus salmoides* and *Lepomis gibbosus* were analyzed as samples of the filet. The smaller organisms (*Fundulus notatus* and *Palaemonetes kadiakensis*) were analyzed whole. Samples were frozen pending analysis, followed by drying at room temperature to a constant weight and analysis for both total and MeHg.

![Map of East Marsh](image)

Figure 4-1 Map of East Marsh located in Magee Marsh Wildlife Area approximately 30 km east of Toledo, Ohio on the southwestern shore of Lake Erie. Yellow border of East Marsh indicates diked area used to manipulate water levels inside the marsh. Google maps source of satellite image. Map inset from USEPA.

### 4.2.1.2 Northern Pantanal

I sampled in the northern Pantanal in sites with a history of gold mining (Figure 4-2) (Leady and Gottgens 2001). I selected a wetland location with minimum
disturbance and with maximum water depth during the dry season. Baia Piuval on the Fazenda Ipiranga is a shallow lake on the Rio Bento Gomes (16°22’30” S / 56°34’00” W) approximately 20 km south of the Poconé gold mining region (Figure 4-2). Vegetation was dominated by floating aquatic species (including *Eichhornia crassipes*, *Salvinia auriculata*, *Azolla* sp., and *Pistia stratoides*), common in neotropical systems with highly-fluctuating water levels (Fortney *et al.* 2004).

Figure 4-2. Map of Pantanal indicating the Baia Piuval on the Rio Bento Gomes. The location is approximately 20km south of Poconé. Google maps source of inset and satellite image.
Organisms were identified to genus or species and frozen. All samples were handled using clean field techniques. *Aphyocharax* sp. and *Palaemonetes* sp. were analyzed whole. The larger fish species (*Tetragonopterus* sp and *Pygocentrus nattereri*) were analyzed as filets. Samples were transported frozen back to the U.S. (with appropriate permits), dried at room temperature to a constant weight and analyzed for both total and MeHg.

4.2.2 Selected Organisms

In each site, I selected organisms representing successive levels in a food chain. Methyl mercury is known to be extremely low in sediments and plants (Roulet *et al.* 2001) so these were not analyzed. In both systems, Grass shrimp (*Palaemonetes* sp.) represented the lowest trophic level. Small fish representing omnivorous and carnivorous species included Pumpkinseed (*Lepomis gibbosus*), Blackstripe top minnows (*Fundulus notatus*), *Aphyocharax* sp., and *Tetragonopterus* sp. Top level piscivorous carnivores were largemouth bass (*Micropterus salmoides*) and Red-bellied piranha (*Pygocentrus nattereri*). Functional positions in the food chain and dietary specific for each species are discussed below.

4.2.3 Mercury analyses

4.2.3.1 Total Mercury

Total mercury was analyzed using cold-vapor atomic fluorescence spectroscopy (CVAFS) at 253.7 nm (USEPA 1995) on a Tekran® Detector (model 2500). Fish and shrimp were first analyzed wet and later converted to a dry-weight basis by analyzing
separate tissue samples for moisture content. Results were expressed both on a wet- and
dry-weight basis. Samples were digested with mixed warm acids for 2 hours. Following
reduction with SnCl\textsubscript{2}, Hg\textsuperscript{+} was purged with ultra high-purity argon gas (125 ml min\textsuperscript{-1}
flow rate), scrubbed through a soda-lime trap, adsorbed onto a pure gold-mesh trap, and
thermally desorbed using a heated Nichrome coil. Determination of total mercury
concentrations in samples, standards, spikes, replicates and certified reference materials
used peak height on a Hewlett-Packard\textsuperscript{®} Integrator (model 395). Detection limit,
computed as twice the standard deviation of five method blanks, was <1 ng g\textsuperscript{-1} after
correction for moisture content.

**4.2.3.2 Methyl Mercury**

Methyl mercury analysis of samples was performed using the distillation method
of Horvat et al. 1993. Samples were placed in glass bottles to which e-pure water,
sulfuric acid, hydrochloric acid and potassium chloride were added. Bottles were placed
in a distillation block maintained at 140\textdegree C. The samples were distilled through Teflon
lines under nitrogen flow of 60ml min\textsuperscript{-1}. The distillate was collected in another glass
bottle containing approximately 10mL deionized water in a closed cooler. Cooling aided
in condensation and kept distillates in the dark. Distillation was halted when
approximately 80 to 90% of the sample was distilled (60-90 minutes).

Distillates were analyzed within 24 hours. The distillate pH was adjusted to about
4.9 using 200ul of acetate buffer, ethylated using 100ul of 1% sodium tetraethyl borate
(NaTEB) and purged with nitrogen onto a graphitized carbon trap (Carbotrap). Mercury
was thermally desorbed from the trap and carried into the analytical stream using ultra-
high purity argon at 20 ml min\(^{-1}\). Mercury peaks were separated using isothermal gas chromatography. The column was composed of Chromasorb WAW-DMSC kept at 60°C. Peaks were converted to inorganic mercury on a pyrolytic column consisting of quartz wool heated to 700-800°C prior to detection by CVAFS. A Tekran model 2500CVAFS was used for peak height detection.

Analytical quality control was performed by analysis of two certified reference materials (CRMs) (DORM-1 and TORT-11). Typically, sixteen samples were distilled at one time consisting of ten samples, one duplicate, three distillation blanks, a spike and a CRM. The mean value for DORM-1 was 0.687±0.040 (reference value 0.731±0.060). The mean value for TORT-11 was 0.120±0.008 (reference value 0.128±0.014). Recovery of MeHg in distillation blanks was less than 5% of the concentrations measured in samples. Recovery of spikes averaged 94.2±0.54%.

**4.2.4 Statistical Analysis**

Concentration data for THg and MeHg were not normally distributed. THg and MeHg concentrations were log transformed prior to analysis. The Rcmdr interface for R was used to perform statistics (Fox *et al.* 2007). Differences between the two locations and between the trophic levels were assumed to exist (Table 4.1). A traditional 2-way ANOVA cannot be applied to these data as confirmation. The same organisms were not present in both sites. Instead, organisms were coded as belonging to a trophic level (O4 – highest trophic level to O1 – lowest trophic level). Then a 2-way ANOVA was used with location and four trophic orders. The Jonckheere-Terpstra test was used to assess an
alternative hypothesis that an ordered increase in THg and MeHg occurred in successive trophic levels in each location (Bewick et al. 2004).

4.3 Results and Discussion

Mercury concentrations are presented in Table 4.1 for both THg and MeHg on both a wet and dry weight basis. THg has been the most common method of assessing Hg because of its relative ease of analysis compared to MeHg. For the three fish species in each location, the percentage of total mercury that is methylmercury (%MeHg) was almost 100%. This same pattern has traditionally been found in other locations (Bloom 1992). The utility of wet or dry weight measurements depends on the goal of the study. Wet weights are more useful when the goal is to address direct effects of Hg on the organism and its consumers. Fish consumption advisories for humans are based on wet weights of food fish. Dry weights are more useful for tracking the accumulation of Hg through a food chain. Both wet and dry weights were used in this study, although I focused on mercury levels on a dry weight basis for the quantification of biomagnification factors.

4.3.1 Lake Erie East Marsh Food Web

Four trophic levels were examined in Lake Erie’s East Marsh. Largemouth bass (Micropterus salmoides) had the highest mercury concentrations in the study. As a top predator subject to the highest level of biomagnification, it was not surprising that their total mercury level in this region of known mercury pollution was by far the highest in the study (Table 4.1). East Marsh is a diked marsh and impoundments have been
identified as enhancing mercury availability to fish (Jackson 1991). Largemouth bass in other locations in the U.S. with high levels of mercury concentration have two or more times the mercury levels found in East Marsh (Table 4.2).

Both THg and MeHg concentrations dropped drastically in smaller carnivorous fish. Diet specifics are given in Table 4.2. Smaller fish were both lower in trophic level and likely younger in age. Based on length, the bass in this study were more than nine years of age (Smith et al. 2007). The Pumpkinseeds were likely 3-4 years old based on size (Smith et al. 2007). Smaller fish that consume prey lower in mercury content and with less time to accumulate mercury were expected to have lower mercury concentrations in their tissue.

Differences in mercury content between the two locations and among trophic levels were evident (Table 4.1). A two-way ANOVA, with location and four coded trophic orders, showed significant differences between the two locations for both total and methyl mercury (p<0.001) and among all four levels in the food web for both total and methyl mercury (p<0.001). Much higher mercury concentrations were found in East Marsh organisms as expected due to Lake Erie’s history of mercury pollution.
Table 4.1 Mercury content of organisms collected from East Marsh, Lake Erie and the northern Pantanal, Brazil. Sample processing is described in detail in the Methods section. Trophic level is based on literature. Concentrations are given as mean±1SD. %Me is calculated by dividing the concentration of MeHg by the concentration THg ng g\(^{-1}\) dry.

<table>
<thead>
<tr>
<th></th>
<th>Organism</th>
<th>Sample Type</th>
<th>Level</th>
<th>ng MeHg g(^{-1}) dry</th>
<th>ng MeHg g(^{-1}) wet</th>
<th>ng total Hg g(^{-1}) dry</th>
<th>ng total Hg g(^{-1}) wet</th>
<th>%Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Erie</td>
<td>Largemouth bass (Micropterus salmoides)</td>
<td>filet</td>
<td>Carnivore</td>
<td>2063.5±52.6</td>
<td>454.0 ±11.6</td>
<td>2066.2 ±52.9</td>
<td>454.6 ±11.6</td>
<td>99.9%</td>
</tr>
<tr>
<td></td>
<td>Pumpkinseed (Lepomis gibbosus)</td>
<td>filet</td>
<td>Carnivore</td>
<td>376.0± 27.1</td>
<td>90.2 ±6.5</td>
<td>381.5 ±26.3</td>
<td>91.6 ±6.31</td>
<td>98.6%</td>
</tr>
<tr>
<td></td>
<td>Blackstripe top minnow (Fundulus notatus)</td>
<td>whole body homogenate</td>
<td>Carnivore</td>
<td>199.3± 9.1</td>
<td>51.8±2.4</td>
<td>206.0 ±15.1</td>
<td>53.6 ±2.1</td>
<td>96.7%</td>
</tr>
<tr>
<td></td>
<td>Grass shrimp (Palaemonetes kadiakensis)</td>
<td>whole body homogenate</td>
<td>Omnivore</td>
<td>38.5± 3.9</td>
<td>6.2 ±0.6</td>
<td>123.3 ±15.5</td>
<td>19.7 ±1.7</td>
<td>31.2%</td>
</tr>
<tr>
<td>Northern Pantanal</td>
<td>Red-bellied piranha (Pygocentrus nattereri)</td>
<td>filet</td>
<td>Carnivore</td>
<td>306.3±40.1</td>
<td>76.6 ±10.0</td>
<td>311.1±39.6</td>
<td>77.8 ±9.9</td>
<td>98.4%</td>
</tr>
<tr>
<td></td>
<td>Aphyocharax sp.</td>
<td>whole body homogenate</td>
<td>Carnivore</td>
<td>49.8±6.3</td>
<td>12.9 ±1.6</td>
<td>51.3±8.2</td>
<td>13.3 ±2.1</td>
<td>97.1%</td>
</tr>
<tr>
<td></td>
<td>Tetragonopterus sp.</td>
<td>filet</td>
<td>Omnivore</td>
<td>18.8±5.4</td>
<td>5.3 ±1.5</td>
<td>20.8±5.0</td>
<td>5.8 ±1.4</td>
<td>90.4%</td>
</tr>
<tr>
<td></td>
<td>Grass shrimp (Palaemonetes pugio)</td>
<td>whole body homogenate</td>
<td>Omnivore</td>
<td>31.8±5.9</td>
<td>5.4 ±1.0</td>
<td>43±7.4</td>
<td>7.2±1.3</td>
<td>74.7%</td>
</tr>
</tbody>
</table>
Table 4.2. Diet specifics for organisms sampled in Lake Erie’s East Marsh and Northern Pantanal’s Baia Piuval. Size range for fish is Total Length (TL) or length from the tip of the snout to the tip of the longer lobe of the caudal fin.

<table>
<thead>
<tr>
<th>Organism</th>
<th>Level</th>
<th>Size range (mm) &amp; Sample size (N)</th>
<th>Diet specifics</th>
<th>Mean Hg levels (from the literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Largemouth bass (Micropterus salmoides)</td>
<td>Carnivore</td>
<td>486-523; N=6</td>
<td>Large invertebrate such as crayfish and carp, minnows, and any other available fish species (including other bass) (Trautman 1981)</td>
<td>Magee Marsh - 1494 ng THg g⁻¹ dry (Cole 1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Great Lakes region - 400 µg THg g⁻¹ wet (Monson et al. 2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sacramento-San Joaquin Delta, CA – 530 ng THg g⁻¹ wet (Davis et al. 2008)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Savannah River - 840 ng total Hg g⁻¹ wet (Burger et al. 2001)</td>
</tr>
<tr>
<td>Pumpkinseed (Lepomis gibbosus)</td>
<td>Carnivore</td>
<td>139-160; N=4</td>
<td>Insects, mollusks and small crustaceans (Keast 1978)</td>
<td>Magee Marsh - 355.5 ng THg g⁻¹ dry (Cole 1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Savanna River - 220 ng g⁻¹ wet (Paller and Litrell 2007)</td>
</tr>
<tr>
<td>Blackstripe top minnow (Fundulus notatus)</td>
<td>Carnivore</td>
<td>49-62; N=4</td>
<td>Terrestrial arthropods, snails, aquatic insects and microcrustaceans</td>
<td>Magee Marsh - 192 ng THg g⁻¹ dry (Cole 1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Atmar and Stewart 1972)</td>
<td>Illinois- 1000 ng THg g⁻¹ wet (Levengood et al. 2013)</td>
</tr>
<tr>
<td>Grass shrimp (Palaemonetes kadiakensis)</td>
<td>Omnivore</td>
<td>Not measured; N=4</td>
<td>Zooplankton, phytoplankton and detritus (Olmi and Lipcius 1991, Morgan 1980, Uguccioni and Posey 1992)</td>
<td>Magee Marsh - 139.6 ng THg g⁻¹ dry (Cole 1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Texan cypress swamp - 601 ng THg g⁻¹ dry (Chumchal et al. 2011).</td>
</tr>
</tbody>
</table>
Table 4.2. continued

<table>
<thead>
<tr>
<th>Organism</th>
<th>Level</th>
<th>Size range (mm) &amp; Number (N)</th>
<th>Diet specifics</th>
<th>Mean Hg levels</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Red-bellied piranha</strong> <em>(Pygocentrus nattereri)</em></td>
<td>Carnivore</td>
<td>123-170; N=6</td>
<td>Adults are fish-eaters but mostly scavenge dead and dying vertebrates (Pauly 1994)</td>
<td>Alto Pantanal, Brazil – 255 ng THg g(^{-1}) wet (Hylander <em>et al.</em> 2000)</td>
</tr>
<tr>
<td>*<em>Aphyocharax sp.</em></td>
<td>Carnivore</td>
<td>32-54; N=4</td>
<td>Zooplanktivore (Russo and Hahn 2006)</td>
<td>Itenez River, Bolivian Amazon – 467 to 1140 ng THg g(^{-1}) dry (Laffont <em>et al.</em> 2009)</td>
</tr>
<tr>
<td><strong>Tetragonopterus sp.</strong>*</td>
<td>Omnivore</td>
<td>75-90; N=4</td>
<td>Plant material, insects and small fish (Corrêa <em>et al.</em> 2011)</td>
<td>Tapajós River, Brazilian Amazon – 403 ng THg g(^{-1}) wet (DaSilva <em>et al.</em> 2005)</td>
</tr>
<tr>
<td>Grass shrimp <em>(Palaemonetes pugio)</em></td>
<td>Omnivore</td>
<td>Not measured; N=4</td>
<td>Epiphytic microalgae on the surface of the vegetation (Morgan 1980)</td>
<td>Non-piscivorous fish – Tapajós River, Brazilian Amazon – 42 ng THg g(^{-1}) wet (DaSilva <em>et al.</em> 2005)</td>
</tr>
</tbody>
</table>

* Characid omnivorous fish – Rio Negro, Amazon - *Triportheus* - 13-135 ng THg g\(^{-1}\) wet (Dorea *et al.* 2006)

* Characid omnivorous fish – Rio Negro, Amazon - *Hemigrammus* 124-368 ng THg g\(^{-1}\) wet (Barbosa *et al.* 2003)

* New Jersey estuary - 7310 ng THg g\(^{-1}\) wet (Bergey *et al.* 2002)

* No specific published data on mercury levels of *Aphyocharax* sp. or *Tetragonopterus* sp. were available. Other similar small fish from the region were used for comparison.
Lake Erie’s wetlands are subjected to a higher degree of contamination due to both direct and indirect industrial and agricultural mercury pollution to a much greater extent than the Pantanal in Brazil. The differences in the level of mercury contamination were apparent in a comparison of modern mercury flux ratios calculated from sediment cores. Leady and Gottgens (2001) found a modern mercury flux for the northern Pantanal of 54.9 ug m$^{-2}$ yr$^{-1}$. In Chapter 2, the modern mercury flux for Lake Erie was found to be 937.4 ug m$^{-2}$ yr$^{-1}$.

Biomagnification produced higher levels of methyl mercury contamination in successively higher levels in the food web (Table 4.1). While an ANOVA confirmed the existence of significant differences in this study, it did not address the question of the directionality of that difference. The Jonckheere-Terpstra test was used to assess an ordered alternative hypothesis (Bewick et al. 2004). In both locations, both MeHg and THg were lower in the lower levels of the food chain and higher in the top level of the food chain. A significant directional increase in both methyl and total mercury was found in both the Lake Erie East Marsh (both p=0.001) and Pantanal trophic levels (THg p=0.0002, MeHg p=0.001).

The majority of the total mercury in fish is methyl mercury (Bloom 1992). As expected, in East Marsh, 96.7-99.9% of the total mercury was MeHg in the three fish species (Table 4.1). The transition from the three fish species to shrimp was a shift away from a high to low percentage of MeHg.

Grass shrimp (*Palaemonetes kadiakensis*) are small benthic crustaceans. They had the lowest THg, MeHg and %MeHg for Lake Erie’s East Marsh organisms sampled. As the lowest trophic level sampled, this was expected. Grass shrimp eat periphyton
which has been identified as a site of important bacterial activity associated with mercury
methylation (Guimaraes et al. 2006). This was evident if we compare grass shrimp
MeHg levels to average sediment MeHg. A survey of 579 sites across northeastern North
America found an average of 3.83 ng MeHg g$^{-1}$ dry weight in sediments (Kamman et al.
2005), an order of magnitude lower than East Marsh grass shrimp. The low %MeHg is
typical of invertebrates as usually less than 60% of the mercury in invertebrates is organic
(Wren et al. 1995).

4.3.2 Northern Pantanal Marsh Food Web

The basic natural history of many organisms in the Pantanal is still a subject of
research. The details of the diet and position (or positions) in the food web for many
species of fish are still poorly known (Corrêa et al. 2011; Wantzen et al. 2002).
Omnivory and feeding in different trophic intervals is common in many neotropical fish
food webs (Winemiller and Jepsen 1998). Stable isotope studies have found fish in the
Pantanalan to feed on a trophic continuum rather than discrete levels (Wantzen et al. 2002).
In contrast, temperate zone isotope studies have found trophic structures to be relatively
stable over the year (Delong et al. 2001).

In the northern Pantanal’s Baia Piuval, four trophic levels were also examined.
Red-bellied piranhas (Pygocentrus nattereri) are top level predators. The piranhas
collected in this study were smaller than the adult average of 30cm (Zelditch and Fink
1995). As young/small fish, Pygocentrus nattereri primarily eat aquatic invertebrates
and add fish scales and fish fins to their diet as they grow (Zelditch and Fink 1995).
Piranha in this study had only 15% of the total mercury burden as Largemouth bass
The piranha body size was much smaller and the fish were likely much younger than the bass. A younger fish would have less time to accumulate mercury. Not surprisingly, almost all the mercury in these fish was MeHg \((306.3 \pm 40.1 \text{ ng MeHg g}^{-1} \text{ dry or } 98.4\% \text{ MeHg})\).

Little information exists on the dietary preferences of the two smaller fish in this study, *Aphyocharax* sp. and *Tetragonopterus* sp. Both, along with *Pygocentrus*, are members of the order Characiformes. This group is ecologically and morphologically diverse, containing members that specialize in trophic levels from herbivores to top carnivores. Based on DNA analysis, *Aphyocharax* sp. and *Tetragonopterus* sp. are fairly close in relationship being members of the subfamily Glandulocaudinae (Ortí and Meyer 1997). *Aphyocharax* sp. is viewed as an important link between primary producers and upper levels of the food web (Russo and Hahn 2006). *Tetragonopterus* sp., although a larger body-size fish than *Aphocharax*, is an omnivore that can shift to higher or lower percentages of fish or vascular plants in their diets (Corrêa *et al.* 2011). Comparisons to other similar fish indicated fish from the Pantanal were lower in THg than small non-piscivorous fish in the Amazon (Table 4.2).

Like grass shrimp in Lake Erie’s wetlands, grass shrimp (*Palaemonetes pugio*) in the Pantanal are omnivores (Morgan 1980). Again, as the lowest trophic order examined, they had the lowest THg \((43 \pm 7.4 \text{ ng THg g}^{-1} \text{ dry})\) and MeHg \((31.8 \pm 5.9 \text{ ng MeHg g}^{-1} \text{ dry})\) of any organism sampled at either location.
4.3.3 Comparing Pantanal and East Marsh

Although a significant pattern was found in both locations, the pattern of biomagnification in the Pantanal was not as clear as that in the Lake Erie marsh food chain (Figure 4-3). This may be due to the more common omnivory and feeding in different trophic intervals in many neotropical fish food webs (Winemiller and Jepsen 1998). As mentioned earlier, stable isotope studies have found fish in the Pantanal to feed on a trophic continuum rather than discrete levels (Wantzen et al. 2002). In the temperate zone trophic positions were found to be relatively stable over the year (Delong et al. 2001).

Differences in biomagnification patterns may also be due to differences in the relative growth rates and age of temperate and tropical fish. *Pygocentrus* and *Micropterus* are both top level predators in their system. Bass in this study are physically larger than the Piranha. The age-length relationship in fish is not linear and bass in a temperate system may be much slower growing and thus much older (and have had more time for biomagnification) than an equal sized Piranha with a faster growth rate. Amazonian fish were labeled as “fast-growth, fast-reproduction and short-life” with large fish reaching reproductive maturity in one to two years and a life span of less than ten years (Gragson 1992).

While there was an overall similarity of the pattern of increase in food chains in both East Marsh and Baia Piuval, I also noted specific differences based on the natural history of the fish involved. This underlines a problem in applying the extensive data on mercury levels in temperate fish directly to tropical fish in terms of fish consumption guidelines for humans. More extensive research on basic natural history to determine
diet during a specific species lifetime is imperative to understanding mercury dynamic in that species. As Boischio and Henshel (2000) pointed out, a lack of natural history data and dire need for protein in the diet make uniformed fish consumption guidelines a serious mistake.

![Graph of mercury content in organisms](image)

Figure 4.3. Total and methyl mercury in organisms (dry weight basis) representing food chains in the northern Pantanal (Brazil) (top panel) and Lake Erie marshes (Ohio, USA) (bottom panel). Note the different scales on the ordinate. Concentrations are given in dry weight as mean±1SD.
4.3.4 Biomagnification Factors.

Biomagnification factors (BMF) were determined by comparing successive trophic levels. This allowed for a comparison of the magnitude of the change in mercury levels between trophic levels within and between systems. BMF have been reported in the literature on a wet and a dry weight basis. Dry weight basis was more accurate in this context because it eliminated variability due to varying water content in tissue levels that may result from different sample preservation and handling techniques. Following MeHg concentrations on dry weight basis, allowed me to follow Hg through a food web regardless of the organism’s water content. BMF were calculated between trophic levels for the dry weight MeHg concentrations (Table 4.3). BMF in the top predator in each system was similar but the magnitude of change from grass shrimp to top predator was drastically different. In East Marsh, a documented long-term history of mercury pollution and high fish mercury concentrations in Lake Erie likely may account for the large jump in BMF from grass shrimp to bass in MeHg. Fish in Papua New Guinea had BMF between omnivores and carnivores ranging from 1.5 to 1.6 based on wet weights (Bowles et al. 2001). Using MeHg concentrations for wet weight to calculate BMF gave higher values for both the Pantanal (2.4 and 5.9) and East Marsh (1.7 and 8.8). It was noted that while their sample site, Lake Murray, is high in mercury for Papua New Guinea, it is not high compared to other tropical or temperate locations with industrial mercury contamination (Bowles et al. 2001).

Length of the food chain plays a critical role in the degree of biomagnification possible in a system. In temperate systems, several studies have found that increasing the length of the food chain increases MeHg content in fish. Lake trout (Salvelinus
namaycush) accumulated higher levels of mercury in lakes with five trophic levels than in lakes where they fed directly on zooplankton (Cabana et al. 1994, Futter 1994). In both Baia Piuval and East Marsh, detailed sampling of the organisms present was not accomplished. Each location might have had a large interconnected web of organisms in the food web or a relatively simple short food web. The number of connections would have influenced the mercury content of the organisms.

Table 4.3. Biomagnification factors calculated for organisms collected from East Marsh, Lake Erie and the northern Pantanal, Brazil. Trophic level is based on data from the literature. BMF (Biomagnification Factor) was calculated by dividing higher trophic level concentration of MeHg by next lower trophic level concentration of MeHg. BMF maximum calculated from lowest (shrimp) to highest (top carnivore) trophic level. All calculations use MeHg concentrations based on dry weight.

<table>
<thead>
<tr>
<th></th>
<th>Organism</th>
<th>Level</th>
<th>BMF</th>
<th>BMF Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lake Erie</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Largemouth bass*</td>
<td>Carnivore</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Micropterus salmoides)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pumpkinseed*</td>
<td>Carnivore</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Lepomis gibbosus)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Blackstripe top minnow*</td>
<td>Carnivore</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Fundulus notatus)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grass shrimp*</td>
<td>Omnivore</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Palaemonetes kadiakensis)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Northern Pantanal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Red-bellied piranha*</td>
<td>Carnivore</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Pygocentrus nattereri)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aphyocharax sp.*</td>
<td>Carnivore</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tetragonopterus sp.*</td>
<td>Omnivore</td>
<td>-0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grass shrimp*</td>
<td>Omnivore</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>(Palaemonetes pugio)</em></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.5 Relationship between fish length and mercury content

The relationship of fish length and mercury content is well known. Significant positive correlations have been found in both temperate systems (Mathers and Johansen 1985; Lange et al. 1994; Watras et al. 1998) and tropical systems (Bowles et al. 2001; Leady and Gottgens 2001). In both the Pantanal and East Marsh, significant positive relationships existed between MeHg in tissue and length of fish in all but one species, *Tetragonopterus* (Table 4.4). *Micropterus* was clearly the largest fish with the highest MeHg content. Comparisons of the rate of MeHg increase with length was made for all fish but *Tetragonopterus* (Table 4.4). The slope of the regression line covering the size range for each fish species was used to derive the rate of change in MeHg ng g$^{-1}$ dry per cm increase in fish length for that species. That rate was highest in the top predator in each system and decreased with decreasing trophic level. This was expected based on predators consuming prey with increasingly biomagnified amounts of Hg. Bowles et al. (2001) used ANCOVA on four tropical fish species from two trophic levels and found significant heterogeneity of slopes. They suggested differences in slope might result from differences in MeHg assimilation from food, changes in trophic position with size within a species or differences in growth rate between species. When the two locations were compared, East Marsh had twice the average rate of MeHg increase as the Pantanal. This was expected based on the much higher rate of mercury contamination in the Lake Erie region, as discussed previously.
Table 4.4. Summary of regression results for fish length (cm) against log MeHg ng g\(^{-1}\) dry weight of six species of fish in Baia Piuval, Pantanal and East Marsh, Lake Erie. Rate of MeHg increase (ng MeHg g\(^{-1}\) dry weight cm\(^{-1}\)) calculated from the slope of the regression line for each species.

<table>
<thead>
<tr>
<th>Organism</th>
<th>N</th>
<th>R(^2)</th>
<th>p-value</th>
<th>Rate of MeHg Increase ng MeHg g(^{-1}) dry weight cm(^{-1})</th>
<th>Average rate of MeHg increase ng MeHg g(^{-1}) dry weight cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lake Erie</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Largemouth bass (Micropterus salmoides)</td>
<td>6</td>
<td>0.75</td>
<td>&gt;0.001</td>
<td>37.4</td>
<td></td>
</tr>
<tr>
<td>Pumpkinseed (Lepomis gibbosus)</td>
<td>4</td>
<td>0.86</td>
<td>0.004</td>
<td>28.4</td>
<td>24.9±14.7</td>
</tr>
<tr>
<td>Blackstripe top minnow (Fundulus notatus)</td>
<td>4</td>
<td>0.33</td>
<td>0.002</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td><strong>Northern Pantanal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Red-bellied piranha (Pygocentrus nattereri)</td>
<td>6</td>
<td>0.58</td>
<td>0.001</td>
<td>17.9</td>
<td>12.3±7.9</td>
</tr>
<tr>
<td>Aphyocharax sp.</td>
<td>4</td>
<td>0.98</td>
<td>&gt;0.001</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>Tetragonopterus sp.</td>
<td>4</td>
<td>0.23</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-4. Regressions of standard length (mm) and MeHg content (ng g$^{-1}$ dry) of three fish species in two locations. On the left are five fish species from both locations. On the right is *Micropterus* from the East Marsh. Note the change between panels in the scale on both axes. ● = fish from East Marsh, Lake Erie. ▲ = fish from Baia Piuval, Pantanal. Regression statistics given in Table 4.4.
4.4 Summary and Conclusions

The goal of this part of my dissertation was to compare and contrast mercury biomagnification in tropical and temperate wetland organisms from locations with histories of regional mercury pollution. I hypothesized that, if the process of mercury biomagnification is similar in Brazilian and Lake Erie wetlands, then a similar pattern of increase should be seen in mercury levels in both food chains. I found clear evidence of directional increases (biomagnification) in both total and methyl mercury tissue levels in Lake Erie’s East Marsh and the Baia Piuval in the northern Pantanal, Brazil. The sharpness of changes in mercury content in trophic levels in East marsh contrasted with the less distinct (although significant) changes in the Pantanal. The higher degree of trophic plasticity of tropical fish was a likely source of this difference. Due to these differences, developing fish consumptions guidelines primarily from data on temperate systems would be problematic. A significant positive relationship between fish length and MeHg tissue levels was found for five of six fish species tested. Rates of MeHg magnification with increasing length of the fish were higher with increasing trophic level. East Marsh had twice the average rate of MeHg increase as the Pantanal. This supported the concept of increasing MeHg during the lifetime of a fish as it increases in age/size and the existence of differences in rates of biomagnification among species of fish and between temperate and tropical systems.
Chapter 5

Synthesis of Literature on the Impact of Selective Predation on Biomagnification Rates – Suggestions for Future Research

Abstract

I investigated the role of selective predation in mercury dynamics in the food web, reviewed and synthesized the literature and presented suggestions for experiments to test hypotheses on the impact of selective predation on biomagnification of mercury. Current models of biomagnification rates are based on sampling average Hg content of predator and prey populations and using various parameters to predict actual mercury burdens. Predatory fish, however, have been shown to select prey based on multiple features. Mercury toxicity has been shown to alter behavior in both predator and prey. Prey that is easier to capture than average (due to mercury damage) would be particularly attractive to any predator, especially one with neurological deficits due to mercury contamination. Biomagnification models that do not take into account changing behavior with changing mercury levels may not accurately reflect the dynamics of the system. Both lab and field studies have demonstrated that mercury body burden in fish has a positive linear
relationship with mercury content in food. Mercury-impacted predators suffering neurological deficits may select for slower, more easily captured prey that have a higher mercury burden than average prey. This might create a positive feedback loop increasing the slope of a relationship between fish age/size and MeHg content in their tissue. If selective predation occurs based on mercury impacted predators and/or prey, then higher rates of biomagnification than predicted should be seen than for average predators consuming average prey. I suggest two laboratory studies to examine short and long-term selective predation. An additional field study is described to confirm results obtained in the lab studies. Actual field studies at realistic levels of mercury contamination are much less common than lab studies at unrealistic mercury concentrations. Results of these studies would greatly increase our understanding of the contribution of mercury’s impact of selective predation on biomagnification.

5.1 Introduction

Biomagnification is the accumulation of a persistent chemical pollutant, e.g. mercury, in the body of an organism because uptake, through food or across gills, exceeds excretion. Organisms higher up the food chain accumulate more of the chemical because their food contains more mercury than organisms lower on the food chain. The longer a fish is alive, the longer the fish has to accumulate mercury from the environment and from its food. Models of biomagnification rates are based on sampling predator and prey populations and using various parameters to predict actual mercury burdens (Tom et al. 2010; Bisi et al. 2012; Kidd et al. 2012). Such modeling is important in understanding mercury dynamics as a basis for regulatory measures aimed at reducing
mercury levels in human food. Most models are based on measures of average predator and prey mercury burdens (Bisi et al. 2012; Kidd et al. 2012; Tom et al. 2009). Predatory fish, however, have been shown to select prey based on various features (Ahrenstorff et al. 2009; Weber and Brown 2012). Mercury has been shown to change the behavior of both predator and prey (Smith and Weis 1997). If both predator and prey are mercury impacted, the model may not take into account changes in behavior that impact the slope of the relationship between length or age of the fish and MeHg content in its tissue.

The goal of this chapter is to examine the potential impact of mercury on selective predation. If impairment due to mercury does result in selective predation, then significant differences should be found in the slope of the relationship between age or size of fish and MeHg content. Lab and field studies are suggested to address this hypothesis.

### 5.1.1 Predator Mercury Burden Increases With Age/Size

It is widely accepted that mercury body burden increases with the age and size of fish. Size may be measured as length or weight. The longer a fish is alive, the longer the fish has to accumulate mercury. Food is the dominant pathway for MeHg accumulation in fish (Hall et al. 1997). Research dating from the 1970s to present supports this age/size relationship in a variety of fish and locations (Scott and Armstrong 1972; Sprenger et al. 1988; Somers and Jackson 1993; Lange et al. 1994; Qian et al. 2001, Barbosa et al. 2003; Trudel and Rasmussen 2006; Saiki et al. 2010).
Other factors have also been proposed as contributing to the age/size relationship. The growth dilution hypothesis states that the Hg concentration should be lower in fast-growing fish than in slow-growing fish because the fast-growing fish can dilute the ingested Hg into a larger body mass (Doyon et al. 1998). The hypothesis was supported in some studies (Doyon et al. 1998; Essington and Houser 2003; Simoneau et al. 2005) but not in others (Stafford and Haines 2001; Trudel and Rasmussen 2006). Bioenergetic changes with fish age have also been proposed as an important factor in determining mercury body burden. Older fish spend more energy on daily activities due to declines in metabolic efficiency with age. The end result is less energy incorporated into growth. The mercury concentration in a fish will increase with body size if gross growth efficiency decreases with body size (Borgmann and Whittle 1992). For a constant amount of mercury being ingested in food, if the body is growing less, the mercury is more concentrated in what tissue is added to the predator body.

5.1.2 Predator Mercury Burden is Correlated With Mercury in Food

Both lab and field studies have demonstrated that mercury body burden in fish (log MeHg) has a positive linear relationship with mercury content in its food (log MeHg). Rainbow trout had a significant increase in MeHg body burden when they were fed *Tubifex* contaminated with MeHg (Philips and Buhler 1978). Likewise, fish fed zooplankton with high concentrations of MeHg had significantly higher mercury content than fish fed low MeHg zooplankton (Hall et al. 1997). Field studies have correlated mercury in average prey sampled from the habitat with mercury body burden in fish.
Changing mercury concentration with the size of fish may also be related to trophic shifts with age/size. Based on stomach contents, Largemouth bass at age two ate 70% fish and 30% insects. At age eight, they ate 50% fish and 50% crayfish. The crayfish were significantly higher in mercury than prey fish (MacRury et al. 2002). In the same study, northern pike did not shift in diet from age two to eight, eating 100% fish throughout. If growth rates are the same in both bass and pike, bass would accumulate more mercury as they age when they consume a higher mercury prey item. The importance of the fact that not all fish are alike is underlined by Kidd et al. 1995. They found some fish did not change their trophic level (determined by δ¹⁵N) with age (lake whitefish, walleye, and burbot) while others did (yellow perch, lake cisco, and lake trout) (Kidd et al. 1995). Recent advances using δ¹⁵N to address trophic status have also supported the hypothesis that as an individual fish grows, its trophic status may change, and Hg body burden increases (DaSilva et al. 2005).

5.1.3 Mercury Impacts Behavior

Mercury has been shown to affect the behavior of predator and prey fish. Even low levels of MeHg caused delayed learning in zebrafish (Danio rerio) trained to food rewards while higher MeHg levels caused severe impairment or inhibition of learning (Smith et al. 2010). Fish impacted by mercury’s neurotoxicity are not as coordinated and have diminished responsiveness (Eisler 1987; Wiener and Spry 1996). Kasumyan (2001) reviewed the deleterious effects of various chemical pollutants, including mercury, on
foraging behavior. Hg effects on predators included reduced feeding rate (Weis and Khan 1990), reduced foraging efficiency (Grippo and Heath 2003), and reduced capture speed (Weis et al. 2001). In fact, mummichogs (*Fundulus heteroclitus*) from a polluted creek were significantly more likely to become prey themselves to blue crabs (Smith and Weis 1997). Actual field studies at realistic levels of mercury contamination are much less common than lab studies at unrealistic mercury concentrations.

Mercury impacted prey are subject to the same issues of neurotoxicity. Reduced predator avoidance was shown in four studies (Kania and O’Hara 1974; Osokov and Weis 1996; Zhou and Weis 1999; Webber and Haines 2003). Others demonstrated reduced olfaction (Tiernay *et al.* 2010) and increased risky behavior (Webber and Haines 2003) in prey with increased mercury burden. In a study of prey fish, golden shiners (*Notemigonius crysoleucas*) fed a high mercury diet had significantly reduced response to a predator (Webber and Haines 2003). Smith and Weis (1997) found that mummichogs (*F. heteroclitus*) with high Hg levels in brain tissue had a significantly reduced ability to capture prey (e.g., grass shrimp). Hg in the brains of striped mullets and tilapia reduced levels of serotonin which was associated with a loss of motor control (Thomas *et al.* 1981; Tsai *et al.* 1995).

5.1.4 Selective Predation

Fish have a variety of feeding strategies. Some predators strain zooplankton from water based on size alone. Other predators sit and wait for prey. Mercury will likely have the greatest effect on a predator that must compete with others and actively hunt for prey. The predator that must make decisions and physically pursue prey will be most at
risk. In optimal foraging theory, predators will attempt to maximize energy gain and minimize energetic costs (Hambright 1991). Predators select prey based on size to maximize energy gain while minimizing costs of handling and pursuit time (Stein 1977). Larger prey have more calories but cost rapidly increases with prey size (Werner 1974). Prey that is easier to capture than average would be particularly attractive to any predator, especially one with neurological deficits due to mercury contamination.

As an example, in 1965, in Niigata, Japan, “cat suicides” occurred because cats were being poisoned by mercury from dead fish on the beaches (Smith and Smith 1972). If those fish died of mercury poisoning, they would have higher body burdens than the average fish caught by researchers to document mercury levels. Higher levels of mercury in this easy to catch prey translated to higher rates of biomagnification in predators.

Prey work to minimize predation mortality using several strategies including behavior. For example, Stein (1977) found crayfish most at risk for predation by bass modified their behavior to reduce their risk by seeking shelter and changing location. As stated earlier, mercury impacted prey may perform more risky behaviors than average prey. This would make them more vulnerable to predation.

Biomagnification of mercury may change the application of optimal foraging theory. A predator consuming the easiest to capture prey with a large caloric reward is now more at risk for increased mercury contamination. No data suggest predators would learn to avoid mercury impacted prey. A diet that increases in mercury content in tissue will further impact the predator’s behavior and ability to capture prey and would by no means be considered “optimal”.
5.1.5 Linking Mercury, Selective Predation and Biomagnification

No study to date on mercury in predator and prey has examined the potential disparity between the mercury content of the average prey population measured and the actual prey population taken by predators. Even in gut content analysis studies, items taken from the guts were not the ones assayed for mercury and tied to their specific consumer. The question whether fish choose more impacted prey over less impacted prey has not been studied. It is reasonable to predict that this has implications for increasing the slope of the relationship between fish size or age and Hg body burden.

The slope of the relationship between age or size of fish and the log MeHg body burden is assumed to be constant (Figure 5-1). If mercury changes predator behavior (selective predation) over time, the slope of the relationship would increase. If a fish consumes as much prey as it wants with no need to hunt or select prey, its body burden of MeHg should increase with age or size over time, as discussed previously. On the other hand, if a fish has to hunt and compete for limited prey using a brain and body impacted by the neurotoxicity of mercury, that relationship would change. A mercury impacted predator is slower and not as able to capture prey. This predator would be choosing easier prey. Easier prey may be easier because they are also mercury impacted. The slope of the line would increase as a positive feedback loop is established (Figure 5-1).
Mathers and Johansen (1985) found high coefficients of variation for THg concentration in muscle within each age-class of walleye and pike that were not explained by total weight, length, or condition factor. They suggested that the variation in mercury content was either due to error or to “differences in the biology of individual fish”. They go on to explain “one individual of a year class could specialize on a prey which has an unusually high concentration of mercury, resulting in an unusual mercury accumulation”. This would be exactly what my hypothesis predicts. Within the average predator population there are more and less impacted predators that behave differently. It is possible that fish that are highly impacted by mercury do not exist in the natural population. Fish may never grow to a larger size or older age because their mercury content puts them at a competitive disadvantage. Mercury content may limit the age or size a particular fish species can attain.
5.2 Suggested Studies

Studies to clarify the role of selective predation due to elevated mercury tissue levels may be conducted in the field or in the lab. Three studies are proposed. The first two are lab studies. Lab studies have the advantage of minimizing confounding variables. The first lab study I propose is a short term experiment designed to verify the impact of mercury on selective predation. The second lab study extends the time frame and expands the population under study to more closely mimic natural conditions. The third study takes place in the wild to compare the results of lab studies to what actually happens under more natural conditions.

The selection of a predator-prey system is important. Mercury is a neurotoxin so it should have the most impact on a predator that actively hunts for its prey. The prey should be small fish. Invertebrate prey introduces the differences in THg versus MeHg percentages documented in Chapter four. The ratio of predator to prey should be such that the predator has to work to find prey. Again, this puts pressure on the mercury impacted predator to perform and the hunted prey to hide.

5.2.1 Short Term Lab Study

The first lab experiment would examine the hypothesis that mercury impacted predators will select for mercury impacted prey (Table 5-1). Predator and prey fish raised from fry would be treated with MeHg in the lab to produce “impacted” versus “non-impacted” populations. Ideally, both predator and prey fish would be implanted with microchips. This would allow identification of each specific individual which is particularly important in light of the results of Mathers and Johansen (1985), as discussed
previously. The fish would be acclimated over some period of time to lab conditions.

The testing tank would resemble natural conditions where prey would have places to hide. Tanks would be set up in four possible fish combinations (Table 5.1). Mixed prey fish would have an equal number of impacted and non-impacted prey fish. After a period of time, individual predator stomach contents would be documented. The microchip scanner would read the microchips placed on individual prey fish to identify how many and what kind of prey were consumed by each individual predator. The average Hg content of prey is determined by multiplying number of prey with their known Hg content and their known weight. If microchipping is not possible, gut contents can be examined by gastric lavage (Mathers and Johansen 1985). If impacted predators select for impacted prey, the impacted predator’s stomach contents should have a higher than expected mercury content in Trial D (Figure 5-1).

Table 5.1. Possible experimental design examining the effect of MeHg in predator fish on the selection of prey.

<table>
<thead>
<tr>
<th>Non-impacted prey fish</th>
<th>Impacted prey fish</th>
<th>Mixed prey fish</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-impacted predator fish</td>
<td>Trial A</td>
<td>Trial C Increase in avg. Hg level of captured prey fish compared to Trial A</td>
</tr>
<tr>
<td>Impacted predator fish</td>
<td>Trial B</td>
<td>Trial D Increase in avg. Hg level of captured fish compared to Trial A and C</td>
</tr>
</tbody>
</table>
Caution should be used when applying lab studies to natural systems. Wild populations facing long-term Hg contamination may have a selected advantage for tolerance to elevated Hg levels. Kraus and Kraus (1986) working with grass shrimp (*Palaemonetes pugio*) found differences in predator avoidance between shrimp from a mercury contaminated area versus shrimp from an uncontaminated area that had been treated with MeHg in the lab.

5.2.2 Longer Term Lab Study

A second lab study would extend the time frame and expand the population under study to more closely mimic natural conditions. This study examines the relationship of time and MeHg content of prey. The time frame should be sufficiently long to track several collections of prey from gut contents but not so long that growth differences between impacted and non-impacted predator groups might become a confounding factor. In this study, two tanks are identical except one contains non-impacted predators and the other impacted predators. The predators hunt for an equal ratio of impacted and
non-impacted prey. Impacted and non-impacted prey fish come from a lab produced population with a known MeHg content. As previously, the tanks would contain refuges for prey and a specific density of prey would be maintained. During each sampling time, each predator is removed from the tank and scanned for its microchip ID. Then its body is scanned to reveal the identity of consumed prey by their microchip in gut contents.

The average mercury concentration in predator guts contents is derived like the short term lab study. The predator is then returned to the tank. Prey fish would be restocked such that ratio of available impacted and non-impacted prey would be reset. The focus is to keep the same level of competition for food over a longer period of time. Each tank of predators would have a relationship between time and MeHg content of prey. Non-impacted predators are expected to have the same average Hg content in prey over time. They will be able to capture any prey easily compared to an impacted predator. If the experiment were extended over months or years, the predator’s Hg content would rise as it consume some amount of Hg impacted prey. This experiment is meant to be several weeks long. If selective predation is significant, impacted predators should have a steeper slope to the relationship between time and MeHg content of prey as they are able to capture only more and more impacted prey. The results, if significant, should produce a figure similar to Figure 5-1, except that the horizontal axis covers only a short window of time (a small segment of length) in a predator’s life (Figure 5-3). The y-intercept is different because the predators begin the experiment as non-impacted (low or no MeHg) or impacted (high MeHg) predators. The differences in slope indicate the change in mercury content of prey over time. The non-impacted predator has an increase in mercury content over time as it is exposed to impacted prey. Even a non-impacted
The impacted predator has a significantly steeper slope as it is forced to seek easier and easier prey that are mostly mercury-impacted prey. The average mercury in gut contents increases as fewer non-impacted prey are able to be taken.

![Graph showing relationship of MeHg in prey of impacted versus non-impacted predators.](image)

Figure 5-3. Relationship of MeHg in prey of impacted versus non-impacted predators.

### 5.2.3 Field Study

In the field, a comparison of gut contents to average prey in the system might reveal differences in the Hg content of prey actually being captured. Gut content analysis has been performed in numerous studies to determine trophic level of the predator and percentages of organisms of different categories in food. To determine Hg content, prey were captured from the environment and reported as average prey Hg content (Bowles et al. 2001; Baeyans et al. 2003; Agah et al. 2007; Hogan et al. 2007; Chumchal et al. 2011,
Lepak *et al.* 2012; and many others). An improvement to specifically address prey selection would be to match Hg content of prey in gut contents to Hg in the predator consuming them. Weis and Candelmo (2012) conducted a similar experiment on PCB and DDT content of prey in bluefish stomachs. They found levels of contaminants in fish from bluefin stomachs were higher than fish caught in trawls and seines. They did not match Hg content in prey to Hg content in its predator.

### 5.3 Summary

Results of the suggested studies should indicate the importance of selective predation in mercury biomagnification through lab studies and in field studies. The concept of the impact of selective predation on mercury body burden has not been specifically addressed in either lab or field studies to date. Optimal foraging theory dictates a predator will maximize energy intake while minimizing energy expenditures. Unfortunately, the easiest prey to obtain may be those most impacted by mercury. The effect of this change in behavior over time has not been included in models of biomagnification. Previous investigators have noted that there are individual differences in Hg content of predators that are not easily explained (Mathers and Johansen 1985). Investigating the impact of the amplification of biomagnification through such selective predation would provide additional information valuable to understanding and managing the impact of mercury on fish and their human consumers.
Chapter 6

Summary and conclusion

Mercury is a naturally occurring element which is acutely and chronically detrimental even in low doses to both wildlife and humans. It has been used in a variety of medical, agricultural, and industrial applications. An increase in the use of mercury in the latter half of the 20th century has led to increasing global contamination. MeHg is not easily metabolized or eliminated and is the most toxic and readily bioaccumulated and biomagnified form of mercury. The proportion of MeHg relative to total mercury increases through the food web. My work addressed four specific objectives with an overall goal of increasing the understanding of the global mercury problem.

My first objective was to examine the utility of lake cores in documenting the mercury history of a system. If cores reflect the history of deposition to a system (“inputs”), that chronology should correspond to historical sources of mercury to the system (globally and regionally). I tested the similarity of records of US industrial mercury consumption (“environmental input”) and tissue levels in walleye (Stizostedion vitreum vitreum) (“biological output”) with mercury stratigraphy in cores from the western basin of Lake Erie. Total US industrial mercury consumption (or “input”) correlated with mercury accumulation rates in one of two 1995 cores of the western basin.
of Lake Erie. Mercury accumulation rates correlated with fish tissue mercury concentrations (or “output”) in both cores. A regression model hind casted a mean of 17 ng Hg g\(^{-1}\) for ca. 1900 fish tissue levels, providing a reasonable restoration target. The regression model was also used to hind cast to 1945 fish mercury levels. Museum fish analyzed in 1972 found 1945 tissue levels of 75 ng Hg g\(^{-1}\). My regression model predicted a fish tissue level of 80 ng Hg g\(^{-1}\). The results support the use of sediment cores to document mercury input and output in a region.

My second objective was to compare mercury dynamics in two regions of a tropical wetland, one in a region of mercury mining and the other in a reference region. If tropical system mercury dynamics are similar to temperate systems, then a comparison of mercury accumulation in a sediment core and in biota of an impacted site should reveal higher levels of mercury than those in a non-impacted control site. Gold mining with mercury (Hg) amalgamation has thrived since 1980 along the northern rim of the Pantanal. Cores and biological samples from the impacted northern Pantanal were compared to a reference site, Acurizal, some 200km into the Pantanal. Average pre-1940 Hg accumulation rates in both locations were not significantly different. Post gold-rush Hg (post-1980) deposition averaged 1.5 times higher in the northern area than in Acurizal cores. Total Hg concentrations in sediments, plants, and fish were significantly higher in the northern region. Invertebrates collected had low levels of mercury in both locations. *Pygocentrus nattereri* length correlated significantly (p<0.001) with Hg content in both regions, but the slope of the regression in the northern Pantanal was 2.6 times the slope for the Acurizal collection, indicating an elevated rate of biomagnification in the Hg-impacted region. My results demonstrated that signals of Hg use in mining can be
quantified in sediment core chronologies and biological tissues, although species at different trophic levels show dissimilar impacts. I noted that mechanisms involved in Hg magnification along food chains deserve more attention, particularly in tropical regions where the threat of chronic exposure to this neurotoxin may have the greatest implications for biodiversity.

My third objective was to compare mercury biomagnification in temperate and tropical systems. If the process of mercury biomagnification is similar in Brazilian and Lake Erie wetlands, then a similar pattern of increase should be seen in mercury levels along a food chain. A significant directional increase in both methyl and total mercury was found in both the Lake Erie East Marsh and Pantanal trophic levels. The pattern of biomagnification in East Marsh was more distinct than that in the Pantanal. Differences between temperate and tropical systems may be attributed to changes in feeding habits during the year and/or differences in the relative growth rate/age of the fish examined. On a dry weight basis, biomagnification factors (BMF) in the top predator in each system were similar but the magnitude from omnivores to top predator was much greater in the Lake Erie marsh. In both the Pantanal and East Marsh, significant positive relationships existed between MeHg and length of fish in all but one fish species. The rate of increase in Hg tissue levels as fish increase in size was highest in the top predator in each system and decreased with decreasing trophic level. When the two locations were compared, East Marsh had twice the average rate of MeHg increase as the Pantanal. Results clearly indicate the need for further natural history information in tropical species. The lack of such info makes understanding mercury dynamics (for use in setting fish consumption advisories, for example) very difficult.
My final objective was to examine the role of selective predation on mercury dynamics through a literature review and synthesis. If mercury impacts selective predation, then higher rates of biomagnification than predicted should be seen compared with average predators consuming average prey. Most biomagnification models are based on measures of average predator and average prey mercury burdens. Predatory fish, however, have been shown to select prey based on various features. A predator’s selective behavior may be impacted by mercury’s neurotoxicity. I suggested three studies to examine the impact of selective predation. Results of these studies would greatly increase our understanding of the contribution of mercury’s impact of selective predation on biomagnification.

Even though much mercury research has been published, interesting research questions remain in several areas. Sediment cores have the potential to supply historical information in systems where long term databases are missing for biological data. Further documentation and analysis of the utility of both forecasting and hindcasting fish tissue levels could provide a useful tool for informed restoration targets. Additional research in basic natural history and tropical food web dynamics is necessary to better understand the transfer and fate of mercury in tropical ecosystems. The impact of selective predation on the rate of biomagnification should be examined more closely. A better understanding of the role of selective predation would increase our understanding of differences in biomagnification rates in different fish species and in different ecosystems. My overall objective was to increase the understanding of the global mercury problem. Applying chemical, biological and sedimentary approaches, I accomplished this goal in both a temperate and a tropical system.
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