

**TROPHIC TRANSFER OF ENERGY AND POLYCHLORINATED  
BIPHENYLS BY NATIVE AND EXOTIC FISH IN LAKE ERIE**

**DISSERTATION**

**Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of  
Philosophy in the Graduate School of The Ohio State University**

**By**

**Gene Wook Kim**

**The Ohio State University  
2007**

Dissertation Committee:

Roy A. Stein, Co-Advisor

Elizabeth A. Marschall, Co-Advisor

Susan W. Fisher, Co-Advisor

Paul C. Baumann

Charles P. Madenjian

Approved by:

---

Co-Advisor

---

Co-Advisor

---

Co-Advisor

Graduate Program in  
Evolution, Ecology, and Organismal Biology

## ABSTRACT

Herein, I describe research that quantifies how native and non-native (henceforth exotic) benthic organisms influence community and ecosystem processes. As aquatic ecosystems are recovering from years of excessive inputs of nutrients and industrial pollution, the influence of benthic food webs on the overall ecosystem likely will increase. By conducting a series of laboratory and outdoor experiments, observational studies, and field assessments in small reservoirs, I quantified how benthic organisms transfer material to higher trophic levels. For the native omnivore, gizzard shad *Dorosoma cepedianum*, growth and survival depended on the quality of sediment detritus, suggesting that detritus quality ultimately can regulate community and ecosystem productivity, mediated by its influence on gizzard shad biomass available for trophic transfer to piscivorous fish (Chapter 2). The addition of an exotic, benthic fish, round goby *Neogobius melanostomus* to the Lake Erie ecosystem, by being preferentially consumed over native prey by smallmouth bass *Micropterus dolomieu* appears to transfer benthic energy and contaminants to the pelagic food web (Chapter 3). A field study and historical data in Lake Erie revealed biomagnification of PCBs by an exotic species component (comprising round goby and dreissenid mussels *Dreissena* spp.) to native terminal predators, smallmouth bass and largemouth bass *Micropterus salmoides*

(Chapter 4). Recovering benthic macroinvertebrate communities in Lake Erie appear influenced by dreissenid mussels and dreissenid mussel interactions with PCBs and organic content of sediments (Chapter 5). As nutrient and contaminant inputs continue to decline and exotic species continue to proliferate, I predict an increase in the relative importance of such benthic transfer pathways in influencing variability in transfer of energy and contaminants from to the pelagic food web.

## **DEDICATION**

For my mother and father,  
without whom I would not succeed.

## ACKNOWLEDGMENTS

I thank my co-advisors, Roy Stein and Elizabeth Marschall, for their continued support, care, and guidance during my doctoral tenure at The Ohio State University. I will always be grateful for my time as their student. Beyond the mere technical aspects of completing a dissertation, they have mentored me in how to be a scientist. Through one-on-one meetings, editing, and group interactions, I now have an ideal blueprint to how to run an effective research program. In addition, I thank Susan Fisher, because without her expertise and guidance, much of the dissertation could not be done. My interactions with these scientists will guide my career.

I thank my committee members, Chuck Madenjian and Paul Baumann, for essential guidance and feedback on my dissertation. To assemble such a great group of scientists was valuable and humbling.

I thank my parents for their continued support and love throughout the dissertation. Without them, I would not succeed.

I thank people who have assisted my research in the field and the laboratory. I thank Tae-dong Kwon for supervising my chemical analyses for this study. I thank the contribution of my lead technicians, Jocelyn Flanary, Matt Gearhiser, and Natalie Rossman. I was lucky to have such a team. Beth DeWitt, Melissa Marburger, and Barb Fate provided invaluable contributions to the financial, personnel, and technical aspects

of research, and I thank them for their tireless assistance. I thank the graduate students at the Aquatic Ecology Laboratory for their help and camaraderie. I will fondly remember my interactions with fellow graduate students.

For help and insight on laboratory analyses, I thank Annie Bowling, Bo Bunnell, Bryce Crumrie, Erin Dunlavy, John Guluzian, Kathryn Jenks, Byung-Soek Kim, Peter Landrum, Matt Lawrence, Emily Lawson, Pete Martin, Samantha Messenger, Shannon Mixon, Amanda Robinson, David Soucek, LeAnn Southward, Jeff Spoelstra, Melissa Tucker, Mike Vanni, Lacey Vulgamore, and Cristal Williams. Special thanks go to Jean Roberts for her contributions to the laboratory analysis.

I thank people who helped in the field, including Kristi Arend, Melissa Kotar, Grace Kilbane, Amy Kulesza, Scott Miehl, Joe Stewig, Michelle Thomas, Melissa Tucker, Eric Wagner, and Chad Whaley. I thank Carey Knight, Roger Thoma, Matt Thomas, Jeff Tyson, and the crews of the Stone Lab R/V Discovery and the Ohio Division of Wildlife R/V Grandon and Explorer for help in the field.

Also, Lynda Corkum, Jaci Savino, Lisa Einfalt, Maria Gonzalez, and Melissa Kostich provided valuable advice on experimental design and housing round gobies. The historical fish tissue data were generously and rapidly provided by Dennis Mishne.

I thank Harry Burroughs, Bonnie Bruce, and Dave Whaley for their generous scheduling of time to write the dissertation. I thank Jeff Reutter for his continued support of my career.

This work was funded by Ohio Sea Grant Project R/ER-55 and Lake Erie Protection Fund Project LEPF 00-12. Also, funds were provided by Federal Aid in Sport Fish Restoration Project F-40-R (administered by the Alabama Department of Conservation and Natural Resources-Division of Wildlife and Freshwater Fisheries Division), National Science Foundation grant DEB-9410323, and Federal Aid in Sport Fish Restoration Funds to the Ohio Division of Wildlife. In addition, GWK was supported by an Ohio State University Graduate Enrichment Fellowship, an Ohio State University Presidential Fellowship, and a Sea Grant John A. Knauss Marine Policy Fellowship.

## VITA

April 14, 1971.....Born – Seoul, South Korea

1974.....Immigration to the United States

1986.....Became a United States Citizen

1995.....B.S. Zoology,  
Miami University

1995.....B.A. Philosophy,  
Miami University

1998.....M.S. Fisheries Ecology,  
Auburn University

1998 – 1999.....University Graduate Enrichment Fellow  
The Ohio State University

1999 – 2004.....Graduate Teaching and Research Associate  
The Ohio State University

2004 – 2005.....Presidential Fellow  
The Ohio State University

2005 – 2006.....John A. Knauss Marine Policy Fellow  
The Ohio State University

## **PUBLICATIONS**

### Research Publications

1. Kwon, T.D., S. W. Fisher, G. W. Kim, H. Hwang, and J.E. Kim. 2006. Trophic transfer and biotransformation of polychlorinated biphenyls in zebra mussel, round goby, and smallmouth bass in Lake Erie, USA. *Environmental Toxicology and Chemistry* 25:1068-1078.
2. Irwin, B.R. Irwin, G.W. Kim, and D.R. DeVries. 2003. Responses to gizzard shad recovery following selective treatment in Walker County Lake, Alabama, 1996-1999. *North American Journal of Fisheries Management* 23:1224-1236.
3. Kim, G.W., and D.R. DeVries. 2001. The influence of adult fish predation on freshwater, limnetic fish larvae. *Transactions of the American Fisheries Society* 130:189-203.
4. Kim, G.W., and D.R. DeVries. 2000. Effects of a selectively reduced gizzard shad population on trophic interactions and age-0 fishes in Walker County Lake, Alabama. *North American Journal of Fisheries Management* 20:860-972.

## **FIELDS OF STUDY**

Major Field: Evolution, Ecology, and Organismal Biology

Specialization: Aquatic Ecology

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## **CHAPTER 1**

### **INTRODUCTION**

Material and energy flow across aquatic habitats influence ecosystem productivity. Although phytoplankton primary production is a principal carbon source for higher trophic levels, a large fraction of this carbon eventually dies and settles to the bottom. As such, this carbon becomes available to the benthic food web. In addition to these internal inputs, allochthonous material can subsidize carbon in benthic habitats (Lindeman 1942; Adams et al. 1983; Polis et al. 1997). These subsidies join internally derived benthic detritus. Unless benthic and pelagic food webs are linked in some way, these nutrients remain unavailable to higher trophic levels in this detritus “sink.”

Given that they drain municipalities, agriculture, and industry, aquatic ecosystems suffer from eutrophication and contaminated sediments. Eutrophication arises when excessive anthropogenic inputs of nutrients over-stimulate primary production and organic material accumulates (reviewed in Smith et al. 1999; Carpenter et al. 1998; Khan and Ansari 2005). The resultant high algal production, frequent harmful algal blooms, and widespread oxygen depletion in bottom waters have caused sensitive benthic organisms to disappear (Carpenter et al. 1998; Khan and Ansari 2005; Makarewicz and Bertram 1991). In addition to nutrients, industrial contaminants such as polychlorinated

biphenyls (PCBs) and suspended sediments from agriculture accumulated in bottom sediments further reduce the abundance and diversity of benthic organisms (Beeton 1961; Carr and Hiltunen 1965).

Recent controls on excessive nutrients and chemical pollution have started to reduce nutrient and contaminant levels and hence their impact on benthic organisms. In 1972, the Great Lakes Water Quality Act imposed a limit of 1 mg/L total phosphorus on large municipalities and banned phosphorus use in detergents (Dolan 1993). In addition, local improvements to municipalities, industry, and agriculture have reduced nutrient inputs to countless lakes and reservoirs (Ney 1996; Jeppesen et al. 2005). After a ban on PCB production in 1977, lake-wide mean total PCB concentrations in Lake Erie sediments have declined from 136 ng/g in 1971 to 43 ng/g in 1997 (Painter et al. 2001); yet, higher concentrations still are found in the western basin and the southern portion of the central basin. To a lesser degree, improved agricultural practices have reduced sediment discharges into Lake Erie (Richards and Baker 1993; Myers et al. 2000). As a result of these changes, recovery has begun in Lake Erie.

As inputs of nutrient and contaminants decline, the influence of benthic food webs to overall ecosystem function likely will increase. Across many experimental systems, as nutrient inputs decrease, the contribution of benthic primary production to overall system productivity increases relative to other energy sources (Vadeboncoeur et al. 2003). Also, as contaminant inputs decline, changes in mid-trophic-level biota may become more important in determining PCB residues in upper trophic levels than variations in source inputs (Smith 2000). Examples of organisms at mid-trophic levels

influencing PCB concentrations in higher trophic levels include opossum shrimp (*Mysis relicta*) and alewives (*Alosa pseudoharengus*) altering PCB concentrations in salmonine predators (Vander Zanden and Rasmussen 1996) and prey fish density affecting the rate of PCB residues in Great Lakes herring gull *Larus argentatus* eggs (Hebert et al. 2000).

Fish can link benthic and pelagic food webs. Recent studies highlight how benthic production contributes to lake primary production and stabilizes ecosystems, as postulated by Lindeman (1942). Driven, in part, by new techniques (i.e., stable isotopes) that identify fish diets beyond conventional gut contents, these studies document that fish link benthic and pelagic food webs (transferring nutrients, energy, and biomass). Indeed, higher trophic levels depend on benthic production in both freshwater (Vadeboncoeur et al. 2002; Vander Zanden and Vadeboncoeur 2002) and marine ecosystems (Doering 1989). By translocating material across habitats, fish provide “new” nutrients and biomass that serve to stimulate primary and secondary production in recipient habitats (Vanni 2002).

The establishment of Ponto-Caspian exotic species provides a new potential for benthic-pelagic coupling in Great Lakes ecosystems. In the mid-1980s, zebra mussels *Dreissena polymorpha* and quagga mussels *D. bugensis* were accidentally introduced via ship ballast and spread rapidly through the Great Lakes and Mississippi River basins (Mills et al. 1993). Abundant zebra mussels reduce algae and seston by filter feeding (Klerks et al. 1996); they also alter nutrient dynamics, contaminant fate, organic material deposition, and habitat complexity (Botts et al. 1996; Ricciardi et al. 1997; Stewart et al. 1998a, 1998b). Recently established in the mid 1990s, round gobies *Neogobius*

*melanostomus* consume dreissenid mussels, thus influencing higher trophic levels. Because round gobies reach high densities (Ray and Corkum 2001) and consume dreissenid mussels as primary prey in their native range (Charlebois et al. 1997), they make energy and contaminants (acquired from dreissenid mussel tissue) available for dietary transfer.

Herein, I describe how native and non-native (henceforth, exotic) organisms can influence benthic communities, as well as the entire aquatic ecosystems. I conducted laboratory and outdoor experiments, observational studies, and field assessments to examine how benthic organisms can transfer material to higher trophic levels.

In Chapter 1, I present results from a laboratory experiment, an outdoor mesocosm experiment, and a field survey quantifying how detritus quality and density-dependence affect growth and survival of age-0 gizzard shad *Dorosoma cepedianum*. Omnivorous gizzard shad appear to be an important link to the detritus subsidy from the watershed, as well as an important prey fish. Compared with estuary and tropical ecosystems where detritivorous fish are common, gizzard shad are the only detritivorous fish species that reach high biomass in U.S. lakes and reservoirs (often > 60% of total fish biomass; Johnson et al. 1988; Vanni et al. 2005).

In Chapter 2, I quantify the potential for, and implications of, round goby inclusion into the Great Lakes food web. Given that transfer of energy, nutrients, and contaminants occurs primarily by dietary transfer, quantifying these predator-prey relationships provides insight into the impact of round goby establishment. I conducted a laboratory predator-selection experiment exposing smallmouth bass to round gobies and two native prey, quantifying smallmouth bass prey selection and predator avoidance by

each prey type. To determine smallmouth bass diet composition, I include stomach contents from field-collected smallmouth bass and estimated round goby densities from Lake Erie trawl samples.

In Chapter 4, I quantify trophic transfer of PCBs between exotic round gobies, dreissenid mussel, and two terminal piscivores (smallmouth bass and largemouth bass *Micropterus salmoides*) after full incorporation of round goby into predator diets. I sampled congener-specific PCB concentrations in sediment and biota in western (Maumee and Sandusky) and central basin (Grand and Ashtabula) areas of Lake Erie, hypothesizing that variability in PCB residues in biota are, in part, attributable to changes caused by Ponto-Caspian exotic species and that these changes vary with basin. To assess temporal trends in Lake Erie sport fish, I compare my current results with historical data.

In Chapter 5, I assess how dreissenid mussels interact with the recovery of benthic macroinvertebrate communities in Lake Erie. I surveyed four harbors (Maumee, Sandusky, Grand, and Ashtabula) along the southern shore of Lake Erie during 2001 and 2002, sampling areas inside and outside harbors. Using a combination of approaches, I sought to determine how benthic macroinvertebrate communities vary geographically, how benthic macroinvertebrates, sediment characteristics, and contaminants are associated with each other, and how important dreissenid mussels are in structuring benthic macroinvertebrate communities, compared with structuring by sediment characteristics and sediment contamination.

From a broad perspective, this study improves our knowledge of how biotic interactions can influence the entire aquatic ecosystem. In the past, when inputs of

nutrients and industrial pollutants into aquatic ecosystems were high, variation in nutrient effects or contaminant residues in biota could be easily predicted by measuring inputs. As source inputs decrease, my work will provide insight into how biotic interactions affect material transfer through aquatic food webs. Both theory and empirical studies show that such interactions will become increasingly important for the understanding of ecosystem variation as aquatic ecosystems recover from decades of serving as disposal sites for pollutants from municipalities, agriculture, and industry.

## CHAPTER 2

# EFFECT OF SEDIMENT QUALITY ON GROWTH AND SURVIVAL OF GIZZARD SHAD: POTENTIAL IMPORTANCE TO BENTHIC-PELAGIC COUPLING

### ABSTRACT

Gizzard shad (*Dorosoma cepedianum*) populations vary with lake productivity, competing with and providing prey for sport fishes. Because age-0 gizzard shad (>30 mm total length) are facultative detritivores, they link benthic energy, carbon, and nutrients to pelagic food webs. To determine how age-0 gizzard shad success varies along a detritus-quality gradient, we completed a 15-d laboratory experiment, during which age-0 gizzard shad fed lake sediment and starved fish both suffered high mortality, whereas fish fed zooplankton grew and survived well. This suggested that detritus alone is insufficient to ensure gizzard shad growth and survival. When sediment quality was high in outdoor mesocosms, density-dependence led to rapid growth only at low fish density; however, survival generally increased with sediment quality, regardless of gizzard shad density. In four small reservoirs, annual growth of gizzard shad increased

with sediment quality. Collectively, our findings suggest that detritus quality ultimately can regulate community and ecosystem productivity, mediated by its influence on gizzard shad biomass available for trophic transfer to predators (i.e., piscivorous fish). Without gizzard shad, allochthonous detritus subsidies from the watershed would remain unused on the lake bottom.

## INTRODUCTION

Material and energy flow across aquatic habitats influences ecosystem productivity. Although phytoplankton primary production is a principal carbon source for higher trophic levels, a fraction of this carbon is incorporated into organism biomass that eventually dies and settles to the bottom. In addition to these internal sources, allochthonous material can subsidize and stabilize aquatic ecosystems (Lindeman 1942, Adams et al. 1983, Polis et al. 1997). If not incorporated into biota, these subsidies join internally derived benthic detritus. Unless benthic and pelagic food webs are linked, these nutrients remain unavailable to higher trophic levels in this detritus “sink”.

Fish can link benthic and pelagic food webs. Recent studies highlight how benthic production contributes to lake production and stabilizes ecosystems, as postulated by Lindeman (1942). Driven, in part, by new techniques (i.e., stable isotopes) that identify fish diets beyond conventional gut contents, these studies document that fish link benthic and pelagic food webs often (transferring nutrients, energy, and biomass) and higher trophic levels depend on benthic production in freshwater (Vadeboncoeur et al. 2002, Vander Zanden and Vadeboncoeur 2002) and marine ecosystems (Doering 1989).

The transfer role by fish results from their mobility and high consumption rate. Because most zooplankton do not move long distances (compared to fish), they typically feed, excrete, and are eaten in the pelagic zone; thus, they only recycle nutrients within that habitat (Vanni 2002). In contrast, fish translocate material across habitats, because they are mobile, have biomass for predators to consume, and excrete nutrients (Vanni 2002). These “new” nutrients and biomass stimulate primary and secondary production in the recipient habitat (Vanni 2002). Consider the impressive example of Pacific salmon (*Oncorhynchus* spp.) translocating material hundreds of kilometers during spawning, stimulating production in both natal streams and surrounding forests (Gende et al. 2002).

Omnivorous gizzard shad (*Dorosoma cepedianum*) link benthic and pelagic zones, providing prey for piscivorous fish. Because in-reservoir primary production often is insufficient to support reservoir fish biomass (Adams et al. 1983), omnivorous gizzard shad appear to be an important link to the detritus subsidy from the watershed. Compared to estuary and tropical ecosystems where detritivorous fish are common, gizzard shad are the only detritivorous fish species that reach high biomass in U.S. lakes and reservoirs (Vanni et al. 2005). Neither strongly regulated by bottom-up nor top-down forces (Stein et al. 1995), gizzard shad often become hyper-abundant in lakes and reservoirs in the eastern U.S., reaching over 60% of total fish biomass (Johnson et al. 1988). At small sizes, they are preferred prey by piscivorous fishes (Hartman and Margraf 1992; Garvey and Stein 1998), but they rapidly grow too deep-bodied for gape-limited piscivores (Stein et al. 1995). Planktivory by abundant age-0 gizzard shad can virtually eliminate large zooplankton (DeVries and Stein 1992). Yet, gizzard shad >30 mm total length (TL) can avoid mortality when zooplankton are scarce by switching to

benthic detritus as a food source (Yako et al. 1996, Schaus et al. 2002). Thus, omnivorous gizzard shad can transfer benthic biomass to pelagic predators (Stein et al. 1995), physically re-suspend detritus (Gido 2003), and excrete benthic nutrients into the pelagic zone (Schaus et al. 1997).

Little is known about how benthic productivity relates to growth and survival of age-0 gizzard shad > 30 mm TL. Rather, studies have related pelagic productivity to larval (Bremigan and Stein 1999, 2001) and adult gizzard shad (DiCenzo et al. 1996, Michaletz, 1998, Clayton and Maceina 2002). Detritus studies have compared detritus presence or absence (Schaus and Vanni 2000) or bulk amount of detritus from the watershed (Schaus et al. 2002). Given that gizzard shad select the nutritious fraction of detritus in laboratory and field studies (Mundahl and Wissing 1987, 1988), quantifying the influence of detritus quality appears fundamental to understand gizzard shad availability as prey and regulation of aquatic ecosystems.

We present results from a laboratory experiment, an outdoor mesocosm experiment, and a field survey quantifying how detritus quality and density-dependence affect age-0 (40-60 mm TL) gizzard shad fitness. At these sizes, age-0 fish typically have higher biomass, mass-specific metabolism, and availability to gape-limited predators than older cohorts. In a laboratory experiment, we compared growth and survival of age-0 gizzard shad consuming detritus versus zooplankton or starvation. In outdoor mesocosms, we varied detritus quality and gizzard shad biomass to determine their effect on gizzard shad growth and survival and production in the rest of the ecosystem. Finally, in a field survey, we compared detritus quality to gizzard shad

condition and growth. We then related our findings to predator-prey dynamics and lake productivity (both primary and secondary production).

## METHODS

### Laboratory Experiment

*Experimental Design*—We conducted a 15-d laboratory experiment during 22 September to 7 October 1994. We measured growth and survival of age-0 gizzard shad in three feeding treatments, each replicated four times: (1) zooplankton only, (2) detritus only, and (3) no food. We added *Artemia* spp. nauplii at 10% of fish wet mass·d<sup>-1</sup> to simulate zooplankton levels in Ohio reservoirs, where copepod nauplii dominate summer zooplankton (DeVries and Stein 1992).

To obtain natural lake detritus, we skimmed the top 2 cm of sediments (i.e., the highest organic content), from the upstream, littoral region of Kokosing Lake (Knox County, Ohio) on 10 September 1994. We prepared treatments by adding 3 cm of detritus to each 160-L experimental aquarium, 48 h before trials to allow suspended sediments to settle. We assumed *ad libitum* amounts of sediments for gizzard shad feeding.

On 24 August 1994, we collected age-0 gizzard shad (40-50 mm TL) from Kokosing Lake, and transported them to the laboratory. During holding, fish ate *Artemia* spp. nauplii and sinking pelleted food. During the experiment, water temperature ranged from 17 to 20°C. Before stocking, each fish was uniquely fin clipped. We stocked five

age-0 gizzard shad (45-55 mm TL) per aquarium. On days 0, 5, 10, and 15 (or on the day a fish died) of the experiment, we weighed each gizzard shad (nearest 0.1 g wet mass). At the end of the experiment, or upon death, stomach contents of each fish were removed, dried for 24 h at 60°C, then weighed (nearest 0.1 mg). Fish that died were removed immediately, but not replaced.

We calculated specific daily growth rates (SGR) of each fish by the following equation,

$$\text{SGR} = \left( \frac{\ln W_2 - \ln W_1}{t} \right) \times 100 \quad (1)$$

where  $W_2$  is end mass,  $W_1$  is start mass, and  $t$  is time in days.

### **Mesocosm experiment**

*Experimental Design*—We conducted a 76-d mesocosm experiment during late summer (18 August to 1 November 2001). We used 23 outdoor, polyethylene mesocosms at Ohio State University (Columbus, Ohio, USA), measuring 1.8 m in base diameter  $\times$  1.0 m in depth (volume=2.5 m<sup>3</sup>) with a standpipe to keep water level at 0.9 m (effective volume=2.3 m<sup>3</sup>). Each pool had continuous flow of dechlorinated water (1.0 to 1.5 L / min) and 3-4 air stones, replacing 63 to 94% of the water each day. The south end of each pool was covered in black plastic and the north end in 0.5-cm bar mesh netting to limit light differences and prevent escape or predation by birds.

We used a 4 $\times$ 2 factorial design, with four levels of sediment (SED) quality (low, medium, and high quality, plus a no-sediment control), high and low gizzard shad density (FISH), and three replicates. Due to limited fish availability, the high FISH-no SED

treatment had only two replicates. Because pools were oriented west to east, we reduced location bias via a stratified, block design (Sokal and Rohlf 1995), assigning one replicate of each treatment randomly within each of the east or west areas, then randomly assigning the remaining replicates.

Gizzard shad stocking levels reflected densities from Ohio reservoirs surveys that range 6 to 31 fish / m<sup>2</sup> (Johnson et al. 1988). Assuming 20-30% stocking mortality (DeVries and Stein 1992, Kim and DeVries 2001), we stocked 10 and 20 fish / m<sup>2</sup>. On 17 August, we collected gizzard shad from Kokosing Lake by electrofishing. To reduce mortality, we transported them with aeration and methane tricainesulfonate (MS-222) and held fish for 24 h before stocking. We fed all treatments equal low rations of zooplankton and trout chow (to reduce stocking mortality) and stocked one sunfish *Lepomis sp* (50-100 mm TL) per pool to control insects.

Our sediment detritus qualities matched values in Ohio reservoirs, where values range from 6 to 27% (% volatile organic, Mundahl and Wissing 1987, 1988, OEPA 1995). We combined garden clay (5.2 %), sediments scraped from a fish hatchery pond (6.1% organic matter dry mass), and ground trout feed (88.0%) at ratios to match the low end of this range (6, 8, and 12%). To expose fish to actual detritus, rather than merely trout chow mixed into sediments, we allowed sediments to putrefy. First, we added sediments to 0.3-m of water without aeration or flow (8 d); second, we filled and aerated pools without flow (7 d); third, we filled pools without fish for 31 d with only scant water flow. We raked sediments four times to ensure homogeneity, and on 18 July we sampled sediments ( $n=3$  per pool).

*Fish Growth and Condition*—We compared age-0 gizzard shad growth, condition, survival, and energy density. Because of handling stress, we photographed fish in shallow water to calculate lengths using a digitizing tablet. At stocking, gizzard shad averaged  $47.2 \pm 0.6$  mm TL, ranging from 40.3 to 52.3 mm TL. At the end of the experiment, we measured length and mass and calculated length-independent condition using the residual from the predicted mass for a given fish length generated from the entire population ( $n=333$  experimental fish recovered). Survival was the percent remaining at the experiment's end, excluding initial ( $< 48$  h) mortality.

We estimated energy density according to Rand et al. (1994) and Kershner et al. (1999). We calculated energy density for up to five fish per 10-mm length class from each mesocosm in a bomb calorimeter (Parr Company, Model 1425). Because of low sample mass, we could estimate only one pellet on 42% of the 188 fish. Of the fish with multiple pellets, 88% differed by  $< 2\%$  (94% differed by  $< 3\%$ ). When the two estimates differed by  $> 2\%$ , we burned a third pellet; no samples required more than three runs. We used a mean value for each fish or a single value when needed. To control for length bias, we used residuals from the predicted energy density (KJ / g wet mass) for a given length, derived from all experimental fish.

*Suspended Solids, Sediments, and Water Quality*—We compared total, fixed, and volatile suspended solids according to standard methods (methods 2540 D and E; APHA 1998). On 27 October, we filtered 0.5-3.2 L of water from 0.25-m depth ( $n=2$  replicates per pool). We combusted filtered, dried samples at  $550^{\circ}\text{C}$ , providing total (pre-combustion dry mass), volatile (total mass minus post-combustion mass), and fixed suspended solids (residue mass after combustion).

We quantified detritus quality on 18 July and at the end of the experiment (1 November) per standard methods (2540 B and E; APHA 1998). We sampled 200 mL of sediments ( $n=3$  replicates per pool). Dried samples were combusted at 550 °C. We calculated percent organic content as [(mass lost upon ignition divided by dry mass)  $\times$  100].

During the experiment, we monitored abiotic water parameters using a Horiba U-10 water quality meter to ensure water quality. We measured water temperature, dissolved oxygen, pH, and turbidity at the surface (0.1 m depth below water surface) and near the sediment-water interface (0.1 m above the sediment) at 7- to 10-d intervals.

*Phytoplankton, Periphyton, and Macroinvertebrates*—To track nutrient fate, we estimated algal biomass in the water column (phytoplankton), attached to mesocosm walls (periphyton), and benthic macroinvertebrates. We estimated chlorophyll-*a* concentration via the spectrophotometric method for each pool, corrected for pheophytin (method 10200 H, APHA 1998); we sampled 0.6-2 L of water from 0.25-m depth 3 d before the end of the experiment. To estimate periphyton, we scraped the inner circumference of each drained pool twice with a razor blade at 0.25-m depth (1 November). We determined biomass of periphyton ( $\text{g} / \text{m}^2$ ), subtracting the mass of inorganic matter via loss upon ignition. At that same time, we collected 1 L of sediments from each pool. We sieved the samples (US Standard No. 30, 0.60-mm mesh) and stored invertebrates (95% ethanol). In the laboratory, we identified macroinvertebrates to family.

## **Field Study**

Study Site and Fish Collection—We collected gizzard shad, detritus, and zooplankton during summer 1998 in four small (2-5 ha) experimental reservoirs on the Auburn University Experiment Station, AL (designated S-8, S-14, S-15, and S-30), where access is restricted and removal of sport fishes occurs by electrofishing only.

We collected gizzard shad by DC electrofishing and gill nets and measured length and mass. We estimated condition by calculating relative weights ( $W_r$ ), comparing the mass of each fish to the 75<sup>th</sup> percentile mass from multiple populations (Anderson and Neumann 1996). We estimated ages of fish using sagittal otoliths (Clayton and Maceina 1999), then estimated growth (mm TL / year) and back-calculated, length-at-age using the direct proportional method.

Detritus Collection and Analysis—We collected sediment samples ( $n=5$ ) from 2-3 m depth at all reservoirs. We collected sediment by diving and carefully collecting the top 5 cm of sediments using PVC tubes. We returned them to the laboratory, and froze them (-20°C). We removed the top 2.5-cm fraction for analysis of organic matter (Mundahl and Wissing 1988).

## **Statistical Analysis**

For the laboratory and field experiments, we compared treatments via a one-way analysis of variance (ANOVA; PROC GLM; SAS version 8.2), with post-hoc Tukey's multiple comparisons. Mesocosm data were analyzed via a two-way ANOVA (PROC GLM; SAS version 8.2), with post-hoc Duncan's Multiple Range Tests. For the field study, we calculated Pearson product-moment correlations to relate sediment quality to gizzard shad growth, condition, and back-calculated length-at-age-1. Before averaging

values for each replicate aquarium, mesocosm, or pond, we transformed (arcsine-square root) proportional data and transformed ( $\log_{10}$ ) variables to help normalize the data and homogenize variance (Sokal and Rohlf 1995).

## RESULTS

### Laboratory Experiment

Gizzard Shad Growth and Survival— In the 15-d experiment, age-0 gizzard shad growth was fastest with zooplankton only. Gizzard shad grew in the zooplankton treatment (Figure 1A); however, those in the lake detritus only and starved treatments lost mass (ANOVA  $F_{2,9} = 35.42$ ,  $P < 0.0001$ ; Tukey's comparison). Gizzard shad fed detritus lost a similar amount of mass to starved fish (Figure 1A), despite having the same mass in gut contents to those fed zooplankton ( $t$ -test,  $P = 0.2743$ ;  $df = 8$ ;  $t = 1.17$ ; Figure 1B). In turn, fish in the zooplankton treatment survived well to day 15 (90% survival), whereas those fed detritus only or starved survived poorly to day 15 (<15% survival; ANOVA  $F_{2,9} = 43.11$ ,  $P = 0.0001$ ; Tukey's comparison; Figure 1C). On average, gizzard shad fed zooplankton survived 14 d versus only 8 d for those fed detritus only and starved (ANOVA  $F_{2,9} = 12.91$ ,  $P = 0.0023$ ; Tukey's comparison).

### Mesocosm Experiment

Sediment treatments differed in organic material at the start of the experiment (ANOVA;  $F_{2,14} = 51.10$ ;  $P < 0.0001$ ). On average, the low sediment quality was 5.6% ( $\pm 0.2$  standard error) organic material ( $n=6$ ); the medium was 7.8% ( $\pm 0.5$  SE;  $n=6$ ); the

high was 12.3% ( $\pm 0.7$  standard error;  $n=5$ ). By the end of the experiment, however, sediment quality among treatments was similar ( $F_{2,14} = 0.90$ ,  $MS = 0.3148$ ,  $P=0.43$ ), ranging 3.3 to 4.1%.

*Gizzard Shad Growth, Condition, and Energy Density*—In the mesocosm experiment, gizzard shad growth varied with both fish density and sediment quality, whereas only sediment quality influenced survival. Growth rates ranged from 0.06 mm TL / d (high fish-no sediment treatment) to 0.32 mm TL / d (low fish-high sediment treatment). Specifically, gizzard shad growth increased with sediment quality only at low densities (Figure 2A; 2-way ANOVA), growing faster in the high-quality sediments than in no sediment or low-quality sediments (Duncan's Multiple Range Test;  $P < 0.05$ ; Figure 2A); low- or medium-quality sediments did not increase growth over no sediments (Duncan's Multiple Range Test; Figure 2A). Growth was density dependent, growing faster at low than high density (Duncan's Multiple Range Test;  $P < 0.05$ ; Figure 2A). Unlike growth, gizzard shad survival was not density dependent. Gizzard shad survived better in high quality sediments than low or no sediment treatments (Duncan's Multiple Range Test;  $P < 0.05$ ; Figure 2B), but no difference existed between fish density treatments. Although these levels of survival were lower than expected due to stocking mortality, we did not observe any events that could explain such high mortality across all pools.

Energy density of gizzard shad depended on both fish density and sediment quality, with fish density differences driven by body length. At high sediment quality, gizzard shad had higher energy density than the other sediment treatments and low fish density yielded higher energy content (Duncan's Multiple Range Test;  $P < 0.05$ ; Figure

2C). However, when standardized for length (Figure 2D), energetic condition was not density dependent (Duncan's Multiple Range Test;  $P = 0.0601$ ; Figure 2D), suggesting that only difference in fish size (Figure 2A) drove the energy density differences (Figure 2C). When standardized for fish size, high sediment quality fish had higher energetic condition than medium sediment quality fish, but was similar to the other treatments (Duncan's Multiple Range Test;  $P < 0.05$ ; Figure 2D).

Suspended Sediments—Differences in sediment quality influenced suspended sediments. High quality sediments had the highest concentrations of volatile (VSS) and total suspended solids (TSS; Figure 3A-B; ANOVA; Duncan's Multiple Range Test;  $P < 0.05$ ). Treatments with sediments had lower proportions of VSS to TSS than without sediments (Figure 3B; Duncan's Multiple Range Test;  $P < 0.05$ ). Suspended solids were not influenced by fish density (Figure 3A-B; FISH and FISH\*SED treatment; ANOVA;  $P > 0.10$ ), suggesting little physical re-suspension of bottom sediments by gizzard shad.

Benthic Primary and Secondary Production—Benthic production appeared to dominate in our mesocosms. Periphyton biomass, our surrogate measure for benthic production, generally increased with increasing sediment quality (Figure 3C; ANOVA; Duncan's Multiple Range Test;  $P < 0.05$ ); however, fish density had no effect. Our surrogate measure for open-water primary production, algal biomass, was extremely low ( $< 1 \mu\text{g} / \text{l}$ , unpublished data), suggesting primary production was mostly periphyton. Macroinvertebrate density (95% of which were chironomid larvae) increased with sediment quality, but not with fish density (Figure 3D; ANOVA; Duncan's Multiple Range Test;  $P < 0.05$ ).

## Field Study

*How Detritus Quality Influences Gizzard Shad Growth and Condition*—Organic content of detritus varied among our four experimental reservoirs (ANOVA,  $F_{3,16} = 4.58$ ;  $P=0.02$ ), ranging from 9.6% ( $\pm 1.2$  standard error) to 17.2% ( $\pm 1.0$ ); the reservoir with the highest organic content in sediments (S-14) differed from the other three reservoirs. From these reservoirs, we collected 104 gizzard shad (1-13 years old), ranging 210 to 467 mm total length (TL). Although condition (Figure 4A) and first-year growth (Figure 4B) did not statistically relate to detritus quality ( $P>0.10$ ), all relationships were positive, as was hypothesized, despite low sample size. Mean annual growth of gizzard shad increased with detritus quality (Figure 6C;  $P<0.05$ ).

## DISCUSSION

Using a multi-scale approach, we documented that age-0 gizzard shad populations vary with detritus quality, potentially mediating how they link benthic and pelagic habitats. In the laboratory, the mere presence of natural sediment detritus was not sufficient for growth and survival of age-0 gizzard shad. Rather, high sediment quality yielded relatively fast growth and energy density in the mesocosm experiment only at low gizzard shad density, because of density dependence. In high-quality sediments, survival was less variable than in the other sediment treatments. These experimental findings were supported in the field, where annual growth increased with sediment quality. Because omnivorous age-0 gizzard shad recover nutrients from benthic sediments that were previously lost to pelagic food webs, including both internally

derived and “new” nutrients from the watershed, they link benthic and pelagic food webs (Schaus and Vanni 2000; Vanni et al. 2005). Our findings suggest that in addition to the bulk quantity of detritus, its quality can ultimately influence productivity, mediated by its influence on gizzard shad biomass available to piscivores fish. This supports detritus quality being critical to aquatic ecosystem productivity, as proposed by Lindeman (1942).

Our multi-scale approach was necessary to examine how detritus-quality gradients affect gizzard shad via their feeding habits. Previous experimental work has quantified the short-term feeding behavior of age-0 gizzard shad switching between detritivory and zooplanktivory (Yako et al. 1996, Schaus et al. 2002), gizzard shad nutrient excretion with and without access to lake sediments (Mather et al. 1995, Schaus and Vanni 2000), and *in situ* studies of nutrient recycling (Schaus et al. 1997, Gido 2003). However, these studies focused on the presence or absence of detritus, not its quality. Individual gizzard shad in both the laboratory and field actively select the nutritious fraction (2- to 3-fold richer than average organic content) of detritus (Mundahl and Wissing 1987, 1988), suggesting the importance of detritus quality on individual foraging behavior. Thus, quantifying how detritus quality influences gizzard shad populations is important to predict how they influence the rest of the ecosystem.

*Gizzard Shad Populations Dynamics along Pelagic Productivity Gradients—*

Although population abundance often increases with productivity (DiCenzo et al. 1996, Michaletz 1998, Clayton and Maceina 2002), density-dependence at the age-0 stage yields different populations along productivity gradients. As pelagic trophic state increases, larval gizzard shad hatch rates, survival, and growth rates increase, increasing age-0 fish abundance (Bremigan and Stein 1999, 2001). Productivity that increases from

mesotrophic to eutrophic Ohio reservoirs yields abundant, but small age-0 gizzard shad (Bremigan and Stein 1999); however, increased trophic state from eutrophic to hypereutrophic resulted in both increased abundance and size of age-0 gizzard shad. Across Missouri reservoirs, age-0 gizzard shad growth increased along with reservoir productivity, with productivity and juvenile density explaining 75% of the variability in age-0 growth (Michaletz 1998, 1999); however, juvenile density did not correlate with reservoir productivity (Michaletz 1999). Generally, adult gizzard shad populations in highly productive systems are dense, grow slowly after age-1, have poor condition, and suffer high mortality (DiCenzo et al. 1996, Michaletz 1998, Clayton and Maceina 2002).

When zooplankton are scarce, omnivory can drive gizzard shad growth, potentially influencing the entire ecosystem. Although gizzard shad can switch to consuming abundant detritus when zooplankton are scarce, detritus is nutritionally poor and results in low growth rates, compared to zooplanktivory (Mundahl and Wissing 1987, Yako et al. 1996, this study). Stable isotope analysis reveals two scenarios (Schaus et al. 2002). First, at low gizzard shad biomass, abundant zooplankton provides most gizzard shad energy, generating rapid growth and nutrient recycling within the pelagic habitat. Second, when rapid growth leads to increased age-0 gizzard shad biomass, zooplankton become scarce, forcing a diet shift to detritus. During detritivory, gizzard shad grow slowly, but transport “new” nutrients and carbon from the benthic to the pelagic zone.

The size range of age-0 gizzard shad in our study represents a life stage that has high biomass and broad diet range. Between hatching and 10 mm TL, gizzard shad larvae consume microzooplankton exclusively, switching to crustacean zooplankton at sizes between 11 and 20 mm (Miranda and Gu 1998). At sizes around 25-30 mm,

development changes start to elongate gut morphology and gill raker structure to allow a broader diet that includes minute algae, protozoans, rotifers, detritus, and phytoplankton (Wier and Churchill 1946; Bodola 1965; Miranda and Gu 1998). Thus, our fish that averaged 40-50 mm TL could consume a wide variety of food, including detritus. This size range also marks the beginning of the period of highest biomass for gizzard shad during the latter part of their first year (Denlinger et al., 2006).

In the mesocosm experiment, sediment quality among treatments may have been manifested in terms of variation in chironomid density and periphyton biomass as the proximate causes of variation in growth and survival of age-0 gizzard shad. Organic content of sediments positively influences growth and development of chironomids (Vos et al. 2000). The sizes of our gizzard shad were probably large enough to consume soft-bodied chironomid, especially early instar stages. In fact, adult gizzard shad have even been observed to surface feed on chironomid remains when this food is abundant (King et al. 1977). In addition, the increased periphyton density with sediment quality also provided food for age-0 gizzard shad. During the experiment, we observed gizzard shad feeding on the sides of pools.

In our view, omnivory buffers gizzard shad against mass mortality when zooplankton is scarce. Even so, when high-quality sediments are available and population density is low, gizzard shad enjoy relatively fast growth. In fact, our highest growth rates (0.32 mm TL / d in low fish-high sediments) were similar to gizzard shad feeding at low zooplankton densities. When zooplankton densities are manipulated in enclosure experiments, age-0 gizzard shad growth rates range 0.3 to 1.2 mm TL / d (Bremigan and Stein 1997, Dettmers and Wahl 1999) for slightly smaller gizzard shad

(22-26 mm starting TL). Thus, in some situations (available high quality-sediments and low gizzard shad), the growth consequences from switching from zooplanktivory to detritivory may be negligible. Thus, even when zooplankton density is high, it is not surprising that the majority of gizzard shad stomach contents still is detritus (Yako et al. 1996).

Gizzard shad influence predators and nutrient transfer differently along productivity gradients. In productive systems with enriched sediments, gizzard shad are dense, grow slowly, and consume primarily detritus after zooplankton are depleted (Schaus et al. 2002). Intense predation on these small gizzard shad can increase biomass of pelagic predators (Kershner et al. 1999). Simultaneously, gizzard shad excrete nutrients from sediments back into the water column, stimulating phytoplankton growth (Schaus et al. 1997). At times, gizzard shad are a significant nutrient source, excreting phosphorus at rates that exceed watershed input (Schaus et al. 1997). The influence of nutrient translocation would have the greatest influence in low to moderate productivity systems with little nutrient loading from the watershed, enriched sediments, and few zooplankton (Schaus et al. 1997).

Despite well-documented relationships between reservoir pelagic productivity and gizzard shad populations, pelagic productivity does not simply correlate to concomitant detritus quality. Among 12 Ohio reservoirs, no correlation exists between pelagic productivity and detritus quality (% organic material;  $P=0.49$ ,  $r=0.21$ ; data from OEPA 1995). Further, as pelagic productivity increased via nutrient input (e.g., cultural eutrophication), benthic primary production either decreased (due to shading) or did not

change in a mesocosm experiment (Blumenshine et al. 1997) and a multi-lake survey (Vadeboncoeur et al. 2003).

We hypothesize that a threshold value exists between our medium and high sediment quality treatments, above which high growth is possible. Our mesocosm sediment quality values were on the lower end of the range found in reservoirs. Field values of sediment organic content range from 6 to 27% (Mundahl and Wissing 1987, 1988, OEPA 1995). Lake sediments in the 15-d laboratory experiment and low- and medium-quality sediments in the 76-d mesocosm experiment yielded poor growth, similar to the no-sediment controls. Unfortunately, we did not measure organic content of the sediment used in the laboratory study. However, they probably were at or slightly below our mesocosm sediments scraped from a production fish hatchery pond, which averaged 6.1% organic content. The highest sediment quality treatment yielded unique patterns in the mesocosm experiment; at this high sediment quality, density-dependent regulation of growth was strongest. However, survival was not density dependent and was influenced only by sediment quality. This is similar to the field pattern observed in Ohio reservoirs of abundant, but small age-0 gizzard shad as systems increase from mesotrophic to eutrophic status (Bremigan and Stein 1999).

The influence of gizzard shad on ecosystem processes depends on both age and size. In many systems, age-0 gizzard shad quickly outgrow predators (DiCenzo et al. 1996). In these systems, trophic transfer of biomass is not realized; yet, their role in sediment re-suspension and nutrient excretion would remain intact. Although age-0 gizzard shad can eat detritus (Mundahl and Wissing 1987), they can actively switch back to zooplanktivory when zooplankton becomes abundant, yielding fast growth (Yako et al.

1996, Schaus et al. 2002). In this case, gizzard shad would have a relatively small role linking benthic and pelagic systems, because they would consume little benthic material, quickly outgrow predators, and excrete less nutrients on a mass-specific basis than their smaller-sized, slow-growing populations (Schaus and Vanni 2000).

In addition to external environmental influences, gizzard shad may be regulated by internal population dynamics, potentially yielding cyclical population patterns. Gizzard shad recruitment often is cyclical or sporadic (Michaletz 1998). Intraspecific competition for age-0 gizzard shad (both intra- and intercohort) may explain their erratic recruitment. After producing many larvae in early spring, abundant age-1+ gizzard shad can decimate zooplankton populations, leaving only detritus for offspring (Schaus et al. 2002). Short-term reductions in growth rates from detritivory (as in our study) have asymmetric effects across cohorts, with only age-0 shad vulnerable to predatory mortality (DiCenzo et al. 1996). Our results suggest that high age-0 gizzard shad density would yield slow growth, especially when high-quality detritus is unavailable. Until older gizzard shad become scarce or senescent, reducing their consumptive demand and reproductive output, age-0 gizzard shad recruitment could suffer greatly from intra- and inter-cohort competition. Similar patterns of asymmetrical competition among cohorts leading to population cycles have been suggested for vendace (*Coregonus albula*; Hamrin and Persson 1986) and yellow perch (*Perca flavescens*; Sanderson et al. 1999).

*The Role of Fish in Benthic-Pelagic Coupling*—Without gizzard shad, benthic and pelagic food webs would remain largely separate in many lakes and reservoirs. Additionally, the allochthonous detritus subsidy from the watershed would remain disconnected to upper trophic levels, including sport fish. Such external subsidies are

especially important for reservoirs, which have a large watershed:surface area ratio and poor conditions for phytoplankton production (high water turnover rate, high turbidity) compared to lakes (Vanni 2002). At times, the benthic detritus pool is the ultimate source for a large proportion of pelagic dissolved nutrients (Schaus et al. 1997) and the gizzard shad available for piscivores (this study), enhancing both primary and secondary production.

With efforts to reduce cultural eutrophication, the role of fish integrating benthic and pelagic food webs likely will increase, generating unexpected outcomes. Although excess phosphorus inputs from agriculture, industry, and municipalities have declined in lakes and reservoirs (OEPA 1995, Ney 1996), water quality returns on this investment may not occur as quickly as anticipated, due to benthivorous fish and pools of high-quality detritus. In systems with reduced pelagic productivity, increased water clarity, and higher periphyton biomass, the contribution of benthic primary production to system productivity increases relative to other energy sources (Vadeboncoeur et al. 2003). Thus, if one of the goals of water quality management is to reduce gizzard shad biomass relative to that of sport fish, this may not be realized in the short-term. As previously anoxic bottom sediments become accessible to fish during oligotrophication, fish-mediated translocation of nutrients among habitats will become more important. Thus, as the eutrophication process “reverses trajectory” towards oligotrophication, resultant water quality increases or fish community changes may be delayed or interrupted until this reserve of high-quality benthic detritus is exhausted or gizzard shad biomass is reduced.

Figure 1. Mean response of age-0 gizzard shad ( $n=5$  per aquarium) to a 15-d laboratory experiment with three feeding treatments: starvation (no food), only detritus (detritus), and only zooplankton (zooplankton) in aquaria. Panel A: specific growth rate (SGR). Panel B: dry mass of food in guts of gizzard. Panel C: percent survival of gizzard shad. Letters within a panel denote different values (one-way ANOVA, Tukey's post-hoc test,  $P < 0.05$ ). Error bars represent  $\pm 1$  standard error.

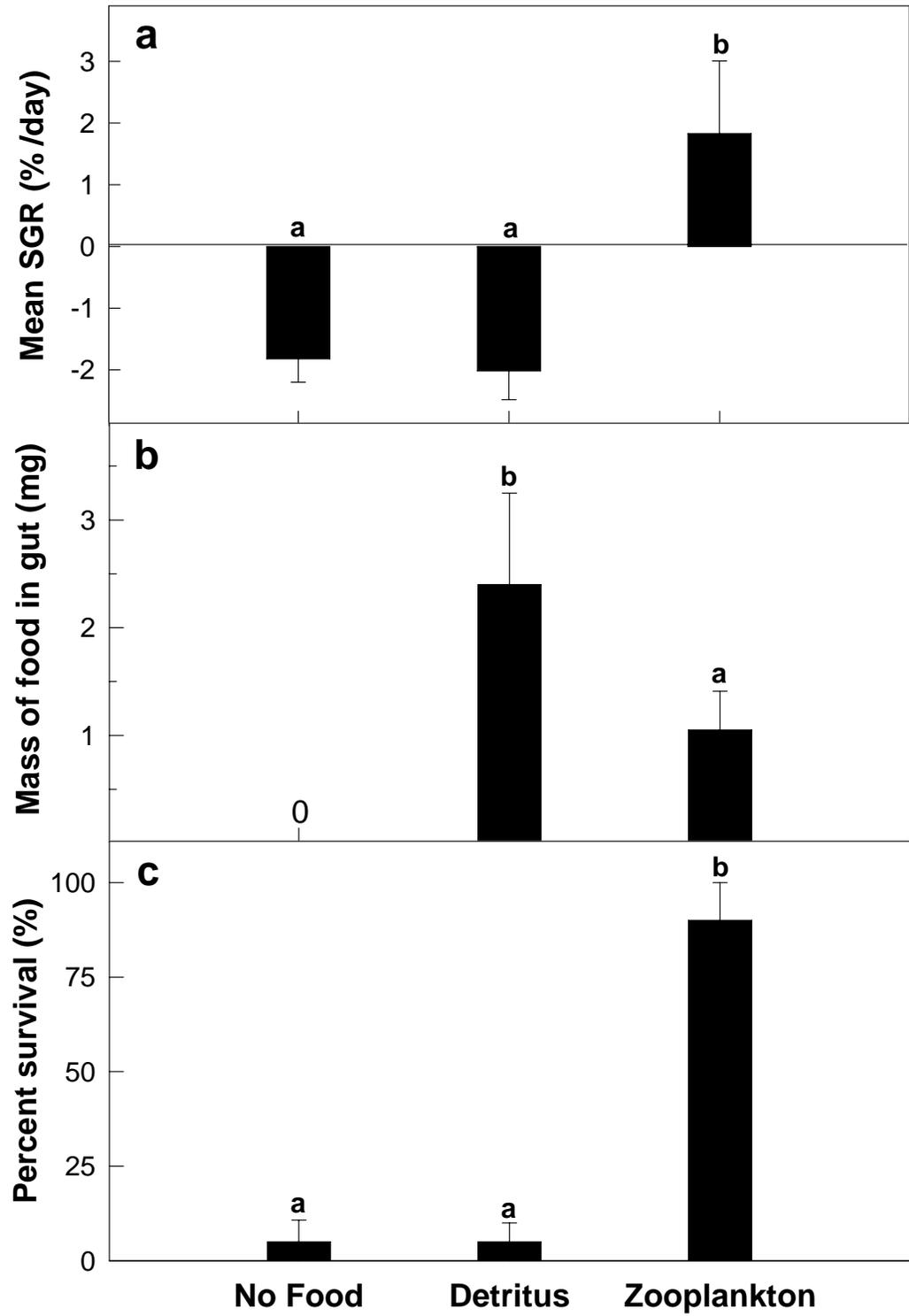


Figure 1.

Figure 2. Mean responses of age-0 gizzard shad (length at stocking averaged  $47.2 \pm 0.6$  mm TL) to fish density and sediment quality treatments in a 76-d mesocosm experiment. Panel A: growth as measured by final length. Panel B: percent survival during the experiment. Panel C: final energetic content. Panel D: fish condition, measured as the residual from predicted energy content. Treatment codes that share an underline did not differ (two-way ANOVA, Duncan's Multiple Range Post-hoc Test,  $P > 0.05$ ). Error bars are  $\pm 1$  standard error. Treatments are coded: LF=low fish density, HF=high fish density, OS=no sediments, LS=low sediment quality, MS=medium sediment quality, and HS=high sediment quality.

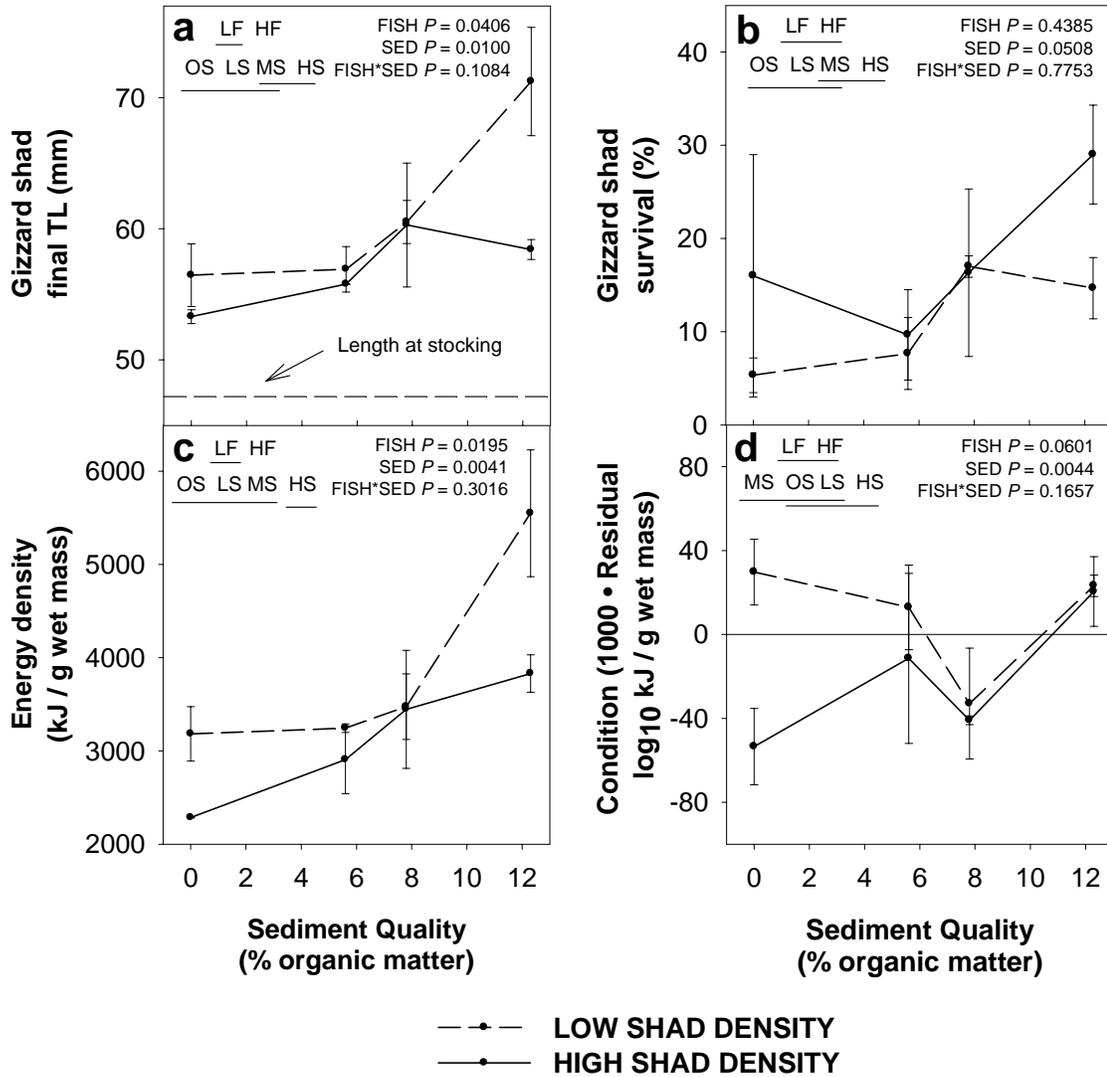


Figure 2.

Figure 3. Water quality and productivity responses to fish density and sediment quality treatments in a 76-d mesocosm experiment. Panel A: volatile suspended solids (VSS). Panel B: proportion of VSS to total suspended solids. Panel C: periphyton (organic fraction) on mesocosm sides. Panel D: benthic macroinvertebrate density in bottom sediments (95% of which were chironomid larvae). Treatment codes that share an underline did not differ (two-way ANOVA, Duncan's Multiple Range post-hoc Test,  $P > 0.05$ ). Error bars are  $\pm 1$  standard error. Treatments are coded: LF=low fish density, HF=high fish density, OS=no sediments, LS=low sediment quality, MS=medium sediment quality, and HS=high sediment quality.

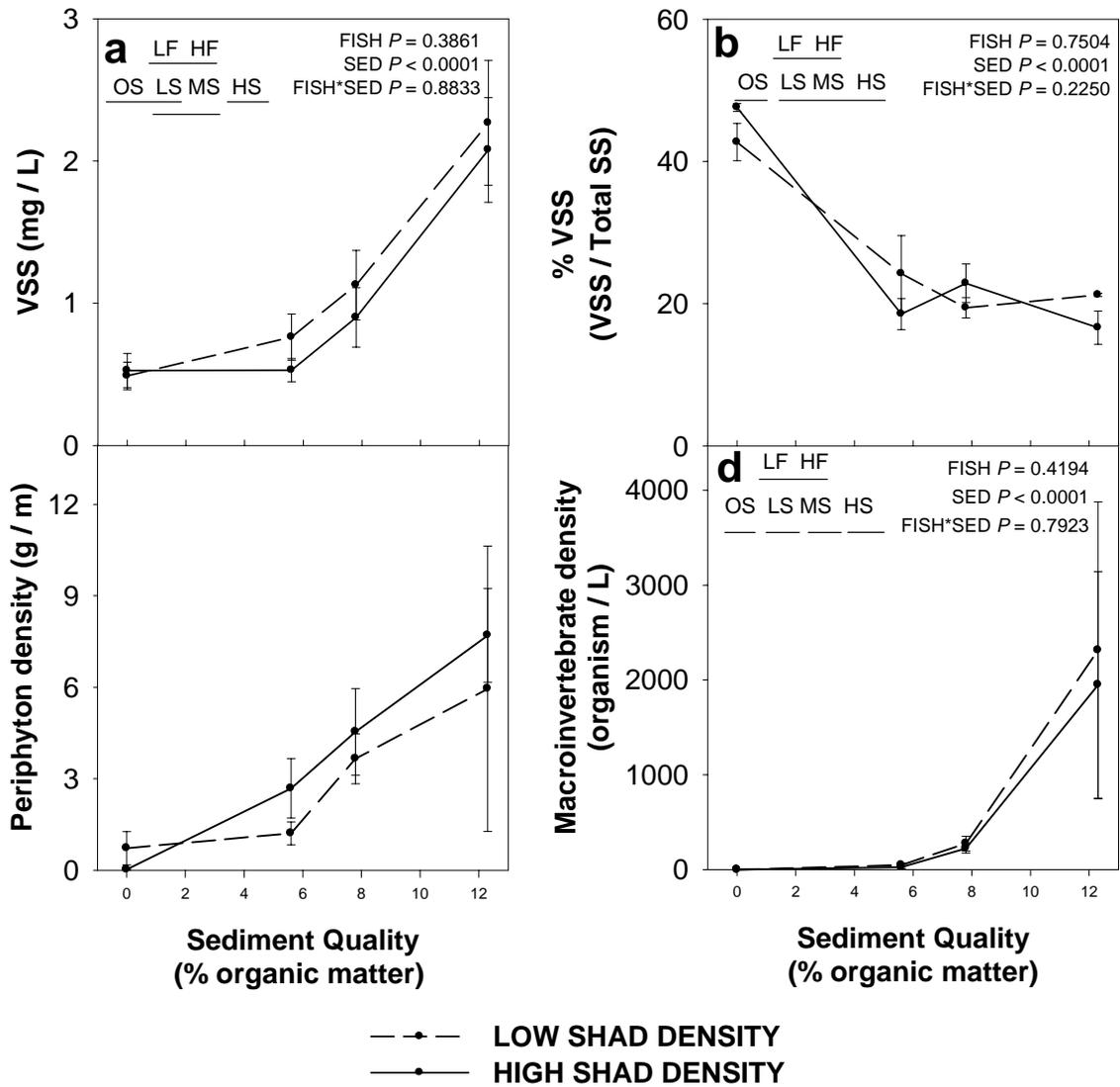


Figure 3.

Figure 4. Results from four small reservoirs, comparing pond sediment detritus quality with (A) mean relative weight, (B) back-calculated first-year growth based on otolith measurements, and (C) mean annual growth rates. Error bars represent  $\pm 1$  standard error.

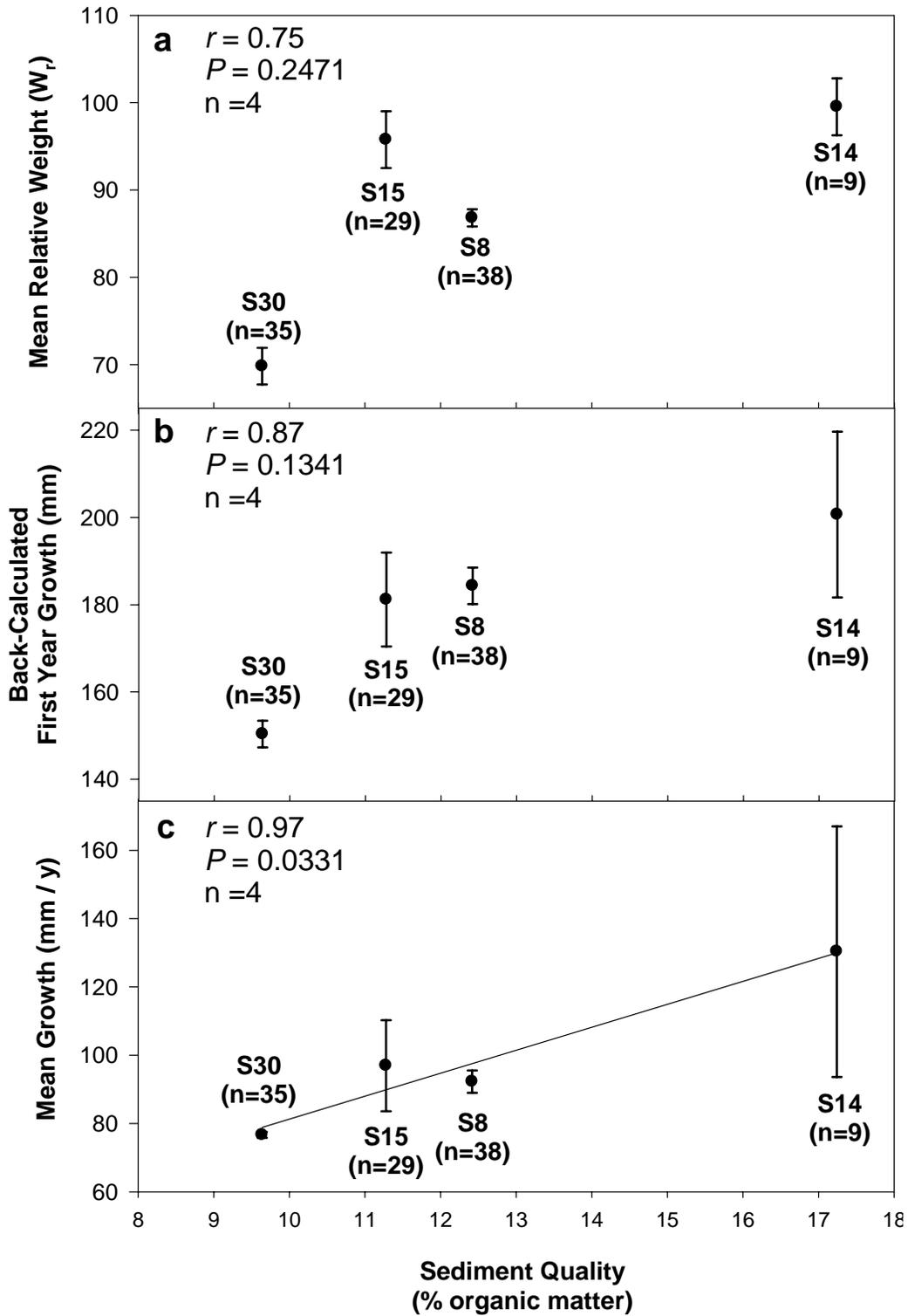


Figure 4.

## CHAPTER 3

### SELECTIVE PREDATION BY SMALLMOUTH BASS ON EXOTIC ROUND GOBIES OVER HISTORICAL LAKE ERIE PREY: COMPARATIVE RESULTS FROM LABORATORY- AND FIELD-BASED ESTIMATES

#### ABSTRACT

This laboratory-field study quantified smallmouth bass (*Micropterus dolomieu*) diets in response to invasion by exotic round goby (*Neogobius melanostomus*). When round gobies, emerald shiners (*Notropis atherinoides*), and crayfish (*Orconectes rusticus*) were simultaneously presented in a 370-L arena, smallmouth bass spent more active time following, pursuing, and attacking both fishes rather than crayfish. However, despite being attacked more frequently than round gobies and crayfish, emerald shiners reduced their vulnerability via superior flight abilities, compared with round gobies (consumed most) and crayfish (consumed least). These findings supported smallmouth bass field diets, in which round gobies increased through time and were more prevalent in diets than emerald shiners or crayfish. Energetically, round goby were intermediate between

prey fish and macroinvertebrates. Sizes easily eaten by smallmouth bass (42-100 mm TL) averaged  $3.50 \pm 0.05$  KJ/g wet mass, compared with  $3.65 \pm 0.05$  KJ/g wet mass for all round gobies sampled (42-151 mm TL). These values generally were lower than prey fishes and higher than invertebrate prey. Therefore, to maintain historical growth rates, smallmouth bass must eat more round gobies than historical prey. Higher density and ease-of-capture of round gobies, compared with historical prey, could mediate this requirement; but, this potentially could increase contaminant uptake. With the expansion of round gobies into new areas (e.g., the Mississippi River Basin), at least for the near future, we expect that the relative importance of round gobies transferring benthic material to pelagic food webs will increase, even as source inputs of nutrients and contaminants decline.

## **INTRODUCTION**

During the past two centuries, the Laurentian Great Lakes have suffered the establishment of more than 140 exotic species (Mills et al. 1993). Many species were introduced via human activities, including exotic species released in ballast water, escaped from fish culture, and distributed via water diversions (Mills et al. 1993). Once established, introduced species are extremely difficult to remove (Elton 1958). Further, introductions may benefit from facilitation by established exotic species, hastening the rate of subsequent invasions (Simberloff and Holle 1999; Ricciardi 2001; Vanderploeg et al. 2002), and resulting in miniature versions of foreign food webs being transplanted into recipient ecosystems.

The recent establishment of zebra (*Dreissena polymorpha*) and quagga (*D. bugensis*) mussels represents an economically and ecologically important exotic species in the Great Lakes. In 1988, these Ponto-Caspian dreissenid mussels likely were introduced via ballast water into Lake St. Clair (Mills et al. 1993). Since then, they have spread swiftly through the Great Lakes and Mississippi basins (Drake and Bossenbroek 2004). By filtering plankton and other seston, they compete with larval fish (Berg et al. 1996) and increase net sedimentation rates (Dobson and Mackie 1998), resulting in a net transfer of energy and contaminants from the pelagic to the benthic food web. At high densities, filter-feeding dreissenid mussels compete with fish for plankton and re-direct energy and contaminants from the pelagic to the benthic food web (Dobson and Mackie 1998). Although few organisms were initially thought to be able to consume the unpalatable shells of dreissenid mussels (French 1993), recent evidence dispels any notion that they are a simply a food web “dead-end”. Adult lake whitefish *Coregonus clupeaformis*, yellow perch *Perca flavescens*, and freshwater drum *Aplodinotus grunniens* can feed heavily on dreissenid mussels at times (French 1993; Pothoven and Nalepa 2006). In addition, diving ducks can consume large amounts of dreissenid mussels during migration (Mazak et al. 1997).

The recent invasion by round gobies *Neogobius melanostomus* may link benthic and pelagic food webs, transferring material from the benthic zone into upper trophic levels. Within 5 y of their 1990 discovery in the St. Clair River (Jude et al. 1992), round gobies spread quickly to all five Great Lakes (Charlebois et al. 1997) and currently are colonizing the Mississippi River basin (Steingraeber 1999). They can reach extremely high densities ( $>100/m^2$ ) in some areas of Lake Erie (Corkum et al. 1998). In their native

Ponto-Caspian range, round gobies have evolved to use dreissenid mussels as their primary prey (Charlebois et al. 1997). Thus, earlier colonization by dreissenid mussels might have facilitated rapid expansion in the Great Lakes (Charlebois et al. 1997; Ricciardi 2001; Drake and Bossenbroek 2004). Whereas only large, native fish can feed directly on dreissenid mussels in Lake Erie, both juvenile and adult fish can consume round gobies, especially benthic piscivores smallmouth bass *Micropterus dolomieu*, burbot *Lota lota*, and yellow perch (Johnson et al. 2005). Given potential biomagnification and selective contaminant retention, this represents a new and potentially important pathway linking higher trophic levels to sediment contaminants.

Herein, we quantify the potential for, and implications of, round goby inclusion into the Great Lakes food web. Given that transfer of energy, nutrients, and contaminants occurs primarily by dietary transfer, quantifying these predator-prey relationships will provide insight into the impact of round goby establishment. Thus, we conducted a laboratory predator-selection experiment exposing smallmouth bass to round gobies and two common smallmouth bass prey, one benthic- and one pelagic-oriented. In these experiments, we quantified smallmouth bass prey selection and predator avoidance by each prey type. To determine smallmouth bass diet composition, we sampled stomach contents of field-collected smallmouth bass and estimated round goby densities from Lake Erie trawl samples. Finally, we estimated energy density of round gobies to forecast growth consequences from inclusion of round gobies in the diets of top predators. We hypothesized that the occurrence of hyper-abundant round gobies in Great Lakes food webs would have important consequences for growth and contaminant transfer rates, depending on predator choice, consumption rate, and energy density of prey.

## METHODS

### Laboratory Experiment

*Experimental Setup and Organisms*— From November through December 2001, we conducted 30-min experimental trials ( $n=39$ ) to quantify predator selection by smallmouth bass when given a choice among round gobies, emerald shiners, and rusty crayfish. Our choice of emerald shiners and rusty crayfish was driven by their constant availability in bait stores and because both are common to areas where smallmouth bass feed in Lake Erie (Stewart et al. 1998a, 1998b; ODOW 2005). We conducted trials in a 500-L tank (outside dimensions: 2.0 x 0.5 x 0.5 m), in which water temperatures averaged  $20.0 \pm 0.2^\circ\text{C}$  (range:  $18.5\text{--}23^\circ\text{C}$ ) and photoperiod was 12 h light:12 h dark. The tank was divided into a small predator-holding chamber (70 L) and a large 370-L predator arena (effective volume based on length: 1.4 m, width: 0.5 m, and 0.47-m water depth) by a remotely controlled opaque divider. During each trial, we exposed one smallmouth bass to two round gobies, two emerald shiners, and two crayfish. About 15 min before each experimental run, we added prey to the tank, while the predator was confined to the predator-holding chamber. After remotely lifting the divider separating predator from prey, the trial began when the predator entered the larger predator arena. We attached plexiglass (about 30-mm width) vertically to each of the four edges (“corners”) of the predator arena (creating two  $45^\circ$  angles) to prevent crayfish from entrenching themselves in a corner, which would make them virtually invulnerable to predation. With a window in front (1.35 x 0.40 m) and a lighted mirror above (1.42 x 0.41 m) the

tank in a dim room, we recorded behavior (video camera for later analysis). To prevent predators from being distracted by observers, we lined the front window with mesh.

We collected smallmouth bass from a site in Lake Erie having all three prey items. Using pulsed-DC electrofishing, we collected 13 smallmouth bass from near South Bass Island from August through September 2001, and round gobies by trawling and angling during October 2001. We transported these fish to the laboratory (The Ohio State University, Columbus, Ohio) under aeration plus sodium chloride, and then placed smallmouth bass in flow-through tanks and round gobies in a 1,500-L closed, re-circulating tank system under the same temperature and light conditions as the experiment. Emerald shiners and crayfish were purchased at bait stores and held in flow-through aquaria, pending the start of the experiments. Water quality (temperature, oxygen, ammonia, alkalinity, hardness, nitrates, and pH) was measured twice per week (Horiba U-10 water quality meter; Hach water quality, model FF-1A).

To standardize predator experience among predators, we fed experimental smallmouth bass equal amounts of all three prey types, beginning 1 mo before the experiment. Each day, we exposed predators to all three prey types under experimental conditions (i.e., in the predator arena). By exposing smallmouth bass to the same prey set, we hoped to diminish individual differences among smallmouth bass experience with a particular prey type. At times (~10%), we substituted fathead minnows (*Pimephales promelas*) for emerald shiners, because of limited availability of the latter.

Predator and Prey Sizes— We carefully selected sizes of predators and prey. Before the experiment, we did not have access to the Lake Erie diet data. Therefore, we

used surrogate values from other systems. For each trial, emerald shiner sizes were chosen based on a relationship from field data (Probst et al. 1984):

$$\text{Log}_{10} \text{CYPRINID TL} = 0.779 + 0.00466 (\text{SMB TL}) \quad (1)$$

where CYPRINID TL = mm total length of cyprinid, and SMB TL = mm total length of smallmouth bass. To determine round goby sizes for each trial, we assumed a similar morphology to sculpins (*Cottus* spp.). Thus, we selected round goby sizes that were 88% of emerald shiner TL (estimated from equation 1), because the largest ingested sculpin was 88% of the largest cyprinid TL found in smallmouth bass stomachs (Zimmerman 1999). We set the maximum carapace length (CL) of 20 mm of experimental crayfish equal to the largest estimated emerald shiner size. We chose this length, because 200 to 300-mm TL smallmouth bass in Wisconsin lakes contained *O. rusticus* that averaged 21 mm CL (Stein 1977) and the most frequent *Orconectes* spp. size in smallmouth bass diets in the New River (WV) was 20 mm CL (Roell and Orth 1993). We then selected crayfish lengths as a proportion of the largest equivalent emerald shiner.

Because hunger level affects predator foraging (Sabo and Orth 2002; Turesson et al. 2006), we used only fish that were on a routine feeding schedule (within 24-48 h of each experiment). If a scheduled fish had not eaten within 48 h, it was passed over in the cue until it began feeding daily. On average, experimental fish ate  $29 \pm 1$  h before each trial.

*Quantifying Predator and Prey Behavior*— We quantified predator and prey behavior from videotapes of each 30-min trial using event-recording software (Beast Professional V 1.01A, Windward Technology). For each prey type, we calculated the percentage of active time the predator devoted to each step of the predation cycle, capture

efficiency (number of captures / number of attacks), and ingestive pause (time between capture and next feeding bout). We excluded stationary or observation time not oriented toward prey from active time. Based on Wahl and Stein (1988), we separated the predation cycle into mutually exclusive categories: search (moving, but not oriented to prey), observe (motionless, but oriented toward an individual prey with caudal and dorsal fins typically beating rapidly), stationary (identical to observe, but not oriented to an individual prey), follow (move slowly at  $<1\text{m/sec}$ , oriented to particular prey item), pursue (follow at burst speed  $>1\text{m/sec}$ ), attack (strike at prey), capture (grasp prey), release (release of prey), and ingest (swallow prey). If the predator was inactive for  $>5$  min, we excluded that trial. Because satiation affects predator behavior (Turreson et al. 2006), we ended the trial if a predator had eaten both individuals of any given prey type. Selection could only be estimated when at least one individual of each prey type was present. Of the 39 total trials, 48.7% ended after all of a given prey type had been eaten, averaging 11.3 min. Of those 19 trials that ended early, smallmouth bass continued to eat additional prey in only three trials (15.8%). Otherwise, the trial lasted the entire 30 min (51.3% of all trials).

We quantified prey behaviors using 10-cm grids marked on the tank. Every 5 min, we measured the distance of the nearest prey of each type to the predator. We defined reactive distance as the closest distance that a predator could approach a prey before the prey reacted defensively (flight or aggression). Flight response was movement away from the predator in response to follow or pursuit movements. Fleeting distance was the distance that a prey moved during a flight response to one attack bout. Instances of crayfish aggression were recorded when they faced the predator with chelae extended.

Both the number of instances and the distance from the predator at the time of the aggressive display were recorded.

We tested each of eight individual smallmouth bass five times (one fish only had four replicates). To avoid flawed interpretations from pseudoreplication (Hurlbert 1984), we compared averages for each fish across all its replicates. Although the design was balanced for many of the early steps of the predation cycle (observe through attack), some measures could not be calculated for later steps. For example, % of active time devoted toward each prey could always be calculated until attack occurred. But, capture success could not be calculated if a fish did not attack a given prey item at least once. We tested differences for each event in the predation cycle, using species as a main effect in a fixed-effects model. To keep comparisons similar across all measures, we used an unbalanced design, one-way analysis of variance ([ANOVA], general linear model procedure [GLM] [SAS 9.1; SAS Institute, Cary, NC, USA]) for all measures. Upon finding significant differences, we used Student-Newman-Keuls (SNK) post-hoc comparisons to separate differences. Before statistical comparisons, we arcsine-square root transformed proportional data and  $\log_{10}(x+1)$  transformed other data to help normalize the data and homogenize variance (Sokal and Rohlf 1995).

## **Field Study**

*Trawl Sampling*—Smallmouth bass and round gobies were collected by bottom trawling (10.4-m head rope, 1.3-m vertical opening, 15.2-m roller sweep, and a 6-mm cod-end liner) in the central basin of Lake Erie. Sampling occurred monthly from May through October, 1994-2005. Although trawl data predate round goby establishment,

unfortunately, no smallmouth bass diet data are available for that time period for comparison to years after round goby establishment. During each sampling survey, we collected smallmouth bass from multiple sites, placed them on ice, and then returned to the laboratory. Gut contents were identified and then measured for length (0.1 mm TL). Prey mass was calculated via length-weight regressions (Ohio Division of Wildlife 2005). We present data only from fish older than 2 years that have food in their stomachs. Because smallmouth bass are not evenly distributed across all trawling locations, we quantified round goby densities from three central basin sites that regularly yielded adult smallmouth bass for diet analysis. These sites were Lorain (mean depth  $\pm$ 1 SD: 14.3 $\pm$ 3.1 m; lat: 41.52° N, long: -82.19° W; first round goby occurrence: 1997), Perry (depth: 18.5 $\pm$ 4.8 m; lat: 41.89° N, long: -81.06° W; first round goby occurrence: 1994), and Ashtabula (depth: 17.7 $\pm$ 4.8 m; lat: 41.96° N, long: -80.81° W; first round goby occurrence: 1995). We estimated density for round gobies in each trawl via a sex-specific age-length key, averaged these values across months, and then calculated the mean density across all sites (detailed in Bunnell et al. 2005). The Lorain site data series began in 1996, 1 year before the first detection of round gobies at that site.

*Energy Density of Round Gobies*—We determined energy density for round gobies collected during May through August 1999 from central basin trawl sampling. Round gobies were returned to the laboratory on wet ice, and then frozen in water. We estimated caloric density via bomb calorimetry (according to Rand et al. 1994; Kershner 1999). After thawing the fish, we recorded total length (nearest 0.1 mm TL) and mass (nearest 0.1 g) for each fish, removed gut contents, and then re-weighed wet mass. After fish were dried to stable mass, we ignited 1-g ground pellets inside a Parr Bomb

Calorimeter (Model 1672) or smaller 0.1-g pellets in a Parr Semi-micro Calorimeter (Model 1425), depending on the available sample mass. We corrected values for sulfuric acid (base titration), sulfur content (fixed average), and fuse combustion. Owing to low sample mass, we could estimate only one pellet on 51% of the fish. Of the fish with sufficient mass for two pellets (48% of fish), energy density differed by less than 3% between pellets for 92% of the fish. If the two estimates differed by more than 2% ( $n=2$ ), a third pellet was necessary. Seven fish were omitted, because they differed by more than 3% and did not have enough mass for more estimates (4% of all fish bombed). We calculated mean energetic density for each fish (or a single value when needed).

## RESULTS

### Laboratory Experiment

Experimental Predators and Prey—We used only fish that readily ate prey during the pre-experiment period. Of the 13 smallmouth bass collected, we used eight fish, which averaged smaller ( $230\pm 6$  mm TL; ranged 202-256) than those not used ( $251\pm 6$  mm TL; ranged 233-271;  $t$ -test;  $t=2.4$ ,  $df=7$ , 4;  $P=0.03$ ). We estimated these fish to be age 2, based on our unpublished length-age-key. During the experiment, we exposed smallmouth bass to optimally sized round gobies (prey TL averaged 27.3% of predator TL), emerald shiners (TL averaged 35.3% of predator TL), and crayfish (carapace length averaged 8.1% of predator TL).

Experimental Predator and Prey Behavior— During the early steps of the predation cycle (observing through attacking), smallmouth bass spent a greater proportion of their active time directed towards fish than towards crayfish. When observing prey, smallmouth bass did not display any preference in the proportion of active time spent observing (Figure 5A; ANOVA,  $F_{2,21}=0.09$ ;  $P=0.9166$ ). However, they spent more time following emerald shiners than following crayfish, whereas time spent following round gobies was intermediate (Figure 5B; ANOVA,  $F_{2,21}=5.26$ ,  $P=0.0140$ ; Student-Newman-Keuls [SNK] post hoc test,  $P<0.05$ ). Later, smallmouth bass spent a similar time pursuing (Figure 5C; ANOVA,  $F_{2,21}=11.86$ ,  $P=0.0004$ ; SNK post hoc,  $P<0.05$ ) and attacking and capturing (Figure 5D; ANOVA,  $F_{2,21}=4.70$ ,  $P=0.0205$ ; SNK post hoc,  $P<0.05$ ) round gobies as they did emerald shiners and spent less time towards crayfish.

During the later steps of the predation cycle (attacking through digestive pause), differences in capture efficiency resulted in more round gobies being ingested, despite smallmouth bass directing most of their attacks at emerald shiners. In fact, smallmouth bass attacked emerald shiners twice as frequently as round gobies and six times as often as crayfish (Figure 5E; ANOVA,  $F_{2,21}=5.34$ ,  $P=0.0133$ ; SNK post hoc,  $P<0.05$ ). However, smallmouth bass were 2.4 times more successful at consuming round gobies than either crayfish or emerald shiners (Figure 5F; ANOVA,  $F_{2,21}=3.73$ ,  $P=0.0430$ ). Successfully capturing an emerald shiner required more effort (on average, 6.2 attacks per successful capture) than the other prey taxa (only 2 attacks required to capture either round gobies or crayfish; ANOVA,  $F_{2,14}=12.13$ ,  $P=0.0009$ ). As a result, more round gobies were consumed in the experiment than crayfish, with emerald shiners intermediate

(Figure 5G; ANOVA,  $F_{2,21}=4.51$ ,  $P=0.0235$ ; SNK post hoc,  $P<0.05$ ). Finally, consuming round gobies resulted in a longer digestive pause than other prey (Figure 5H; ANOVA,  $F_{2,21}=4.51$ ,  $P=0.0234$ ; SNK post hoc,  $P<0.05$ ).

Differences among prey behavioral responses help explain prey capture rates. When not under attack, all three prey taxa remained the same distance from the predator (Figure 6A; ANOVA,  $F_{2,15}=1.39$ ,  $P=0.2800$ ). However, reactive distances for both fish species were twice that for crayfish (Figure 6B; ANOVA,  $F_{2,15}=45.84$ ,  $P<0.0001$ ; SNK post hoc,  $P<0.05$ ). The greatest disparity among prey occurred with flight response; emerald shiners fled twice as far from the predator as round gobies, whereas crayfish moved very little (Figure 6C; ANOVA,  $F_{2,15}=196.75$ ,  $P<0.0001$ ; SNK post hoc,  $P<0.05$ ).

### **Field Study**

*Trawl Sampling*—Round goby contribution to smallmouth bass diets increased through time, despite a stabilization of round goby density. Round gobies were first collected during 1993 at Grand River Harbor (Charlebois et al. 1997) and during 1994 in ODOW trawls (ODOW 2005). Round goby density peaked during 1998 (Figure 7A), then stabilized after 1998. Despite this stabilization, the contribution of round goby to smallmouth bass diets (measured as % dry mass) increased through time. Although this value peaked during 2002 (77% of diets by dry mass), round gobies still contributed more than 50% of smallmouth bass diets (by dry mass) from 2003 to 2005 (Figure 7B). The frequency of occurrence of round gobies in smallmouth bass diets increased from only 4% of sampled smallmouth bass diets in 1994 to more than 90% of smallmouth bass diets after 2003 (ODOW 2005). Crayfish were found in smallmouth bass' diets only in 6 of

the 12 sampling years, whereas round gobies and emerald shiners were eaten during all years (Figure 7B).

Energy Density of Round Gobies—Energy density of round goby was low, relative to other prey. Energy density of round gobies was intermediate between historical Lake Erie prey fish and crayfish (Figure 8A). Energy densities averaged  $3.65 \pm 0.048$  KJ/g wet mass for all sampled round gobies ( $n=138$ ; range: 42-151 mm TL),  $3.42 \pm 0.053$  KJ/g wet mass for the sizes used in the experiment ( $n=65$ ; 45-87 mm TL), and  $3.50 \pm 0.045$  KJ/g wet mass for a size range that likely could be eaten by adult smallmouth bass ( $n=98$ ; 42-100 mm TL).

Energy density of round gobies increased with body size. Whereas energy density increased in a linear fashion with round goby total length (Figure 8A), it increased in a nonlinear fashion with wet mass according to the equation:

$$ED = 2.89 \cdot (\text{wet mass})^{0.104} \quad (1)$$

where ED is energy density in KJ/g wet mass, and wet mass is measured in g ( $r^2=0.36$ ). In addition, the dry:wet mass ratio appeared to be an adequate predictor of round goby energy density (Figure 8B). No sex-specific differences in energy density were evident; however, large individuals ( $>21$  g or 112 mm TL) were exclusively male.

## DISCUSSION

Our laboratory and field studies quantified increasing preference for and importance of hyper-abundant, calorie-poor round gobies in diets of Lake Erie smallmouth bass, relative to historical prey. When presented equal ratios of round gobies,

emerald shiners, and crayfish, smallmouth bass in the laboratory spent more active time following, pursuing, and attacking both fish species than crayfish. However, when attacked, the longer flight distance of emerald shiners afforded them more protection from predation than round gobies. This was reinforced by smallmouth bass field diet data, in which round gobies increased through time and were more prevalent than emerald shiners or crayfish.

Round goby are important prey for native smallmouth bass. They can occur at high densities (typically up to 9 fish/m<sup>2</sup>), but sometimes reach extremely high densities (>100/m<sup>2</sup>; Corkum et al. 1998; Ray and Corkum 2001). As a result of their high densities, round gobies can compete with, and reduce, densities of other small, benthic fishes, such as mottled sculpin *Cottus bairdi* (Janssen and Jude 2001). As a result, encounter rates between smallmouth bass and round gobies are probably much higher than for other prey fishes. Further, round gobies are soft-rayed, have shallow body depth, spawn early, and produce multiple cohorts through summer (Charlebois et al. 1997). Thus, round gobies supply abundant, small prey through the growing season of nearly all smallmouth bass life stages.

Round goby energy density (3.65 KJ/g wet mass) was intermediate between prey fish and macroinvertebrate prey common to Lake Erie. Round goby energy density was slightly higher than crayfish (3.60 KJ/g wet mass, *Procambarus* sp., Eggleton and Schramm 2002; 3.12 KJ/g wet mass, *O. virilis*; Kelso 1973). However, if measured on a dry-mass basis, the differences likely would be greater. Round goby energy density fell well below other Lake Erie prey fishes, including yellow perch (*Perca flavescens*, 4.66 KJ/g wet mass, 97-204 mm TL, Bryan et al. 1996), emerald shiner (5.14 KJ/g wet mass,

49-88 mm, Bryan et al. 1996), rainbow smelt (*Osmerus mordax*, (5.41 KJ/g wet mass, 75-177; Bryan et al. 1996), white bass (*Morone chrysops*, 3.83 KJ/g wet mass, 44-77 mm SL; Wissing 1974; 5.46 KJ/g wet mass, 80-150 mm TL, Eggleton and Schramm 2002), and gizzard shad (*Dorosoma cepedianum*; 5.11 and 6.74 KJ/g wet mass, 99-272 mm TL, Miranda and Muncy 1989; 5.925 KJ/g wet mass, 20-200 mm TL, Eggleton and Schramm 2002).

Despite their modest energy density, round goby can be energetically profitable. For young-of-year smallmouth bass, round goby energy density is much higher than invertebrate prey (Cummins and Wuychuck 1971). Indeed, by consuming abundant round gobies, young-of-year smallmouth bass begin to eat fish prey earlier in life, generating faster growth rates than historical populations (Steinhart et al. 2004). Also, lower handling time during capture and faster digestive processing can make one prey type more energetically profitable than another, even if their absolute energy densities are the same (Stein 1977; Miranda and Muncy 1989). In this manner, the high encounter rates between adult smallmouth bass and abundant, easily caught round gobies could allow more round gobies to be digested than other calorie-rich prey fishes, likely increasing growth.

Compared with round gobies, crayfish were a minor component of our central basin Lake Erie smallmouth bass diets and were not preferred by experimental smallmouth bass. Of the three experimental prey, smallmouth bass attacked and consumed crayfish least frequently, despite crayfish reacting and fleeing only short distances. Because predators respond to prey activity, moving little and using chelae to ward off predators can make crayfish less susceptible to predation (Stein 1977). Thus,

the combination of low availability (field data) and low capture success (experiment) indicate low importance of crayfish to diets of Lake Erie smallmouth bass.

Emerald shiners are of minor importance to our central basin smallmouth bass diets, relative to round gobies. Emerald shiners are numerous and consistently caught in the trawls. However, compared with benthic round gobies, they are more pelagic-oriented and may not be abundant through the season, particularly from May through August (Trautman 1981; ODOW 2005). As such, low emerald shiner availability (field data), hence low encounter rate, and greater escape ability (experimental data) suggest lower importance of emerald shiners to diets of Lake Erie smallmouth bass, compared with round gobies.

The contribution of round gobies to smallmouth bass diets likely will continue to increase. Even though round goby densities in our central basin sites peaked in 1998, they are increasing at other Lake Erie sites, in all five Great Lakes, and in the Mississippi River basin (Charlebois et al. 1997; Steingraeber 1999; ODOW 2005). In addition, their upstream advance into tributaries likely will change diets of riverine populations of smallmouth bass (Carman et al. 2006). Thus, the inclusion of round gobies into predator diets will affect transfer rates of energy, nutrient, and contaminants throughout and well beyond the Great Lakes Region.

*Potential Experimental Biases*—We chose equal numbers of each prey without habitat to reduce bias toward any one prey. Had we provided benthic habitat (e.g., sand, pebble, cobble, or shelter), benthic-oriented round gobies and crayfish would have been less vulnerable to predation than pelagic-oriented emerald shiners (Stein 1977; Belanger and Corkum 2003), resulting in an inflation of predation rates of benthic prey in our

experiments. Moreover, selecting a size or type of substrate (as in Stein 1997) or complex shelter (as in Belanger and Corkum 2003) could result in differential protection for prey types.

On the contrary, had the predator arena been larger or circular, emerald shiner probably would have benefited more from their superior flight behavior. Average emerald shiner flight distance (179 cm) was longer than the length of the predator arena (140 cm). Further, using only two of each prey type nullified any defensive benefits that emerald shiners realize from schooling (Turesson and Brönmark 2005). So, while having no substrate likely overestimated vulnerability to predation for benthic-oriented prey, other prey-arena attributes probably did the same for emerald shiner. In spite of the limitations of the predator arena, our experimental preferences matched field diet data.

*Community Effects of Round Goby*—Round goby are clearly becoming important prey for fish in Lake Erie, as shown by our field and laboratory study. Benthic-oriented predators in Lake Erie (smallmouth bass and burbot *Lota lota*) quickly increased their consumption of round gobies and now both species acquire about 75% of their diet from round gobies (Johnson et al. 2005). In contrast, benthic yellow perch derive less of their diet from round gobies. About 30% of the diet of Lake Erie yellow perch is round gobies (Johnson et al. 2005) and only 11% of adult yellow perch in southern Lake Michigan contained round gobies (Truemper and Lauer 2005). Pelagic predators, such as walleye *Sander vitreus* and white bass, have little spatial overlap with benthic round gobies and derive less than 10% of their diet from round gobies (Johnson et al. 2005).

Round gobies also are attacked from the land and air. Round gobies now constitute >92% of the prey consumed by the federally threatened Lake Erie Water Snake

(*Nerodia sipedon insularum*), resulting in more rapid growth and larger body size (King et al. 2006) after only 1-2 generations of exposure (8-9 years). Above the waterline in western Lake Ontario, 18% of nests of double-crested cormorant (*Phalacrocorax auritus*) chicks contained regurgitated round gobies, second only to alewife (*Alosa pseudoharengus*) prey (Somers et al. 2003).

Owing to their intermediate position in food webs, round gobies can influence multiple trophic levels simultaneously. In our field study, round goby abundance increased through time in Lake Erie, stabilizing at extremely high biomass among prey fish. Because they consume benthic macroinvertebrates, abundant round gobies compete directly with other mid-trophic-level, benthic fish. For example, round gobies and mottled sculpins overlap spatially (*Cottus bairdi*; French and Jude 2001) and interact aggressively (Dubs and Corkum 1996). Thus, round gobies are thought to have caused localized extinctions of mottled sculpins (Janssen and Jude 2001). Also by selectively eating smaller dreissenid mussels, round gobies can shift mussel size distributions to larger sizes (Barton et al. 2005), potentially affecting algal populations via a trophic cascade. Finally, round gobies can reverse roles and prey upon higher trophic level fish by eating eggs of smallmouth bass (Steinhart et al. 2005), lake trout (*Salvelinus namaycush*; Fitzsimons et al. 2006), and walleye (Roseman et al. 2006).

*Ecosystem Effects of Round Goby*—A body of evidence is growing that discounts simple changes attributable to round goby. Rather, outcomes vary with life stage, habitat, and species. Compared with the historical pathway of piscivorous fish ultimately tracing their energy back to zooplankton and non-dreissenid benthic prey, this newly transplanted

dreissenid-round goby-smallmouth bass pathway appears to add “new” material to upper trophic levels (Bunnell et al. 2005; Johnson et al. 2005).

The ultimate impact of round gobies on predators will depend on both life stage and location. Positive (increased growth of young-of-year smallmouth bass; Steinhart et al. 2004) and negative (egg consumption; Steinhart et al. 2005) outcomes have been documented for early life stages. Conflicting evidence exists for hypothesis of round goby increasing contaminant biomagnification. Some of this uncertainty may be due to differences in predator ingestion of round gobies and the resultant growth rate changes at specific sites. In our view, our findings help unravel these interactions toward better forecasting of growth and contaminant outcomes for native predators as round gobies continue to expand.

Round goby consumption by predators could herald the efficient transfer of benthic energy, nutrients, and contaminants to upper trophic levels. Material, previously inaccessible to the majority of fishes, including age-0 life stages, now becomes available. This has led to hypotheses regarding the round goby-mediated transfer of energy, nutrients, and contaminants in the Great Lakes. Although models have examined the potential for the round goby invasion to affect the fate of PCBs (Morrison et al. 2000, 2002) and phosphorus (Bunnell et al. 2005), field collections surrender variable outcomes. Such variability in trophic transfer can arise from differences in local site contamination, species-specific contaminant uptake and elimination rates, growth dilution, food webs, and prey consumption by predators (Fisher 1995). Examples of organisms at mid-trophic levels influencing PCB concentrations in higher trophic levels include opossum shrimp (*Mysis relicta*), *Diporeia* spp., and alewives (*Alosa pseudoharengus*) altering PCB

concentrations in salmonine predators (Vander Zanden and Rasmussen 1996; Jackson et al. 2001).

Reliance on low-calorie prey could affect PCB concentration in sport fish. Because round gobies are energy-poor prey, compared with historical prey fish, smallmouth bass would need to consume more round goby biomass to maintain growth rates. If PCB retention remains constant, smallmouth bass PCB concentrations potentially could increase, compared with pre-goby times. Thus, a lake site with abundant dreissenids and round gobies and few alternative prey fish or crayfish would yield the highest potential for biomagnification via round gobies. These mechanisms could be tested by comparing PCB residues in round gobies to all other prey fishes, a field study comparing temporal trends in PCB residues and growth rates in smallmouth bass, or an uptake experiment to quantify growth and PCB transfer from round goby prey to predators.

*In Conclusion*—Our experimental and field data both confirmed that round gobies are increasingly important for predator diets, as well as community and ecosystem processes. After only 5 y since their arrival, exotic round gobies have become the most important prey fish in diets of native smallmouth bass in Lake Erie. Their intermediate position completes a transfer chain that potentially can recycle energy, nutrients, and contaminants from sediments back to upper trophic levels. As such, round gobies appear to be significant in that they can increase predator growth rates. However, because calorie-poor round gobies replaced calorie-rich prey in predator diets, this could increase contaminant body residues in smallmouth bass.

Second, with reductions in cultural eutrophication, the importance of round gobies integrating benthic and pelagic food webs likely will increase in the Great Lakes and beyond. Given that round gobies are expanding into the Mississippi River basin (Steingraeber 1999), they likely will have a similar impact on that ecosystem. In recent decades, reductions in excess phosphorus inputs in the Great Lakes have yielded reductions in pelagic productivity and increases in water clarity (Hartig et al. 1991, Ludsin et al. 2001). In such systems, the contribution of benthic primary production to overall system productivity increases relative to other energy sources (Vadeboncoeur et al. 2003). Also, as contaminant inputs decline, changes in mid-trophic-level biota may become more important in determining PCB residues in upper trophic levels than variations in source inputs (Smith 2000). We suggest that the role played by round goby, transferring benthic material to pelagic food webs, will increase through time, as source input of nutrients and contaminants decline. However, as PCBs in aquatic ecosystems decrease through time to virtual elimination (likely on the order of decades), the importance of this role played by round gobies eventually will decrease to levels below background “noise”. Until then, however, monitoring of round goby appears to be a vital component to predicting biomass and contaminant variations in upper trophic levels.

Finally, round gobies connect a miniature version of the Ponto-Caspian benthic food webs to upper trophic levels. Shortly after invasion by zebra (1988) and quagga mussels (1989) into the Great Lakes, their presence appears to have facilitated further colonization of other Ponto-Caspian confederates (Ricciardi 2001; Vanderploeg et al. 2002), including round goby in 1990 (Jude et al. 1992) and the benthic amphipod *Echinogammarus ischnus* in 1995 (Witt et al. 1997). Similar to facilitation during

colonization, the outcomes from exotic food webs could exceed that of its exotic species components. Studies and monitoring should track invasions in light of synergy among transplanted exotic food chains as these organisms spread outside the Great Lakes basin.

Figure 5. Proportion of time spent in predatory behaviors by smallmouth bass fed round gobies (goby), emerald shiner (shiner), and crayfish (crayfish) during 30-min experiments. Panel A: percent of active predatory time spent observing prey. Panel B: percent of active predatory time spent following prey. Panel C: percent of active predatory time spent pursuing prey. Panel D: percent of active predatory time spent for attack and capture. Panel E: rate of attacks. Panel F: capture efficiency. Panel G: proportion of each prey type eaten. Panel H: percent of active predatory time spent for digestive pause. Different letters within a panel denote different values (one-way ANOVA, Student-Newman-Keuls post-hoc test,  $P < 0.05$ ). Error bars represent  $\pm 1$  standard error.

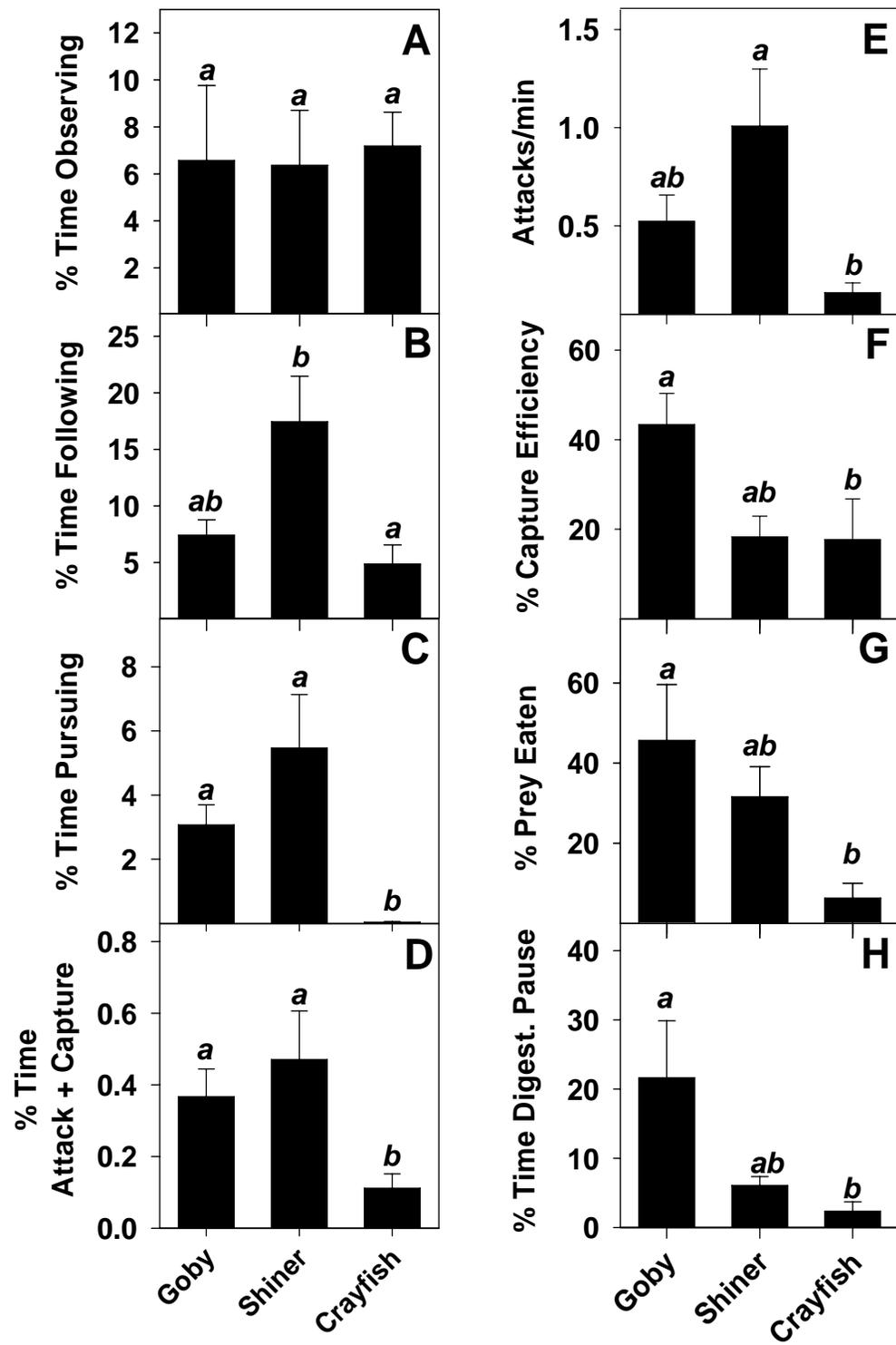


Figure 5.

Figure 6. Prey defensive behaviors that influenced prey vulnerability to predation by smallmouth bass during 30-min experiments. Panel A: mean distance between each prey type and the predator during the trial. Panel B: smallest distance between predator and prey to elicit a defensive response from prey. Panel C: prey fleeing distance from the predator. Different letters within a panel denote different values (one-way ANOVA, Student-Newman-Keuls post-hoc test,  $P < 0.05$ ). Error bars represent  $\pm 1$  standard error.

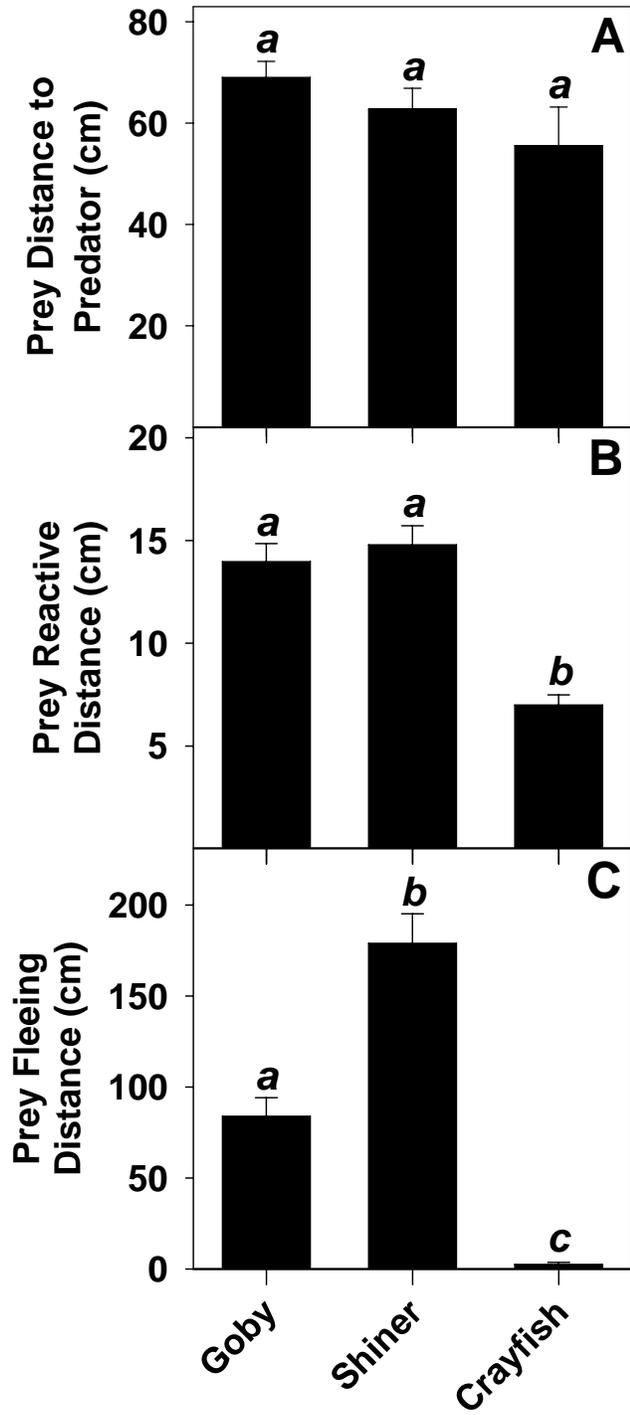


Figure 6.

Figure 7. Results from central basin Lake Erie trawling during 1994 through 2005.

Panel A: mean round goby density ( $\pm 1$  SE standard error) at three central basin Lake

Erie sites with abundant smallmouth bass densities (Lorain, Ashtabula, and Perry). Panel

B: Percent dry mass contribution of prey in smallmouth bass (age 2 and older) diets from

central basin Lake Erie. Parenthetical numbers denote sample sizes for each year.

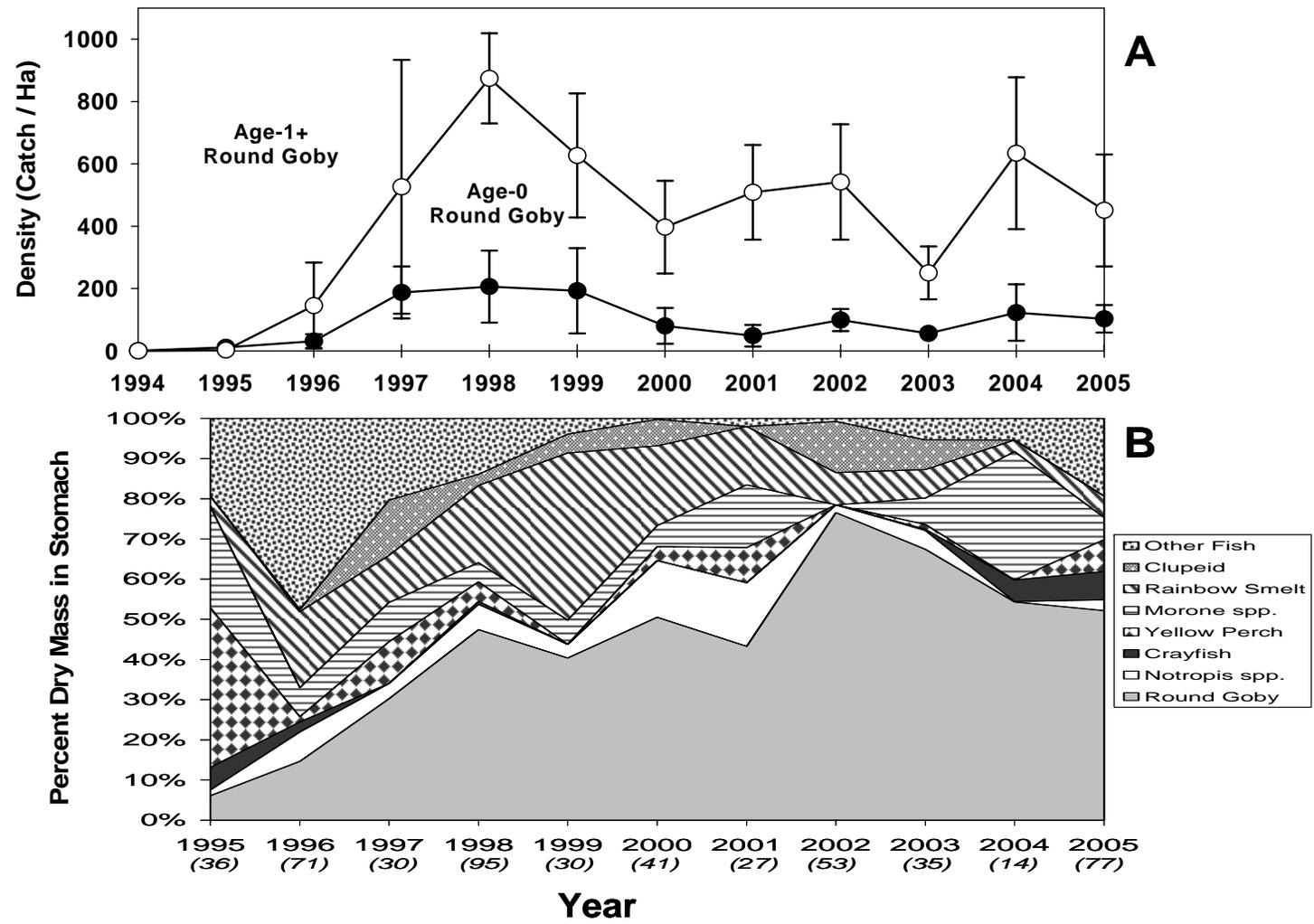


Figure 7.

Figure 8. Energy density (ED) for 138 round gobies from central basin Lake Erie trawl sampling (May to August 1999), as a function of round goby total length (mm TL; Panel A) and dry mass:wet mass ratio (DWR; Panel B). Note that the lengths of optimal round goby prey in the experiment averaged  $64.7 \pm 0.9$  (range: 45-87 mm TL), which corresponds to  $3.42 \pm 0.053$  KJ/g wet mass. Mean values for various prey taxa, common to Lake Erie, are indicated by horizontal lines (see results for sizes of fish).

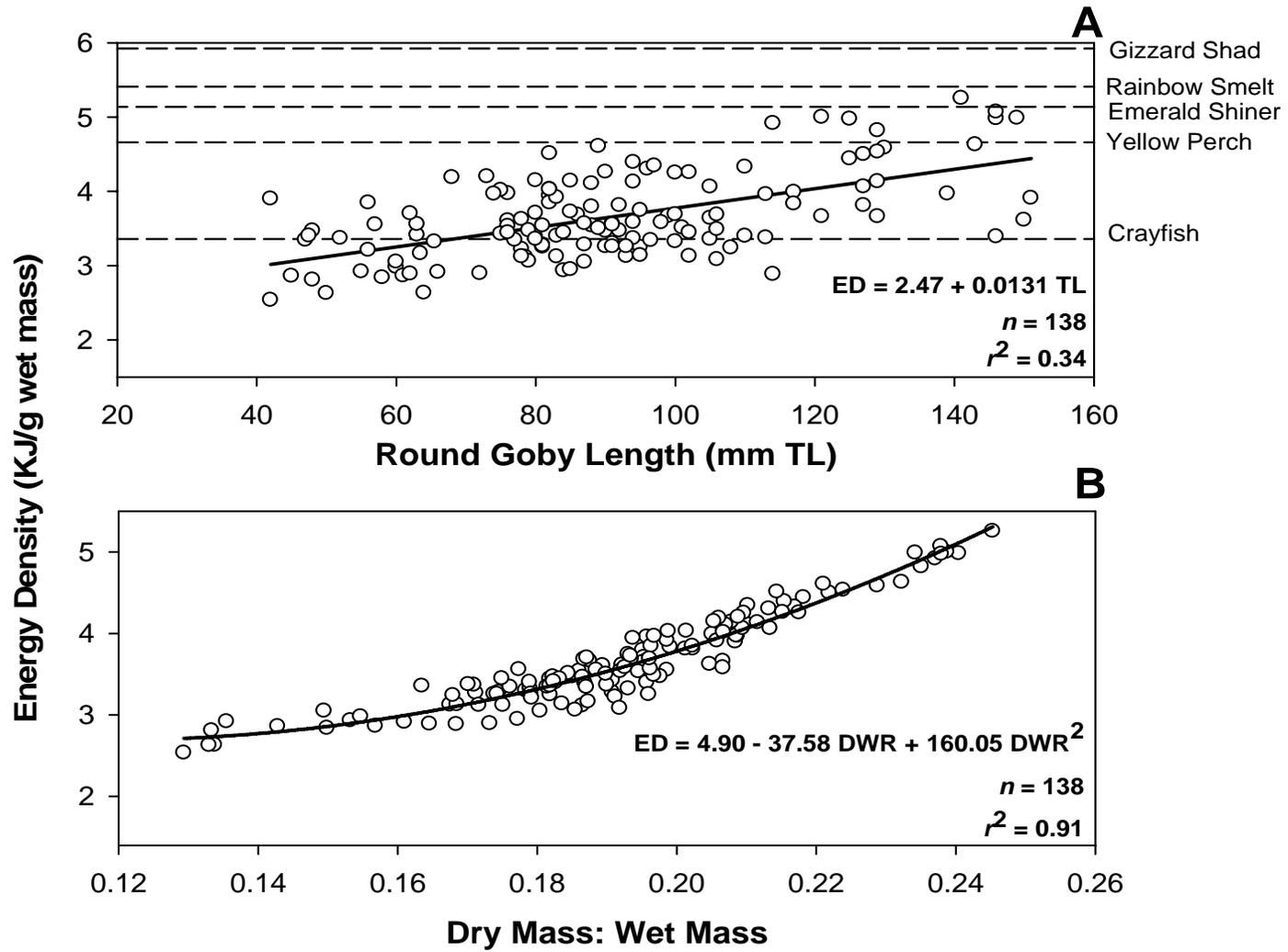


Figure 8.

## CHAPTER 4

### EXOTIC SPECIES INFLUENCE BIOMAGNIFICATION OF POLYCHLORINATED BIPHENYLS IN A GREAT LAKES BENTHIC FOOD WEB

#### ABSTRACT

We demonstrated biomagnification of polychlorinated biphenyls (PCBs) in a Lake Erie food chain by an exotic species component (comprised of round goby and dreissenid mussels) to native terminal predators (smallmouth bass and largemouth bass). In a field study, total PCB concentrations and average chlorination increased with trophic level similarly at four sites in western (Maumee and Sandusky harbors) and central (Grand and Ashtabula harbors) Lake Erie, despite differences in sediment PCB levels, which averaged higher in the central than in the western basin. When normalized to organism lipid content, however, PCB biomagnification was more pronounced in the central than the western basin. For all study species, mean biota-sediment-accumulation factors for dominant PCB congeners increased with hydrophobicity until a log  $K_{ow}$  value around 7.6, and then declined. In contrast, as hydrophobicity increased, mean trophic

transfer factors of dominant congeners increased in round gobies, remained constant in smallmouth bass, and decreased in largemouth bass. The largemouth bass pattern could be a result of their habitat, which likely increased exposure to PCB-laden sediments and decreased predation on round gobies. Historical data (1990-2005), including pre- and post-round goby incorporation into the Lake Erie food web supported this interpretation. Benthic piscivores and molluscivores that consumed exotic species had increasing Arochlor 1260 residues through time, whereas pelagic piscivores and benthic omnivores did not. The degree to which this exotic food-chain affected trophic transfer of PCBs from sediments to piscivores appeared to vary among species, but was consistent across different sizes and life stages, locations, and through time. As nutrient and contaminant inputs into Lake Erie continue to decline, we expect that the importance of this transfer pathway will increase, explaining variation in upper trophic levels.

## **INTRODUCTION**

Exotic species affect the Laurentian Great Lakes ecosystem. In the past two centuries, countless organisms have been introduced by intentional stocking, aquaculture, and ballast water discharge, yielding over 140 established exotic species (Mills et al. 1993). Once established, abundant exotic species affect native flora and fauna directly, via competition and predation, or indirectly, by altering the transfer of energy and contaminants in food webs (Elton 1958). Owing to continued shipping activity and facilitation between established exotic species and recent arrivals, the establishment rate

of exotic species in the Great Lakes may hasten (Ricciardi 2001, 2006). Thus, miniature versions of foreign food webs continue to become transplanted in the Great Lakes.

The establishment of Ponto-Caspian exotic species has irreversibly changed the Great Lakes ecosystem. In the mid-1980s, zebra mussels (*Dreissena polymorpha*) and quagga mussels (*D. bugensis*) were accidentally introduced via ship ballast and spread rapidly in the Great Lakes and Mississippi River basins (Mills et al. 1993). At high densities, filter-feeding dreissenid mussels compete with fish for plankton and re-direct energy and contaminants from the pelagic to the benthic food web (Dobson and Mackie 1998). Although few organisms were initially thought to be able to consume the unpalatable shells of dreissenid mussels (French 1993), recent evidence dispels the notion that they are simply a food web “dead-end”. Adult lake whitefish *Coregonus clupeaformis*, yellow perch *Perca flavescens*, and freshwater drum *Aplodinotus grunniens* feed heavily on dreissenid mussels at times (French 1993; Pothoven and Nalepa 2006). In addition, diving ducks consume large amounts of dreissenid mussels during migration (Mazak et al. 1997).

Recently established round gobies *Neogobius melanostomus* interact with dreissenid mussels and likely influence higher trophic levels. Within 5 years since their discovery in 1990, Ponto-Caspian round gobies were captured in all five Great Lakes (Charlebois et al. 1997) and the upper Mississippi River basin (Steingraeber 1999), re-tracing vector and establishment paths of dreissenid mussels. Because round gobies reach high densities (Ray and Corkum 2001) and consume dreissenid mussels as primary prey in their native range (Charlebois et al. 1997), they make energy and contaminants

(acquired from dreissenid mussel tissue) available for dietary transfer. Whereas only large fish can feed directly on dreissenid mussels, both juvenile and adult fish can consume round gobies, especially benthic piscivores smallmouth bass *Micropterus dolomieu*, burbot *Lota lota*, and yellow perch (Johnson et al. 2005). Given potential selective contaminant retention and biomagnification, this represents a new pathway linking higher trophic levels to sediment contaminants. Without dreissenid mussels, bioavailability of contaminants sequestered in sediments likely would be low.

In contrast to increasing exotic trends, environmental contaminants in Great Lakes biota appear to be slowing to stable, low levels (Smith 2000). After a ban on polychlorinated biphenyl (PCB) production in 1977, lake-wide mean total PCB concentrations in Lake Erie sediments decreased from 136 ng/g in 1971 to 43 ng/g in 1997 (Painter et al. 2001); yet, higher concentrations still occur in the western basin and the southern portion of the central basin. The relative recalcitrance of hydrophobic PCBs varies with location and food-web structure in Lake Erie. As contaminant inputs decline, biotic interactions become increasingly important in driving fish contaminant residues (Hickey et al. 2006). Many organisms at mid-trophic levels influence PCB concentrations in higher trophic levels, including *Mysis relicta*, *Diporeia* spp., and alewives (*Alosa pseudoharengus*), which serve to alter PCB concentrations in salmonine predators (Vander Zanden and Rasmussen 1996). Basin-specific changes in Lake Erie prey fish affect PCB declines in herring gull *Larus argentatus* eggs (Hebert et al. 2000).

Herein, we quantify the potential for, and implications of, contaminant transfer in this transplanted exotic food chain in Lake Erie. We sampled congener-specific PCB concentrations in sediment and biota in western (Maumee and Sandusky) and central

basin (Grand and Ashtabula) areas of Lake Erie, hypothesizing that variability in PCB residues in biota are, in part, attributable to changes caused by Ponto-Caspian exotic species and that these changes vary with basin. Two of our sites, Maumee and Ashtabula, are Areas of Concern (AOCs), due to industrial pollution, degraded biotic health, habitat modification, and/or runoff from agriculture and landfills (Yang and Baumann 2006; IJC 2003; Breneman et al. 2000). Because pollution levels decrease with distance from harbors (Carr and Hiltunen 1965; Goodnight 1973; Krieger and Ross 1993), we sampled sediments directly inside each harbor and nearby areas outside of harbors. Thus, we assessed biomagnification of PCBs in areas with relatively high sediment PCB concentrations to test predictions that round goby influence on PCB residues in sport fish varies between basins (Morrison et al. 2000, 2002). Although a previous study (Kwon et al. 2006) assessed similar sites during 1996, round gobies were not distributed throughout the lake and abundant in predator diets by then (Johnson et al., 2005; ODOW 2005). However, in 1998 central basin round goby density peaked (ODOW 2005) and round gobies began to contribute > 50% of smallmouth bass diets (Johnson et al. 2006). Thus, we quantified trophic transfer via exotic round gobies and dreissenid mussel after full incorporation of round goby into diets of native piscivores.

## **METHODS**

### **Field Study**

*Collection of Organisms*—We sampled biota from western and central basin sites along the Ohio shore of Lake Erie during July through August 2000. Beginning in the

west, the two western basin sites were Maumee River Harbor (Toledo, OH, USA; 41°42'08"N, 83°27'57"W) and Sandusky River Harbor (Sandusky, OH, USA; 41°29'46"N, 82°45'17"W); the two central basin sites were Grand River Harbor (Fairport, OH, USA; 41°45'53"N, 81°16'31"W) and Ashtabula River Harbor (Ashtabula, OH, USA; 41°55'04"N, 80°47'13"W). At each site, we collected sizes of organisms that could be consumed by the next trophic level for PCB analysis (ODOW 2005). We choose 6 to 12-mm dreissenid mussels, because the maximum size consumed by round gobies was 13 mm (Ghedotti et al. 1995). Given that the percentages of dreissenid mussels in round goby diets increases linearly from 0% to 80% between 40 and 100 mm total length (TL), respectively (Lederer et al. 2006), and round gobies consumed by predators averaged 72±4 mm TL (Belanger and Corkum 2003), we targeted round gobies that were 60 to 120-mm TL. Finally, we targeted 200 to 400-mm TL smallmouth bass and largemouth bass. For dreissenid mussels, we collected rocks by hand in shallow areas near break walls and with an Eckman dredge sampler in deep areas (>2 m). We collected fish by boat-mounted, DC electrofishing near break walls and angling (for additional round gobies). Upon capture, we measured total length (nearest 0.1 mm) and mass (nearest 0.1 g) of each fish, wrapped it in pre-cleaned aluminum foil inside plastic bags, and then transported it to the laboratory on dry ice, where it was stored at -20 °C until analysis.

We collected sediment samples according to standard procedures (OEPA 2001) during May through June 2001. At each site, we sampled locations inside the harbor and nearshore areas adjacent to the harbor. We selected sites at random, but avoided sites that contained >70% sand, yielding sites of 3 – 15 m depth (Appendix I). Using a

stainless-steel Eckman dredge sampler, we collected 4 – 5 grabs of sediment, homogenized sediments using solvent-washed, stainless-steel equipment, packed samples in pre-cleaned amber jars, and then transported them to the laboratory on ice, where they remained at -20 °C, pending analysis.

We analyzed chemical and physical characteristics of sediments. We quantified water content (drying at 100°C to stable mass) in triplicate and grain size in duplicate, according to methods in Folk (1980), estimating percent distribution of sand (50 to <2,000 µm), silt (2 to <50 µm), and clay (<2 µm) via a sieve-pipette procedure using sodium oxalate. To achieve grain-size estimates within 10% between two replicates, seven (16%) samples required a third run, none required a fourth run, and two (4%) had sufficient sample mass for only one run. Total organic carbon was measured for each replicate using a Fisons NA 1500 Elemental Analyzer with acidification to remove carbonates (Penn State Agricultural Analytical Services Lab, University Park, PA).

*Sample Preparation for PCB Analysis for Biota*— We purchased surrogate (PCBs no. 14, 65, and 166; International Union of Pure and Applied Chemistry [IUPAC]) and internal standards (PCBs no. 30, 204) from AccuStandard (New Haven, CT, USA). Each peak was identified by the internal standard method. Our calibration standard was a mixture of Arochlors 1232, 1248, and 1262, as described by Mullin et al. (1984).

We quantified diets, ages, and sizes of organisms before homogenization. After thawing, we excised stomach contents for diet analysis, recording species and TL (nearest 0.1 cm). We then selected fish of similar size for PCB analysis and extracted smallmouth and largemouth bass sagittal otoliths, estimating ages by counting annuli (Hoyer et al. 1985; Heidinger and Clodfelter 1987). We homogenized shucked dreissenid mussel

tissue, as well as whole-body composites of round gobies, largemouth bass, and smallmouth bass. To achieve sufficient mass for analysis, we analyzed composite samples of similar-sized round gobies (2-4 round gobies; 10-15 g samples) and dreissenid mussels (>100 dreissenid mussels; 15-20 g samples). Smallmouth and largemouth bass were analyzed as individual fish (10 g samples).

We quantified total lipid concentrations according to Van Handel (1985), with modifications. After homogenization, we extracted about 0.04 g of tissue (3-4 replicates/fish) in a test tube containing 5 ml of chloroform and methanol (2:1 v:v ratio), sealing each tube for overnight refrigeration. We analyzed lipids in 0.5 ml of the homogenate using the colorimetric method and used these values to lipid-normalize PCB concentrations using direct ratios.

We quantified PCB concentrations for biota according to methods detailed in Dabrowska et al. (2006) and Kwon et al. (2006). We performed extraction, followed by two cleanup steps. We first dehydrated homogenized samples by grinding them with an excess of anhydrous sodium sulfate (40-50 g; Sigma-Aldrich, St. Louis, MO, USA; cleaned by baking at 500°C for 4 h). We loaded samples onto chromatographic columns (2.5 x 60 cm) with 70 ml of dichloromethane and hexane (1:1 v/v) for 12 h. Before extraction, we added surrogate standards (PCB 14, 65, and 166) to all samples and blanks, and then eluted samples with 210 ml of dichloromethane and hexane (1:1 v/v). After concentration in a rotoevaporator, we transferred extracts to Florisil (6 g; 60-100 mesh) and activated silica gel (70-230 mesh) columns for two cleanup steps, both topped with a 3-cm layer of sodium sulfate (to minimize disturbance of the adsorbent and to remove remaining moisture) and eluted with 50 ml of hexane. After cleanup, we re-suspended

samples and added internal standards PCB 30 and 204 to 1 ml (round gobies and dreissenid mussels) or 2 ml (smallmouth bass and largemouth bass) of isooctane.

We identified and quantified PCB congeners on a Hewlett-Packard 5890 Series II gas chromatograph with an electron capture detector and a splitless injection port. We used a fused silica capillary column (J&W DB-5 column; 60 m long, 0.25 mm i.d., 0.25 µm film thickness). Samples were loaded via autosampler and analyzed with Hewlett-Packard Chemstation software. The GC operating conditions were splitless injection; injection temperature 250°C; detector temperature 325°C; initial oven temperature 100°C; first ramp rate 1°C/min to 265°C; second rate ramp 20°C/min to 300; constant head pressure 65 psi; carrier gas H<sub>2</sub>; and makeup gas N<sub>2</sub>.

Quality assurance was achieved by sample replication and procedural blanks in each batch of eight samples, which were prepared and analyzed identically to biotic samples. We evaluated method detection limits with a subset of congeners representing specific homologue groups (replicated seven times in clean fish tissue), yielding method detection limits of 0.02 to 2.05 ng/ml. Reported PCB concentrations were not corrected for recovery. A recovery test using a PCB mixture containing 99 congeners was performed; recovery rates were 75 – 135%. Both PCB standards and isooctane blanks were run routinely to track retention time and clean the column. For duplicate samples, average relative percent differences were <30% for 95% of the PCB peaks and were >50% for 3% of the PCB peaks. For the procedural blanks in each sample batch, responses were generally lower than the respective method detection limits.

*Sample Preparation for PCB Analysis for Sediments*—Sediment PCB concentrations were quantified by AXYS Analytical Laboratory (Sidney, BC, Canada)

using the High Resolution GC/Low Resolution Mass Spectrometry method (AXYS method MLA-007). Briefly, after homogenizing and drying, 10 g of sediments were spiked with isotopically labeled surrogate standards, dried with sodium sulfate, and then Soxhlet extracted with dichloromethane. The extracts were separated on a Florisil column, concentrated, and then received  $^{13}\text{C}$ -labelled internal standards. When necessary, samples were cleaned up on gel permeation and alumina columns to avoid matrix interferences. The extract was analyzed using High Resolution GC/Low Resolution Mass Spectrometry on a GC equipped with a quadrupole mass spectrometer with a J&W DB-5 column (60 m long, 0.25 mm i.d., 0.10  $\mu\text{m}$  film thickness) coupled directly to the MS source, using a splitless/split injection sequence. Each sediment sample batch was run with a concurrent procedural blank, a spiked matrix sample, and a duplicate sample.

Quality acceptance was evaluated for sediment samples. Target concentrations were determined by isotope dilution or internal standard qualification methods using HP PROLAB software. The percent difference between calibration standards was < 20% and the recovery rates ranged 70 to 130%. Detection limits were 0.01 – 0.47 ng/g; procedural blanks generally were below detection limits.

### **Historical Fish Tissue Data**

We used the database of the Ohio Sport Fish Consumption Advisory Program (OEPA 1996) to examine trends in PCB residues in Lake Erie fish during 1990 through 2005. Individual fish or composites (2-5 similar-sized fish) were either skin-on fillets with scales removed (walleye, smallmouth bass, freshwater drum, white bass, and white perch) or skin-off fillets (channel catfish). Lipid content and PCB concentrations were

quantified based on Arochlor values (1016, 1221, 1232, 1242, 1254, and 1260) using OEPA method 590.

We used the following criteria for inclusion: (1) fish were collected in Lake Erie or its harbors, excluding tributaries, (2) at least 3 years of data were available that spanned the time period before (pre-1998) and after round goby incorporation in piscivore diets (post-1997), and (3) measured values exceeded detection limits for at least half of the samples. We included walleye, smallmouth bass, freshwater drum, white bass *Morone chrysops*, white perch *M. americana*, and channel catfish *Ictalurus punctatus*; no other fish met our criteria. Notable exclusions included common carp (criterion 2) and yellow perch (criterion 3). We used only Arochlor 1260 concentrations because all other Arochlors (1016, 1221, 1232, 1242, and 1254) did not meet criterion 3. Because of significant changes in methods, we excluded data prior to 1990. For values below detection limits, we assigned values as half the detection limit.

### **Hypotheses and Statistical Analysis**

We calculated total PCB concentrations as the sum of all individually quantified PCB congeners. We calculated biotic PCB concentrations on a wet-mass and lipid wet-mass basis and sediment PCB concentrations on a wet-mass and carbon-normalized wet-mass basis to facilitate comparisons to other studies and to control bias in lipid levels associated with size, trophic position, and sediment organic content. Unless stated otherwise, all comparisons and reporting were conducted on wet-mass measurements for biota and dry mass measurements for sediment comparisons. Before statistical analysis, we  $\log_{10}$  transformed variables to help normalize data and homogenize variance. Proportional data were arcsine-square-root-transformed, because variances tend to be

associated with the mean for proportional data (Sokal and Rohlf 1995). Using Pearson product-moment correlations ( $\alpha=0.05$ ), we compared total PCBs in organisms to lipid content, as well as total PCBs in sediments to organic carbon, water content, percent silt, and percent clay.

We compared biota and sediments between basins (western [Maumee and Sandusky site mean] or central basin [Grand and Ashtabula site mean]). For biota, we tested differences in lipid and PCB concentrations with species and basin as main effects; for sediment data, we tested differences in carbon and PCB concentrations with basin and harbor location (within the harbor or outside the harbor) as main effects. For both comparisons, we used a two-way analysis of variance ([ANOVA], unbalanced design; general linear model procedure [GLM]; [SAS 9.1; SAS Institute, Cary, NC, USA]). Upon finding significant differences, we used post-hoc Tukey's multiple comparisons for sediment data and Duncan's multiple range tests for biota.

To test for differences in biota, we assumed that organisms fed and remained at each of the sites. We invoked this assumption for both sessile dreissenid mussels and mobile fishes. Round goby are territorial within localized rocky habitats (Charlebois et al. 1997). Compared with the distances between our sites (~50 to 150 km), home ranges are relatively small (1 to 4 km) for field-tracked largemouth bass (Fish and Savitz 1983; Mesing and Wicker 1986) and smallmouth bass (Hubert and Lackey 1980; Cole and Moring 1997) in multiple-season studies. Thus, spatial differences in PCB concentrations in fish reflect local risk to consumers of these fish, including mammalian and avian predators. Species differences in lipids reflect trophic level and potential capacity for storage of hydrophobic PCBs. Sediment concentrations represented the total

PCBs potentially available, whereas dreissenid mussels served as sentinel species of contaminant bioavailability (Cope et al. 1999). Testing for species differences within sites assessed biomagnification as the step-wise increase of lipid-normalized PCB concentration with increasing trophic level (Vander Zanden and Rasmussen 1996). We tested differences in the frequency of recovered round gobies in predator stomachs with Chi-squared analysis.

We compared transfer rates of PCB congeners to hydrophobicity. We calculated trophic transfer factors ( $TTF_{lip}$ ) as the ratio of each PCB congener concentration in the higher trophic level to the lower, using lipid-normalized, wet mass concentration means (Equation 1):

$$TTF_{lip} = C_p / C_d \quad (1)$$

where  $C_p$  is the lipid-normalized, PCB concentration of congener  $x$  (any given PCB congener) in the predator, and  $C_d$  is the lipid-normalized, PCB concentration of congener  $x$  in the prey. We used values for dominant congeners only, defined as congeners that contributed on average >0.5% of the total PCBs in any of sample species for each sampling site. These 51 dominant PCB congeners represented 93.4% of total PCBs of all 93 congeners. Using only the dominant congeners that co-occurred in sediments and biota at each sampling site (31 congeners), we calculated biota-sediment accumulation factors (BSAF) using mean lipid-normalized, wet-mass PCB concentrations for biota and carbon-normalized, dry-mass PCB concentrations for sediment. We assumed that sediment PCB concentrations at our sites did not change between 2000 and 2001. For each PCB congener, we associated values for hydrophobicity (octanol-water partition

coefficient; log  $K_{ow}$ ), homolog groups, and molecular weight (Shiu and MacKay 1986; Hawker and Connell 1988).

## RESULTS

### Field Study

Predator Diets—Round gobies were slightly more prevalent in diets of smallmouth bass than largemouth bass. In total, we sampled 24 smallmouth bass (mean: 232±13 mm TL, range: 141-410 mm TL) and 28 largemouth bass (mean: 310±11 mm TL, range: 133-426 mm TL) for diet analysis, including 14 fish from Put-in-Bay, Ohio in September 2000. Excluding empty stomachs, which were more frequent in largemouth bass than smallmouth bass (Chi-squared analysis:  $\chi^2 = 11.6$ ,  $df=1$ ,  $P < 0.0001$ ), round gobies were marginally more frequent in smallmouth bass (45% of 18) than largemouth bass stomachs (31% of 13; Chi-squared analysis:  $\chi^2 = 3.33$ ,  $df = 1$ ,  $P = 0.068$ ); in addition, we found shiners *Notropis* spp., gizzard shad *Dorosoma cepedianum*, sunfish *Lepomis* spp., yellow perch, and crayfish in diets. Size of consumed round gobies did not differ between predator species ( $t$ -test,  $df = 10$ ,  $t$ -value = -0.52,  $P = 0.64$ ), averaging 62±4 mm TL ( $n=12$ , range: 43-94 mm TL) and 28±4% of predator TL (range: 13-50%).

Organic Enrichment and Total PCBs in Sediments—Western basin (Maumee and Sandusky) sediments were organically enriched relative to the central basin (Grand and Ashtabula), due to highly enriched sediments inside harbor locations in the western basin (two-way ANOVA, basin  $df = 1$ , 20, harbor  $df = 1$ , 20, and site x harbor interaction  $df = 1$ , 20, Figure 9A). Organic carbon content in harbor locations was about twice as high as

locations outside of the harbors in the western basin; however, inside and outside harbor locations did not differ for central basin sites.

Sediment total PCB concentrations at our sites varied, depending on organic enrichment of sediments, as well as harbor location and basin effects. When expressed as total PCB concentration, sediment PCB concentrations averaged higher in the central versus western basin sites, and higher outside versus inside harbors (two-way ANOVA, basin  $df = 1, 20$ , harbor  $df = 1, 20$ , and site x harbor interaction  $df = 1, 20$ ; Figure 9B). These differences were magnified for carbon-normalized PCB concentrations (two-way ANOVA, basin  $df = 1, 20$ , harbor  $df = 1, 20$ , and site x harbor interaction  $df = 1, 20$ ; Figure 9C). In the western basin, total PCB<sub>carbon</sub> concentrations averaged 3.2 times higher at locations outside of harbors versus inside (Figure 9C; Table 2). Sediment PCB concentration was not correlated with organic carbon, water content, percent silt, or percent clay (all  $P > 0.10$ ;  $n = 24$ ).

*Lipids and Total PCBs in Biota*— Sizes of round gobies analyzed for PCBs did not differ among sites (TL ANOVA: degrees of freedom [ $df$ ] = 3, 16,  $P = 0.080$ ). Across all sites, round gobies averaged  $89 \pm 4$  mm TL and  $9.5 \pm 1.2$  g wet mass. Largemouth bass size did not differ among sites (TL ANOVA  $df = 2, 9$ ,  $P = 0.108$ ), averaging  $269 \pm 9$  mm TL and  $303.0 \pm 34.5$  g wet mass. Except for one age-3 fish, all largemouth bass were age 2. Smallmouth bass were collected at all sites except Maumee and did not differ among sites (TL ANOVA  $df = 2, 9$ ,  $P = 0.816$ ), averaging  $259 \pm 8$  mm TL and  $289.8 \pm 27.1$  g wet mass. Eight of the 12 smallmouth bass were age 2 (ages: 1 to 3 years).

Organism lipid level varied with species and basin, revealing trophic level differences (Figure 10A). When pooled across all sites, organism lipid levels generally

increased with trophic level, except that smallmouth bass averaged higher lipids than largemouth bass: dreissenid mussels < round gobies < largemouth bass < smallmouth bass (mean values  $\pm$  SE: 1.5 $\pm$ 0.1, 3.1 $\pm$ 0.4, 4.2 $\pm$ 0.4, and 6.0 $\pm$ 0.6%, respectively). However, this differed between basins. Fishes, excluding round gobies, collected from the central basin averaged higher lipid concentrations with increasing trophic level and were more distinctly separated than western basin fishes (two-way ANOVA; basin  $df$  = 1, 50,  $P$  = 0.0037, species  $df$  = 2, 50,  $P$  < 0.0001, basin x species interaction  $df$  = 3, 50,  $P$  = 0.0048, Figure 10A). Lipids in dreissenid mussels consistently were lower than fishes, whereas round goby lipids in the western basin were similar to other fishes. In the central basin, all species differed (Figure 10A).

Organism total PCB concentrations increased with trophic level. When pooled across all sites, total PCB concentrations increased with trophic level, with largemouth bass averaging higher than smallmouth bass: dreissenid mussels < round gobies < smallmouth bass < largemouth bass (mean values  $\pm$  SE were 34.8 $\pm$ 1.4, 78.1 $\pm$ 5.7, 256.7 $\pm$ 26.1, and 352.3 $\pm$ 26.8 ng/g wet mass). Generally, PCB concentrations increased with trophic level, but PCB concentration was slightly higher in central- versus western-basin organisms (two-way ANOVA; basin  $df$  = 1, 50, species  $df$  = 3, 50, basin x species interaction  $df$  = 3, 50; Figure 10B). A similar step-wise increase was apparent for lipid-normalized PCBs, except dreissenid mussels were similar to round gobies (two-way ANOVA; basin  $df$  = 1, 50, species  $df$  = 3, 50, basin x species interaction  $df$  = 3, 50; Figure 10C).

When biota were considered together, total lipids explained 47% of variation in PCB concentration (Figure 11). This was driven almost entirely by lipid differences

among species. No intra-specific patterns in PCB concentrations occurred with lipids, except that total PCBs in dreissenid mussels increased linearly with lipids ( $r = 0.64$ ,  $P = 0.024$ ,  $n = 12$ ).

*PCB Congener and Homolog Distributions in Biota and Sediment*—Although the magnitude of BSAF values differed between basins, the general patterns with  $\log K_{ow}$  did not. When averaged across all sites, organism BSAFs for total PCBs ranked round gobies = dreissenid mussels < smallmouth bass < largemouth bass (mean values  $\pm$  SE were  $0.5 \pm 0.1$ ,  $0.5 \pm 0.1$ ,  $1.0 \pm 0.4$ , and  $2.3 \pm 0.8$ , respectively). The BSAF values were generally higher in the western basin, especially for top predators, than the central basin (two-way ANOVA; basin  $df = 1$ , 50,  $P < 0.001$ , species  $df = 3$ , 50,  $P < 0.001$ , basin x species interaction  $df = 3$ , 50,  $P = 0.007$ , Table 2, Figure 12A-D). Examining BSAF values for 31 dominant congeners reveals that accumulation of PCB congeners increased until a  $\log K_{ow}$  value around 7.6, then declined afterwards (Figure 12A-D). This pattern was similar for all species, despite differences in the magnitude of BSAF values (Figure 12A-D).

In general,  $\log K_{ow}$  and  $TTF_{lip}$  were negatively correlated in largemouth bass, not correlated in smallmouth bass, and positively correlated in round goby (Figure 13A-F). However, western basin largemouth bass and smallmouth bass had higher  $TTF_{lip}$  values, and round gobies had lower  $TTF_{lip}$  values, than their central basin counterparts. Largemouth bass displayed the greatest difference between basins; those in the western basin displayed high variability in  $TTF_{lip}$  for congeners with  $\log K_{ow} < 6$ , relative to the central basin (Figures 5A and 5D). For smallmouth bass consuming round gobies,  $TTF_{lip}$  was constant as  $\log K_{ow}$  increased and  $\geq 1$  for nearly all congeners, despite higher values

and variability in western basin smallmouth bass (Figure 13B and 13E). Compared between round gobies and their dreissenid prey,  $TTF_{lip}$  was generally higher for central versus western basin round gobies (Figure 13C and 13F);  $TTF_{lip}$  values  $> 1$ , suggesting selective retention, occurred at  $\log K_{ow}$  values  $> 6.5$  in the western and  $> 6.0$  in the central basin for most congeners (Figure 13C and 13F).

Comparing across all sites, degree of chlorination (i.e., average number of carbons with chlorine substitutions) increased from sediments (46.3%), to dreissenid mussels (54.5%), to round gobies (58.1%), to largemouth (56.1%) and smallmouth (58.5%) bass. However, homolog patterns for sediments and largemouth bass differed between sites. High total PCB concentrations in largemouth bass at Maumee and Ashtabula (Table 2; Figure 14) coincided with lower average chlorination compared with those at Sandusky and Grand. Despite these differences, homolog patterns in dreissenid mussels, round goby, and smallmouth bass did not vary greatly.

### **Historical Fish Tissue Data**

Historical trends yielded four different patterns of PCB Arochlor 1260 residues during 1990 through 2005 (Figure 15). First, in walleye and white bass, Arochlor 1260 concentrations did not change greatly over time (Figure 15); the increased lipid-normalized Arochlor 1260 in white bass occurred despite no change in wet-mass values, indicating that reduced lipids drove this trend. Second, in largemouth bass and channel catfish, Arochlor 1260 residues did not change over time (Figure 15). Third, in freshwater drum, only wet-mass Arochlor 1260 and lipid levels increased over time (Figure 15). Fourth, in white perch and smallmouth bass, both wet mass and lipid normalized Arochlor 1260 values increased over time (Figure 15). We excluded two

smallmouth bass (193 and 198 mm) and large channel catfish (698 and 704 mm) to avoid length-bias from these outliers. This had negligible effect on the Arochlor 1260 or lipid residues. If included, values did not differ for smallmouth bass (Arochlor 1260:  $n = 93$ ,  $r = 0.66$ ,  $P < 0.001$ , Arochlor 1260, lipid-basis:  $n = 92$ ,  $r = 0.60$ ,  $P < 0.001$ , percent lipid:  $n = 92$ ,  $r = 0.23$ ,  $P = 0.026$ ) or channel catfish (Arochlor 1260:  $n = 55$ ,  $P = 0.884$ , Arochlor 1260, lipid basis:  $n = 55$ ,  $P = 0.993$ , percent lipid:  $n = 55$ ,  $P = 0.935$ ).

## DISCUSSION

We documented PCB biomagnification in a Lake Erie food chain that contained an exotic species component (round goby and dreissenid mussels) and native terminal predators (smallmouth bass and largemouth bass). This occurred despite differences in sediment PCB concentrations between the central and western basins. However, when normalized to organism lipid content, biomagnification was more pronounced in the central than the western basin.

Selective retention of PCB congeners, compared between prey and sediments, varied with fish species and basin. All fishes displayed a similar curvilinear relationship between hydrophobicity and BSAF, despite higher values in the western than the central basin. In contrast, both species- and basin-species differences were apparent for trophic transfer factor. As hydrophobicity increased, trophic transfer factors declined in largemouth bass, remained constant in smallmouth bass, and increased in round gobies. Given the apparent selective retention of less-chlorinated congeners by largemouth bass, especially in the western basin, we suggest that their habitat preference could place them

in close proximity to PCBs adsorbed to re-suspended sediments relative to other fishes in Lake Erie. Historical field data between 1990 and 2005 supported this assertion that life history attributes can predict PCB residues in fishes. Arochlor 1260 residues increased over time in benthic piscivores (smallmouth bass and white perch) and molluscivores (freshwater drum) that prefer rocky and sandy bottom habitat and consume these exotic species. In addition to largemouth bass, other fishes that did not change in Arochlor 1260 concentrations over time included pelagic piscivores (walleye and white bass) and benthic omnivores (channel catfish), which likely consume few exotic species.

The consistency between our new data, our analysis of historical data, and a previous analysis of data from the very beginning of the round goby invasion (Kwon et al. 2006) is remarkable. The combined data support our hypothesis that this exotic food chain increases biomagnification of PCBs to a benthic piscivore (smallmouth bass) in Lake Erie for multiple sizes and life stages, through time, and across basins. Concentrations of PCBs consistently increased with increasing trophic level, even at body sizes that were scaled down at each trophic level to our piscivores, which are smaller than are typically harvested or sampled for fish consumption advisories (Ohio Sport Fish Consumption Advisory Program). Thus, incorporation of round gobies in predator diets drives increased biomagnification of PCBs for smallmouth bass, both directly (increased trophic transfer) and indirectly (earlier transition to piscivory). This warrants continued and careful monitoring to provide information for anglers to make educated decisions (see below for consumption guidelines).

*Organic Enrichment and Total PCBs in Sediments*—Our sediment PCB concentrations fall in the lower range of values in a recent lake-wide survey of Lake Erie

(Painter et al. 2001; Marvin et al. 2004). In that survey, the lakewide average declined from 136 ng/g in 1971 to 43 ng/g in 1997. If we compared our total PCB concentration with the 1997 total PCB lakewide average, we would find that 23 of 24 of our sites exceeded that value. However, direct comparison may be inappropriate, given analytical differences and co-eluting congeners. In fact, the 24 PCB congeners in that survey represent only 43.1% (range: 38.6 - 46.5%) of our total PCB concentrations. If we reconstruct estimates to match those 24 PCB congeners, our samples averaged  $34.6 \pm 4.2$  ng/g dry mass (11.0 - 103.1). As a consequence, only five of our central basin sites exceeded the 1997 average (located at the Ashtabula and Grand sites).

Sediment PCB concentrations suggest that harmful effects still are likely. A consensus-based threshold effect concentration of 59.8 ng/g dry mass has been established; above this value, harmful effects are likely to be observed in benthic organisms (MacDonald et al. 2000). Sixteen of our 24 samples exceeded this threshold, as did the mean values for inside and outside Ashtabula Harbor and outside Grand River Harbor. If we use the more conservative Canadian sediment quality guideline of 34.1 ng/g dry mass (cited in Marvin et al. 2004), all but two of our samples exceed this threshold.

Profiles of PCB congeners in sediments may derive from degradation and proximity to industry. During 1957 through 1977, most (52%) domestic PCB production was the Arochlor 1242 mixture (Brown 1994). Our sediment had chlorination (46.3%) elevated beyond Arochlor 1242, which averages only 33.6%, perhaps due to selective adsorption of PCBs to sediments and biodegradation. Compared with PCB congeners with high chlorine content, lightly chlorinated congeners (<5 chlorines) are more volatile

and water soluble (Shiu and MacKay 1986) and are selectively biodegraded by aerobic bacteria (Harkness 1993). Harbor locations at the two AOCs, Maumee and Ashtabula, had high sediment concentrations with low mean chlorination, suggesting close proximity to industrial activities or recent inputs. Short-term changes in sediment contamination are not apparent. Our sediment PCB concentrations in Ashtabula Harbor were similar to a previous study of Ashtabula harbor (1993-1995), where six samples averaged 93.5 ng/g dry mass (52-190 ng/g; Pickard et al. 2001).

Our sites are likely influenced by inputs from both local and distant sources. Agriculture-dominated watersheds in the western basin coincided with higher organic enrichment in harbors, compared with central basin watersheds that were a mixture of urban and industrial land uses (Myers et al. 2000). The relatively high PCB concentration in outside central basin harbors could ultimately be from the Detroit River. The Detroit River is the largest source of water and contaminants to Lake Erie and still contains sediment sites that average 112 (Metcalf et al. 2000) to 4,500 ng/g dry mass PCBs in sediments (Drouillard et al. 2006). Of the sediment-bound pollutants from the Detroit River, about 73% accumulate in the shallow western basin with about 20% accumulating in the central basin (Carter and Hites 1992).

Areas in the current path of the Detroit River outflow can be highly contaminated. For example, sediments near Middle Sister Island in western basin Lake Erie averaged  $1,990 \pm 125$  ng/g dry mass in 1997 (Gewurtz et al. 2000). Prevailing currents carry Detroit River sediments eastward between the Bass Islands and Pelee Island, forming a counter-clockwise gyre in the central basin (Beletsky et al. 1999). This could explain the high sediment PCB concentrations outside of the central basin harbors. In contrast, locations

outside of harbors in the western basin would be less exposed to these currents, explaining their similarity between inside and outside harbor locations.

Different PCB sources may explain the lack of positive correlation between sediment PCB concentration and organic carbon, which has been found in many sediment surveys (Burgess et al. 2001; Pickard et al. 2001; Ghosh et al. 2003; but see Josefsson et al. 2006). Detroit River sediments likely elevated PCB concentrations outside central basin harbors, where sediment organic carbon was moderate. In western basin harbors, where sediment organic carbon was high, those watersheds were dominated by agriculture, compared with the more industrial watersheds of the central basin (Myers et al. 2000).

*Lipids and Total PCBs in Biota*—Compared with sediment PCB congener profiles, dreissenid mussels had higher average chlorination at all sites. Examining BSAF values reveals that accumulation of PCB congeners increased until a log  $K_{ow}$  value around 7.6 (PCB 196+203), then declined afterwards, yielding higher chlorination in tissue versus sediments. A similar parabolic curve was found by Gewurtz et al. (2000), but with higher BSAF values and a slightly lower peak log  $K_{ow}$  value around 7.1 (Gewurtz et al. 2000). Our BSAF values for dreissenid mussels (0.5 to 1.5) at Ashtabula match the range for benthic oligochaetes *Lumbriculus variegates* exposed to Ashtabula sediments, which ranged from 0.27 to 1.69 (Pickard et al. 2001). These PCB residues in dreissenid mussels represent a distinct transfer pathway to upper trophic levels, even without round goby consumption of dreissenid mussels. Direct consumption by adult lake whitefish, yellow perch, and freshwater drum (Pothoven and Nalepa 2006) and diving ducks (Mazak et al. 1997) can complete this transfer pathway.

Our mean PCB concentrations in dreissenid mussels (31 to 41 ng/g wet mass) were low relative to other Great Lake samples collected from more polluted sites. During 1998-1999, mean PCB concentrations in dreissenid mussels from Michigan AOC tributaries ranged 31 - 2,920 ng/g wet mass (Hanari et al. 2004). Dreissenid mussels in the Detroit River averaged PCB concentrations of 767 ng/g lipid at a reference site and 15,103 ng/g lipid at an impacted site (Metcalf et al. 1997). At open-water western basin sites downstream of the Detroit River, values averaged  $6,530 \pm 221$  ng/g lipid during 1997 (Gewurtz et al. 2000).

Our PCB residues in fish were lower than other studies in contaminated tributaries and the central basin of Lake Erie. Whereas mean total PCBs in our round gobies ranged 60 - 87 ng/g wet mass, mean PCB concentrations in round gobies from Michigan tributaries ranged 81 - 4,710 ng/g wet mass 1990 and 1999 (Hanari et al. 2004). Also, our PCB concentrations were low compared with a past study that included the Ashtabula and Grand sites, as well as a site near Sandusky in 1996 (Kwon et al. 2006). In that study, mean values for dreissenid mussels were 29 - 97 ng/g wet mass, round gobies were 118 - 256 ng/g wet mass, and smallmouth bass were 1,091 to 1,520 ng/g wet mass. Although the exact sizes are unavailable for those fish, we attribute the lower values in our study to smaller organisms sampled in our study (their protocol targeted larger organisms) and the likelihood for lower lipids in our organisms. Our organisms were collected during July through August, while Kwon et al. (2006) sampled during September. Round gobies, smallmouth bass, and largemouth bass spawn during late May through early July (Scott and Crossman 1998; MacInnis and Corkum 2000), while dreissenid mussels spawn during May and June (Claxton and Mackie 1998). Because we sampled closer to

spawning than Kwon et al. (2006), low lipid concentration in post-spawning organisms likely resulted in low PCB concentrations. For example, bioconcentration factors are higher and uptake kinetics are faster for hexachlorobiphenyls in high lipid, pre-spawning dreissenid mussels than low lipid, post-spawning individuals (Bruner et al. 1994a). Thus, the difference in PCB concentrations is not surprising. What surprises us is the consistent 2 to 5-fold increases in PCB concentration and 1 to 4-fold increases in lipid-normalized PCBs with increasing trophic level, even when compared with our two predator fishes that were smaller than are typically harvested or sampled for fish consumption advisories (e.g., the Ohio Sport Fish Consumption Advisory Program).

Incorporation of round gobies in predator diets results in biomagnification, even at small sizes. One reason for this is that round gobies provide abundant prey for all list stages of smallmouth bass, including age-0 fish (Steinhart et al. 2004). In western Lake Erie, one outcome of the round goby establishment is earlier transition to piscivory for age-0 smallmouth bass (Steinhart et al. 2004). Given that fish, on average, have higher PCB burdens than invertebrates, consuming round gobies at small sizes could both directly and indirectly result in biomagnification of PCBs for smallmouth bass.

The PCB concentrations in our smallmouth bass and largemouth bass were well below federal consumption guidelines, but merit continued concern. Although the average size of fish sampled in our study fell below the minimum harvest size (356 mm for smallmouth and largemouth in Ohio and Michigan waters), our size range overlapped the lower range of harvested fish. Our highest PCB concentration of 497 ng/g wet mass, a largemouth bass from Ashtabula, was well below the fish consumption tolerance level of 2,000 ng/g for the edible portion, excluding head, scales, viscera, and bones (Title 21

of the U.S. Code of Federal Regulations, Section 109.30). Larger fish, however, would contain higher PCB concentrations; thus, our values should be considered conservative. The historical data illustrate this point quite nicely, as they sample fillets from harvest-sized smallmouth bass (mean: 355 mm, range: 266-440 mm). If we compare the grand mean for the years after round goby incorporation into predator diets (1998 and after mean = 214 ng/g Arochlor 1260) to the years before incorporation (before 1998 mean=83 ng/g Arochlor 1260, excluding 1996 when only one smallmouth bass was sampled), we find nearly a three-fold increase in Arochlor 1260 concentrations. Trends in Kwon et al. (2006) and the large fish in the historical data mesh with our findings for sub-harvest smallmouth bass to suggest that biomagnification by these exotic species to sport fish warrants continued and careful monitoring to educate consumers of fish in the Great Lakes.

Congener-Specific Patterns in PCBs—The pattern for trophic transfer as  $\log K_{ow}$  increased (hence, selective retention) differed among fish species. Our trends for round gobies and smallmouth bass were similar to those in Kwon et al. (2006); the high variability  $TTF_{lip}$  for lower-chlorinated congeners in smallmouth bass in Kwon et al. (2006) was not apparent in our data, because we used only dominant congeners. Selective retention of PCB congeners (i.e.,  $TTF_{lip} > 1$ ) occurred at  $\log K_{ow}$  values above 6 for round gobies, resulting in elevated chlorination in round gobies relative to their dreissenid mussel prey. In contrast, nearly all dominant congeners were selectively retained by smallmouth bass feeding on round goby prey, explaining their similar degree of chlorination. This relatively simple partitioning coefficient has been used to predict PCB bioaccumulation. Although assimilation efficiency increases with contaminant

hydrophobicity, it becomes increasingly difficult for higher-molecular-weight congeners to pass through biological membranes (reviewed in Fisher 1995). Thus, a dome-curvilinear relationship is predicted for top piscivores (Thomann 1989). However, departures from this idealized relationship are common, varying with season (LeBlanc et al. 2006), species, and trophic levels (Maruya and Lee 1998; Kwon et al. 2006).

Contrary to expectations, less-chlorinated PCB congeners were selectively retained by largemouth bass. We propose four potential reasons for this pattern: PCB uptake and metabolism, diet, lipid content, and habitat affinity. To our knowledge, no studies directly compare uptake efficiency or metabolism of PCBs between smallmouth bass and largemouth bass. However, at sites in the Hudson River, NY where they co-occur, no consistent differences occurred in PCB residues or endocrine disruption measures (Baldigo et al. 2006). As closely related species, no *a priori* reason exists to suggest that such differences explain our patterns. Although terrestrial prey may contribute more to largemouth bass diets in small lakes (Scott and Crossman 1998), a survey of 16 larger lakes (41 - 809 ha) found diet similarity between species (Olson and Young 2003). Therefore, diet differences likely do not explain species discrepancies.

Differences in organism lipids and fugacity of chemical compounds could prove useful in explaining differences in trophic transfer between basins. Trophic transfer between piscivores and round gobies was higher in the western basin than the central basin. For highly hydrophobic contaminants, such as PCBs, fugacity ( $f$ , the “escaping tendency” of a chemical from its medium) =  $C/Z$ , where  $C$  is the chemical concentration and  $Z$  is the fugacity capacity (Clark et al. 1990). The higher lipid values and lower chlorination of western basin round gobies, compared with central basin round gobies,

may increase  $f$  for western basin round gobies, explaining the high rates of PCB trophic transfer to western basin predators.

Habitat preferences may explain the pattern of PCB residues in largemouth bass. Even though these species often co-occur, especially where we sampled near breakwalls, their habitats seldom overlap (Scott and Crossman 1998). Whereas largemouth bass prefer shallow areas with warm water temperatures, soft bottom substrates, and dense aquatic vegetation, smallmouth bass prefer rocky and sandy substrate and cooler water temperatures (Scott and Crossman 1998). Thus, largemouth bass likely are confined to nearshore areas of Lake Erie, especially to harbor locations with high nutrients that support vegetation and soft-sediment substrates.

Habitat differences also could affect encounter rate with round gobies and exposure to PCB adsorbed to suspended sediments. Smallmouth bass habitat preference overlaps directly round gobies (Ray and Corkum 2001), suggesting high encounter rates between smallmouth bass and round gobies. Second, the habitat preference of largemouth bass places them in closer proximity to contaminated, soft bottom sediments that are subject to frequent wind re-suspension. As a result, bioavailability of PCBs in sediments increases, increasing the likelihood for direct uptake of PCBs from ingested sediments or contaminated invertebrate prey (Morrison et al. 2000). Unfortunately, no smallmouth bass were sampled in Maumee, which would allow direct comparison.

Historical data, 1990 – 2005, support our supposition that habitat preference and consumption of round gobies can explain differences in PCB residues in Lake Erie. Arochlor residues in walleye and white bass did not change during round goby establishment. Both are pelagic piscivores that derive < 10% of their diet from round

gobies (Johnson et al. 2006). Arochlor residues in largemouth bass and channel catfish did not change over time. Although channel catfish are a benthivores, their diet is largely omnivorous (Scott and Crossman 1998), suggesting that exotic species would have little impact on them. Although the lack of change in largemouth bass over time supports our hypothesis, sample sizes were quite low relative to other fishes. However, Arochlor 1260 residues in freshwater drum, smallmouth bass, and white perch increased over time. The increase in Arochlor 1260 residues in freshwater drum was marginal, compared with smallmouth bass and white perch; wet-mass PCBs increased, but lipid-normalized concentrations did not. This marginal increase can be understood, considering that benthic freshwater drum are primarily molluscivores that can readily consume dreissenid mussels at the sizes sampled, in addition to fish (Scott and Crossman; French 1993). The fishes that displayed consistent increases in wet-mass and lipid-normalized Arochlor 1260 residues are most likely to be frequent consumers of round gobies. In fact, smallmouth bass consume up to 75% of their diet from round goby (Johnson et al. 2006). Although white perch are habitat generalists, migrating between deep and shallow water (Scott and Crossman 1998), they probably consume round gobies, given their consumption of large numbers of benthic prey, including fish, fish eggs, amphipods, and mayfly nymphs (Roseman et al. 2006). These findings suggest that diet can influence PCB concentrations in fish.

*Long-term Forecast for PCBs in Great Lakes Biota*—Round gobies in Lake Erie are a new source of energy and contaminants for benthic piscivores. Because dreissenid mussels and round gobies often co-occur at high densities, this transfer pathway exposes upper trophic levels to elevated PCB concentrations via selective retention and

biomagnification. Compared with the historical pathway of piscivorous fish ultimately tracing their energy back to zooplankton and non-dreissenid benthic prey, this newly transplanted dreissenid-round goby-smallmouth bass pathway adds “new” material to upper trophic levels (Johnson et al. 2005).

The effect of round goby on PCB fate is variable. In riverine versions of this dreissenid-round goby-smallmouth bass food chain, Hanari et al. (2004) found no support for biomagnification of PCBs in the Raisin, Saginaw, or St. Clair rivers, Michigan, USA. However, perfluorooctanesulfonate (PFOS) does biomagnify in this food chain at multiple riverine sites in Michigan, USA (Kannan 2005). In contrast, at multiple nearshore sites on the southern shore of Lake Erie, PCB and mercury biomagnification occurs in this transplanted food chain (Kwon et al. 2006; Hogan et al., 2007).

Our study, as well as model projections, can clarify these disparate findings. Biota in areas with less PCB contamination and less re-suspension from sediments ultimately derive a larger fraction of their PCB body burdens from sediments (via dietary transfer) versus direct uptake from water (Morrison et al. 2002). In this context, we were not surprised that biomagnification in the round goby-mediated food chain was documented more clearly in the central basin. In contrast, Hanari et al. (2004) sampled rivers, where contaminated sediments that could easily be re-suspended.

Overall, as inputs of nutrient and contaminants decline, we believe the role of round goby in cycling energy and contaminants will likely increase. As nutrient inputs decrease, the contribution of benthic primary production to overall system productivity increases relative to other energy sources (Vadeboncoeur et al. 2003). Also, as contaminant inputs decline, changes in mid-trophic-level biota may become more

important in determining PCB residues in upper trophic levels than variations in source inputs (Hebert et al. 2000; Smith 2000; Hickey et al. 2006). Owing to a combination of declining inputs of nutrients and contaminants, expansion of this exotic food chain (both spatially and into predator diets), and the persistence of PCBs in sediments, we suggest that the role played by round goby, transferring benthic material to pelagic food webs, not only will increase through time, but also will vary with location and biotic interactions.

Site	Location	Sample	Latitude	Longitude	Depth (m)
Maumee	Inside	1	41° 42.042 N	-83° 27.686 W	3.7
		2	41° 41.926 N	-83° 28.090 W	2.9
		3	41° 42.532 N	-83° 26.145 W	4.7
	Outside	1	41° 42.158 N	-83° 23.637 W	2.3
		2	41° 42.900 N	-83° 23.888 W	2.8
		3	41° 43.410 N	-83° 23.627 W	3.0
Sandusky	Inside	1	41° 27.710 N	-82° 44.365 W	2.4
		2	41° 28.136 N	-82° 45.966 W	2.6
		3	41° 29.351 N	-82° 47.210 W	2.3
	Outside	1	41° 29.120 N	-82° 39.126 W	7.8
		2	41° 28.653 N	-82° 39.100 W	7.7
		3	41° 27.311 N	-82° 37.031 W	6.7
Grand	Inside	1	41° 45.881 N	-81° 16.551 W	5.6
		2	41° 46.010 N	-81° 16.695 W	6.4
		3	41° 45.949 N	-81° 16.905 W	4.6
	Outside	1	41° 48.284 N	-81° 17.525 W	14.8
		2	41° 47.883 N	-81° 16.869 W	13.9
		3	41° 48.165 N	-81° 16.937 W	14.9
Ashtabula	Inside	1	41° 55.061 N	-80° 47.331 W	4.9
		2	41° 54.950 N	-80° 47.041 W	4.3
		3	41° 54.691 N	-80° 47.562 W	5.5
	Outside	1	41° 55.111 N	-80° 48.801 W	12.2
		2	41° 55.781 N	-80° 47.141 W	13.1
		3	41° 55.901 N	-80° 45.701 W	14.3

Table 1. Location and physical characteristics of sediment sampling locations during May and June 2001 at Maumee, Sandusky, Fairport, and Ashtabula harbors, Ohio. Locations were either within the harbor proper (Inside) or adjacent to the harbor (Outside).

	Maumee Harbor		Sandusky Harbor		Grand Harbor		Ashtabula Harbor	
	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside
Total PCB (ng/g wet mass)	37.2 (3.8)	36.1 (13.4)	28.7 (2.8)	34.8 (6.3)	23.0 (7.1)	61.9 (12.9)	47.5 (17.5)	66.3 (25.2)
Total PCB <sub>carbon</sub> (ng/g wet mass)	1,442.7 (109.0)	2,780.5 (1,015.1)	1,027.5 (129.2)	2,371.6 (508.5)	2,078.1 (773.6)	3,083.7 (549.0)	3,220.9 (744.9)	4,916.4 (1,245.0)
Total PCB (ng/g dry mass)	48.3 (8.0)	68.4 (15.4)	40.8 (6.4)	73.0 (11.0)	58.9 (16.3)	106.4 (9.3)	103.9 (32.5)	152.4 (53.9)
Total PCB <sub>carbon</sub> (ng/g dry mass)	1,867.2 (257.2)	5,404.0 (1,749.7)	1,427.5 (56.6)	4,961.0 (922.4)	5,212.6 (1,976.6)	5,369.8 (387.8)	7,149.1 (1,109.1)	11,536.2 (2,026.0)
Chlorination (% dry mass)	44.1	43.9	48.0	48.0	47.0	48.0	44.8	47.0
Carbon (% dry mass)	2.6 (0.1)	1.4 (0.1)	2.9 (0.4)	1.5 (0.1)	1.2 (0.2)	2.0 (0.1)	1.4 (0.2)	1.2 (0.3)
Clay (% dry mass)	55.2 (9.4)	31.0 (12.0)	48.4 (5.7)	28.4 (5.7)	24.1 (2.9)	34.1 (3.2)	30.2 (1.0)	28.8 (7.9)
Silt (% dry mass)	27.3 (12.6)	41.2 (11.6)	34.7 (3.6)	57.1 (9.3)	44.1 (7.3)	49.5 (9.5)	62.0 (1.0)	50.2 (3.7)

Table 2. PCB concentrations and physical characteristics of sediment collected at four Lake Erie sites: (from west to east), Maumee (Maumee R. Harbor), Sandusky (Sandusky R. Harbor), Grand (Grand R. Harbor), and Ashtabula (Ashtabula R. Harbor). All values were the mean of three replicates and parenthetical values are standard error.

Figure 9. Chemical characteristics of sediments collected in 2000 at four sites along the southern shore of Lake Erie, USA. Listed from west to east, the sites are Maumee (Maumee River Harbor), Sandusky (Sandusky River Harbor), Grand (Grand River Harbor), and Ashtabula (Ashtabula River Harbor) and locations were inside the harbor (IN) and nearshore locations outside of the harbor (OUT). Panel A: percent organic carbon on a dry-mass basis. Panel B: mean total PCB concentrations (ng/g dry mass). Panel C: carbon-normalized PCB concentrations (total PCB / [%carbon/100]). Basins or harbor locations that share the same underline did not differ (two-way ANOVA, Tukey's post-hoc test,  $P > 0.05$ ). All values are the mean of 3 replicates. Note y-axis scales for panels B and C are  $\log_{10}$  scale. Error bars represent  $\pm 1$  standard error.

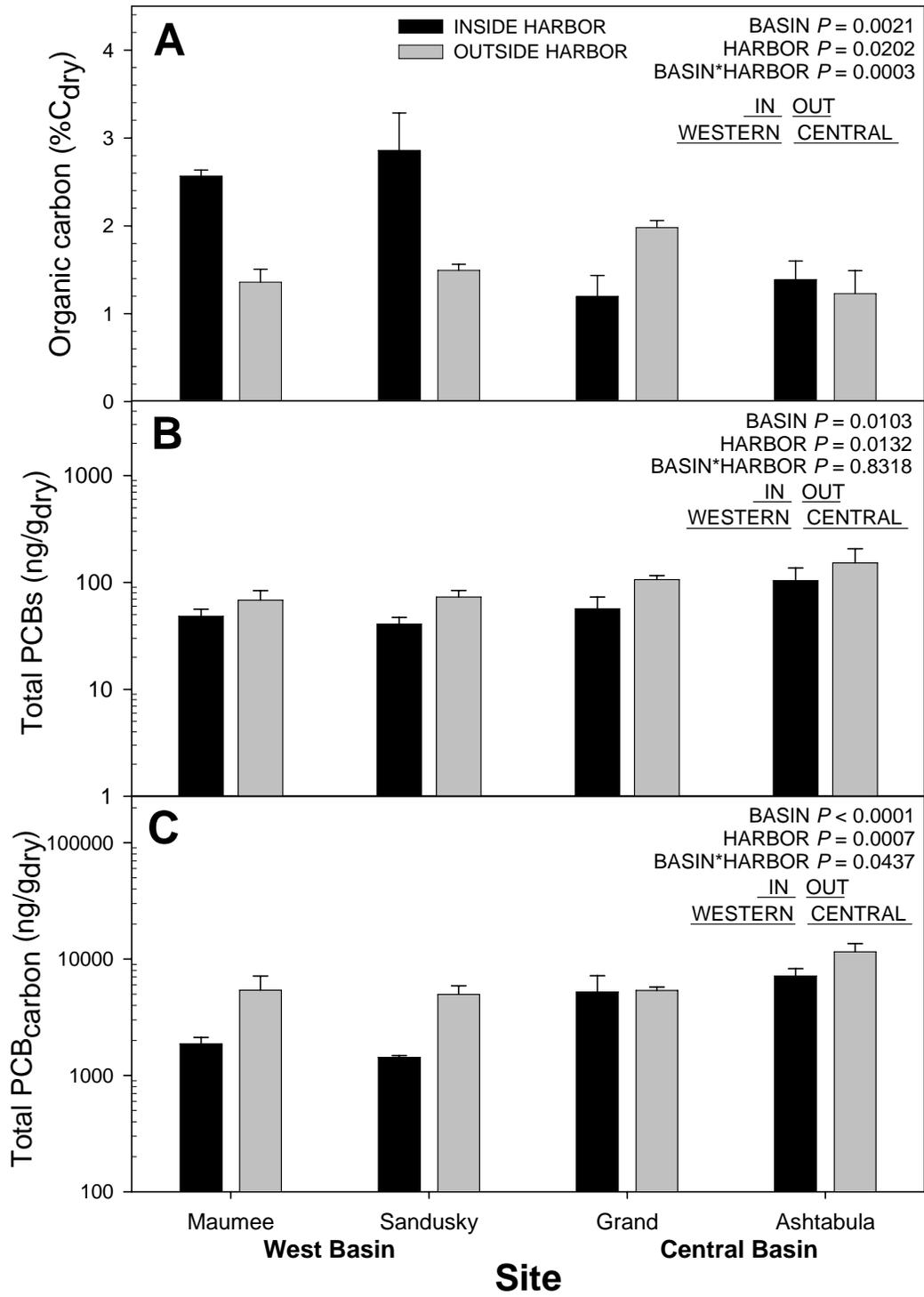


Figure 9.

Figure 10. Lipid and PCB concentrations in organisms collected at four sites during 2001 along the southern shore of Lake Erie, USA. Listed from west to east, the sites were Maumee (Maumee River Harbor), Sandusky (Sandusky River Harbor), Grand (Grand River Harbor), and Ashtabula (Ashtabula River Harbor). Panel A: total lipids (% lipid wet mass). Panel B: total PCB concentration (ng PCB/g wet mass). Panel C: lipid-normalized total PCB (total PCB / [%lipid/100]). Species or basins that share the same underline do not differ (two-way ANOVA, Duncan's multiple range post-hoc test,  $P > 0.05$ ). Error bars represent  $\pm 1$  standard error.

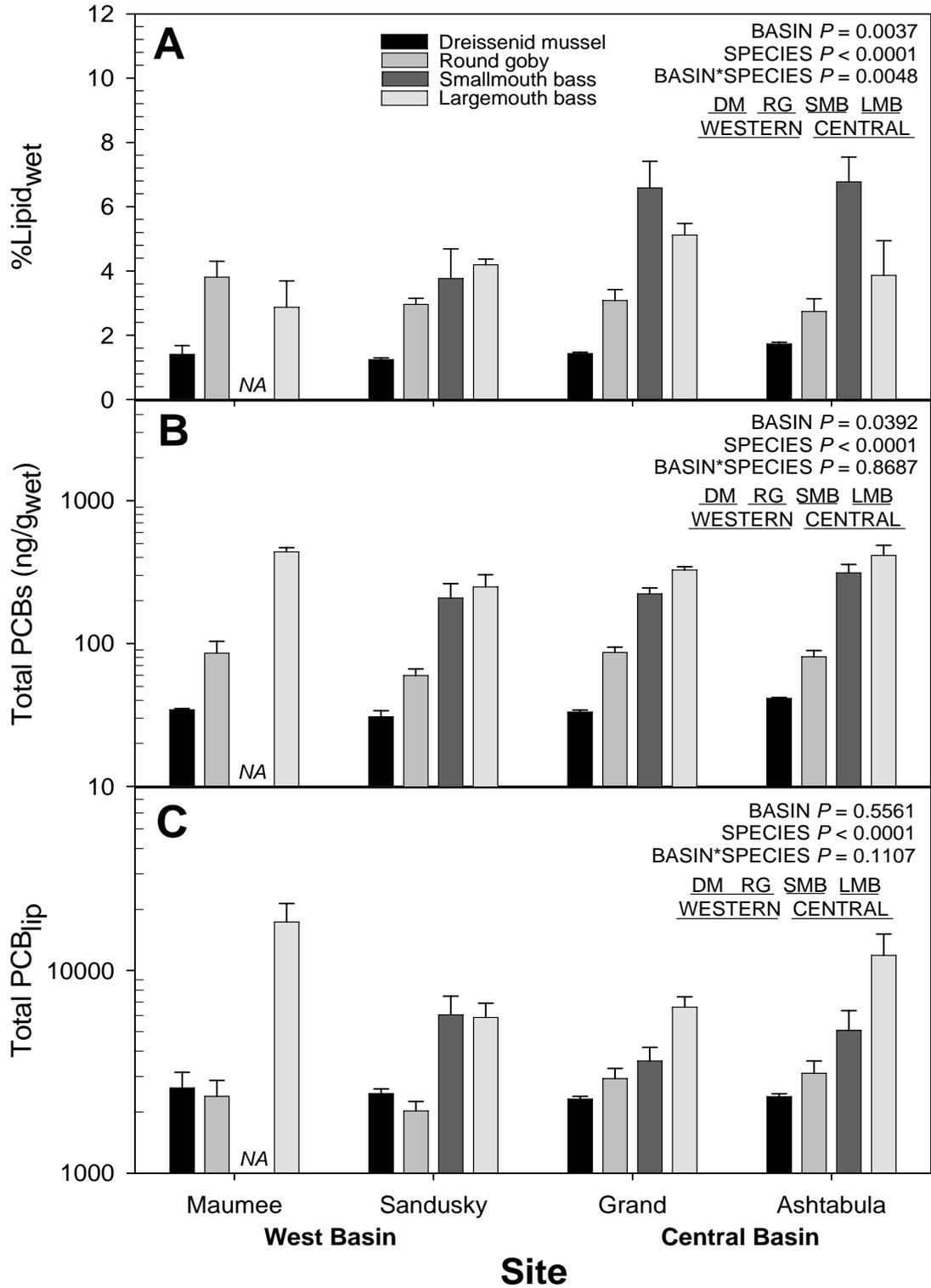


Figure 10.

Figure 11. Pearson product-moment correlation between total lipid content (% wet mass) and PCB concentrations (ng PCB/g wet mass) in dreissenid mussels (DM), round gobies (RG), smallmouth bass (SMB), and largemouth bass (LMB). Organisms were collected in Lake Erie, USA, during 2001. Linear regression used arcsin-square-root transformed total lipid content. All sites were combined.

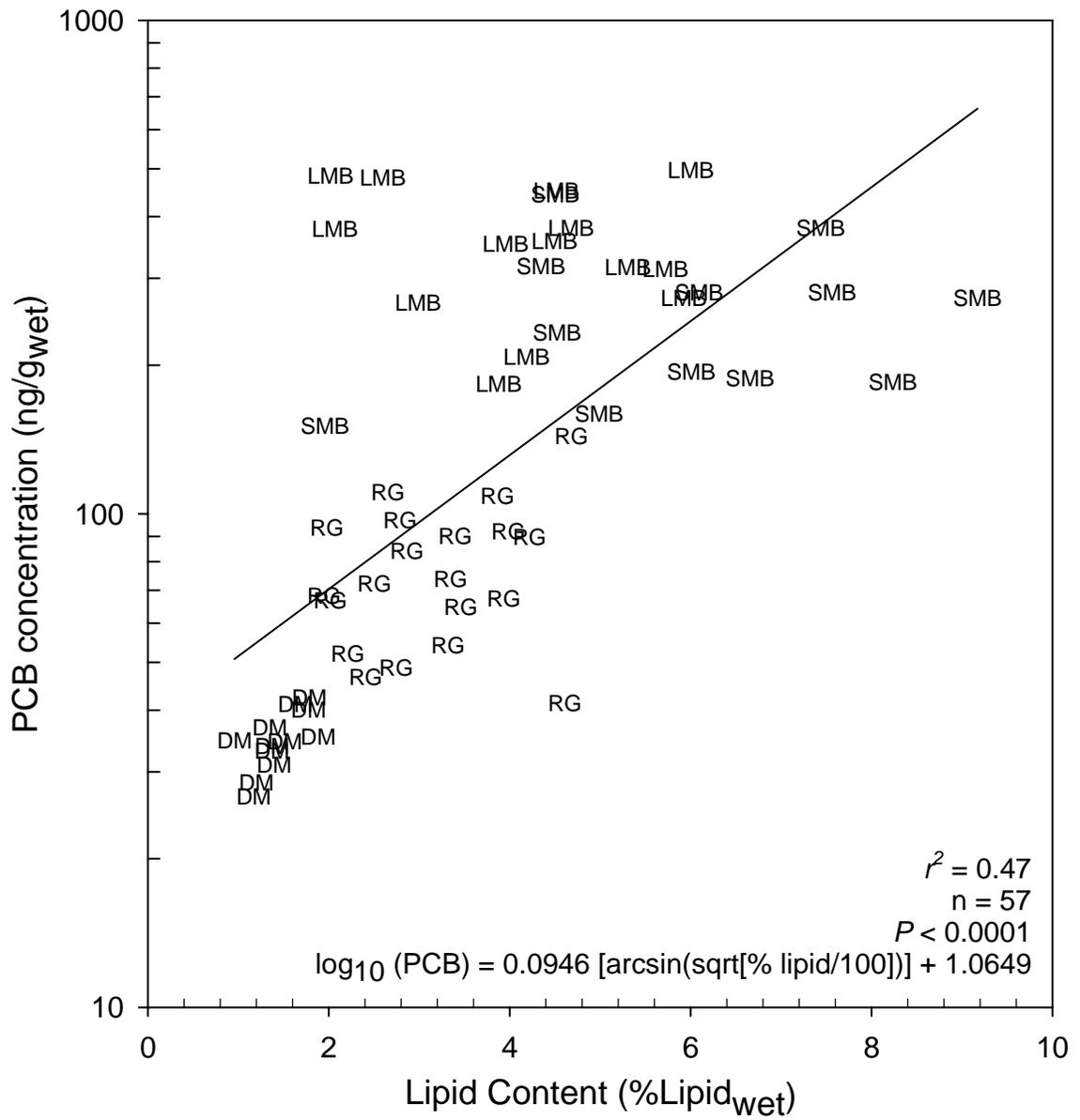


Figure 11.

Figure 12. Relationship between hydrophobicity ( $\log K_{ow}$ ) and mean biota sediment accumulation factor (BSAF) for largemouth bass, smallmouth bass, round gobies, and dreissenid mussels collected in western (Panels A-D) and central basin (Panels E-H) Lake Erie, USA, during 2001. Each data point represents the values for each dominant PCB congener for a given species, averaged first by site, then by basin. Note: smallmouth bass values in the western basin represent only the Sandusky site.

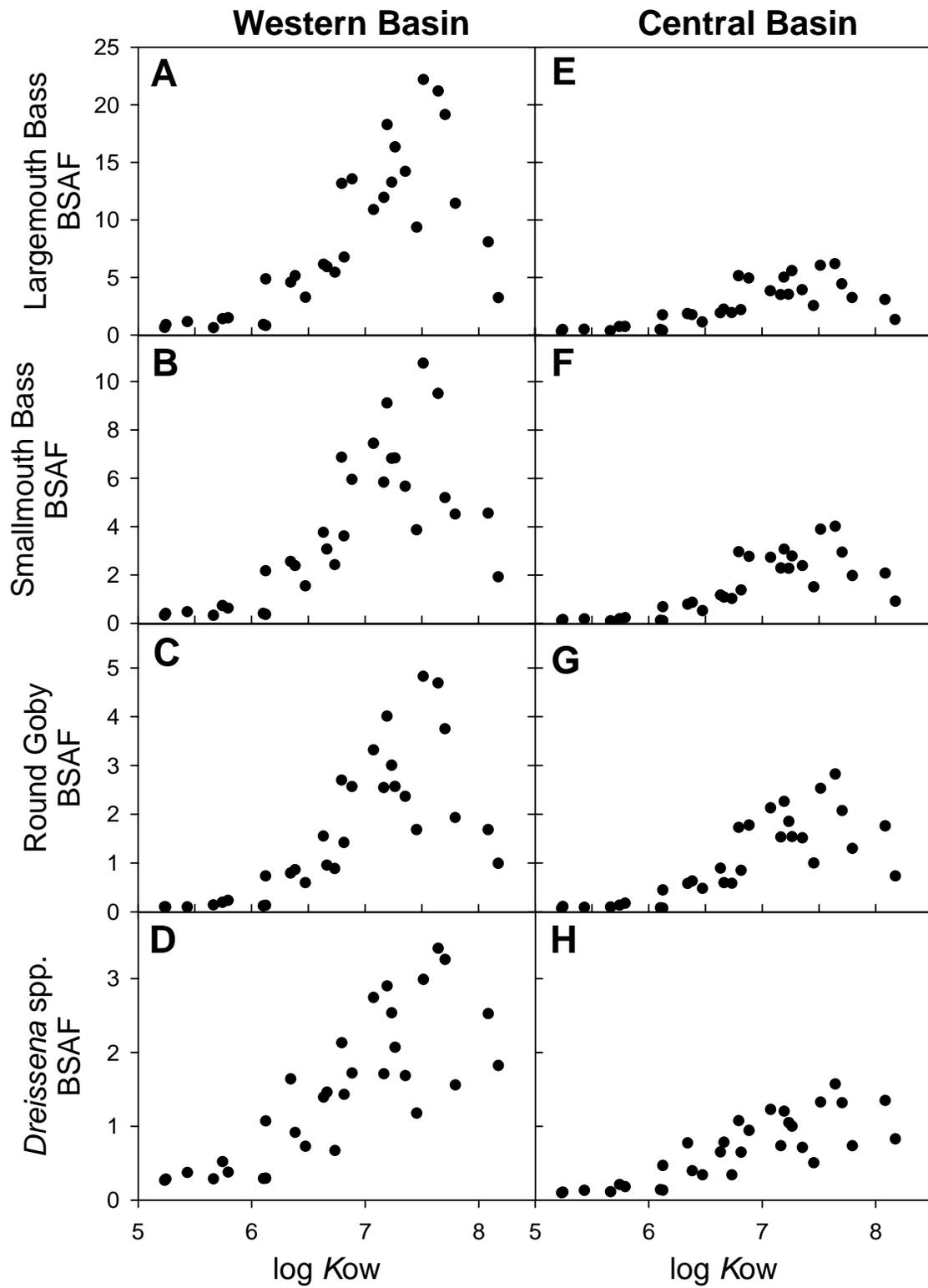


Figure 12.

Figure 13. Relationship between hydrophobicity ( $\log K_{ow}$ ) and mean trophic transfer factor ( $TTF_{lip}$ ) for largemouth bass, smallmouth bass, round gobies, and dreissenid mussels collected in western (Panels A-C) and central basin (Panels D-F) Lake Erie, USA, during 2001. Values above the 1:1 ratio (dashed line) indicate selective retention. Each data point represents the values for each dominant PCB congener for a given species, averaged first by site, then by basin. Note: smallmouth bass values in the western basin represent only the Sandusky site.

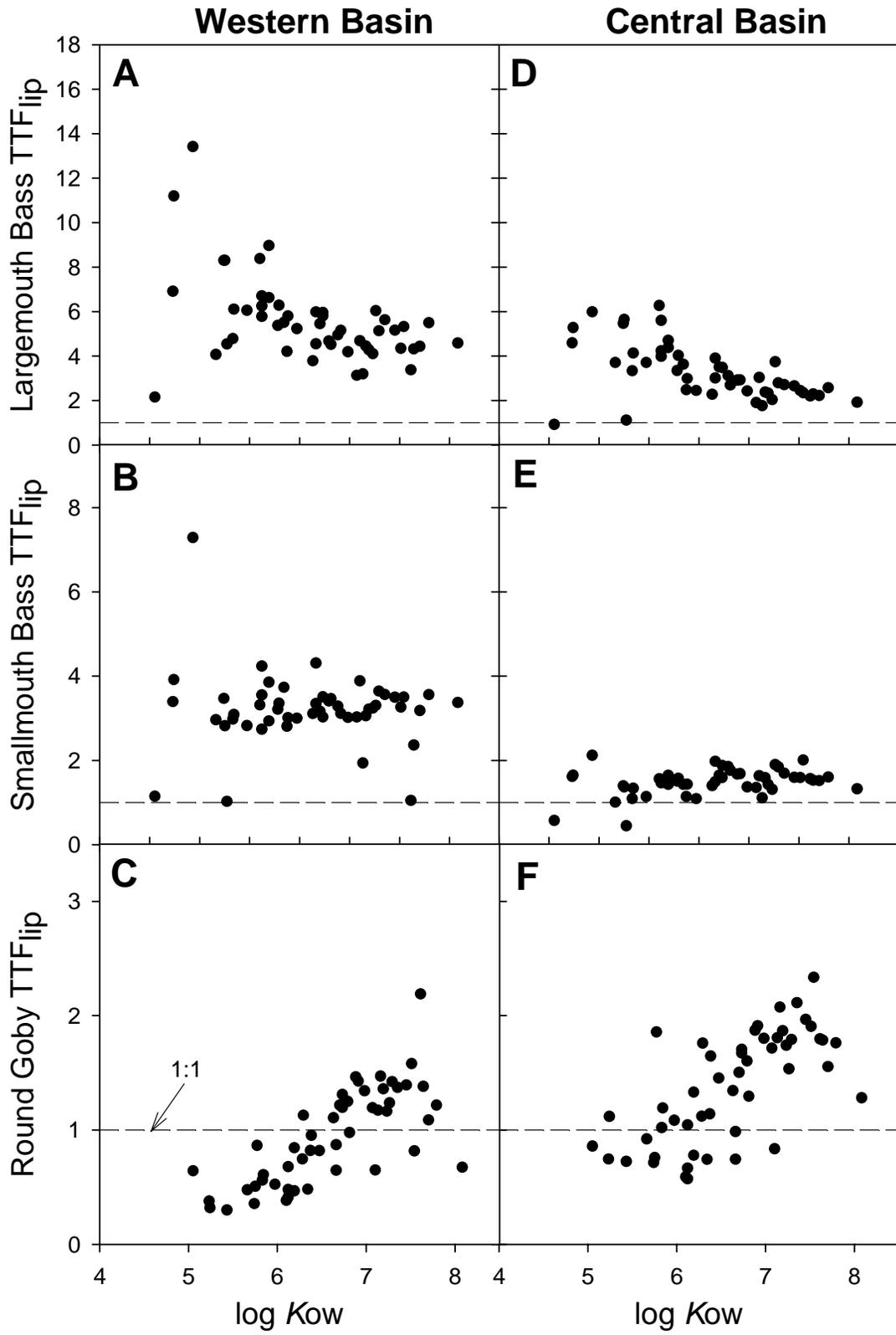


Figure 13.

Figure 14. PCB homolog distribution for organisms and sediments collected at four sites along the southern shore of Lake Erie, USA. Listed from west to east, the sites are Maumee (Maumee River Harbor), Sandusky (Sandusky River Harbor), Grand (Grand River Harbor), and Ashtabula (Ashtabula River Harbor) during 2001. Asterisks indicate median homolog values for each panel. Sediment values were averaged across both inside and outside harbor locations.

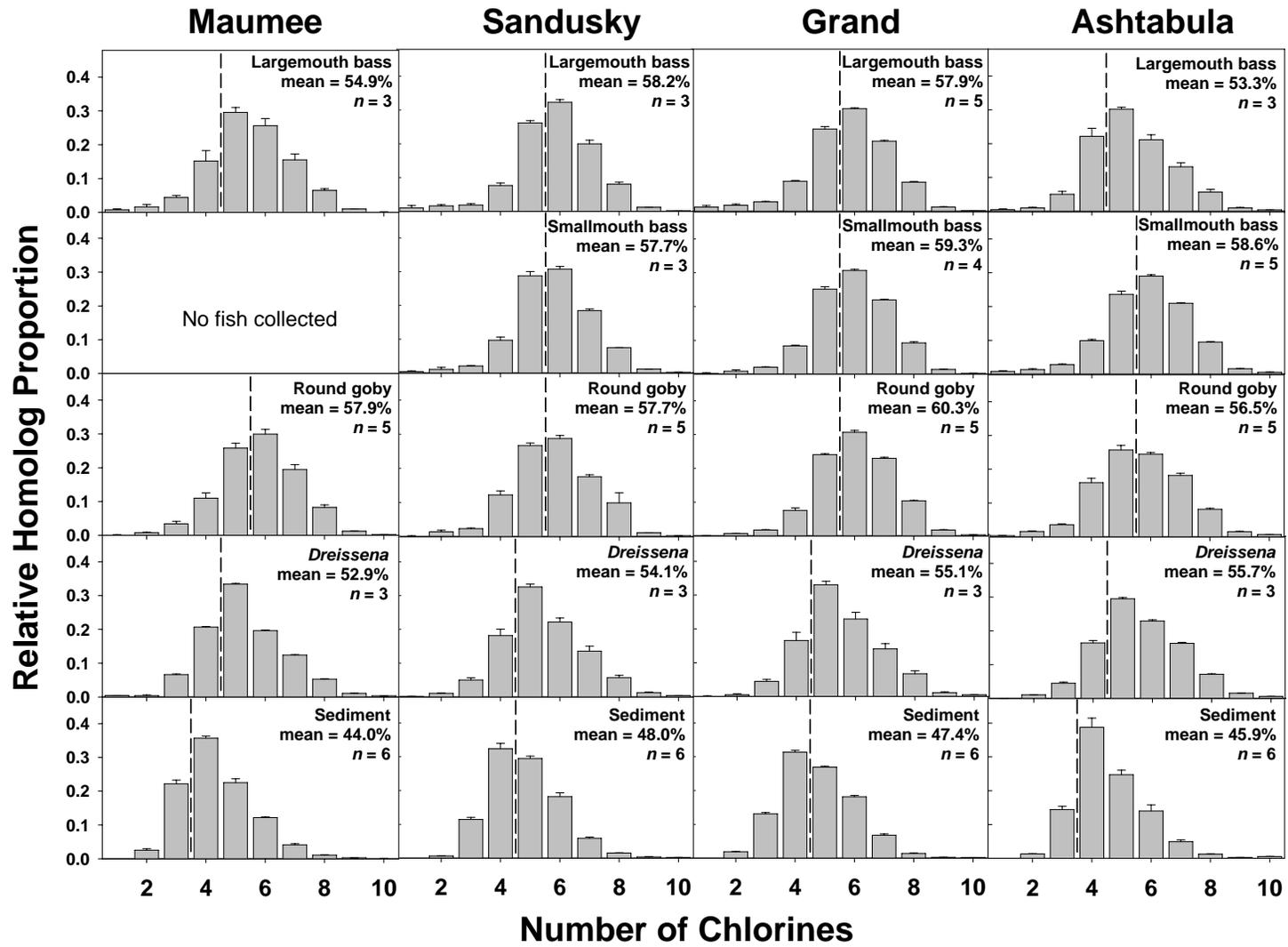


Figure 14.

Figure 15. Historical fish tissue data (1990-2005) from the Ohio Sport Fish Consumption Advisory Program (OEPA 1996) for central basin (triangles), western basin (circles), and unknown locations in Lake Erie (stars). Variables were organized by row: Arochlor 1260 as ng/g wet mass (Row 1), lipid-normalized Arochlor 1260 as  $\text{Arochlor 1260} / [\% \text{lipid}/100]$ , lipid total PCBs as ng/g wet mass (Row 2), total lipids as % lipid wet mass (Row 3), and fish length as mm TL (Row 4). Species were organized by columns.

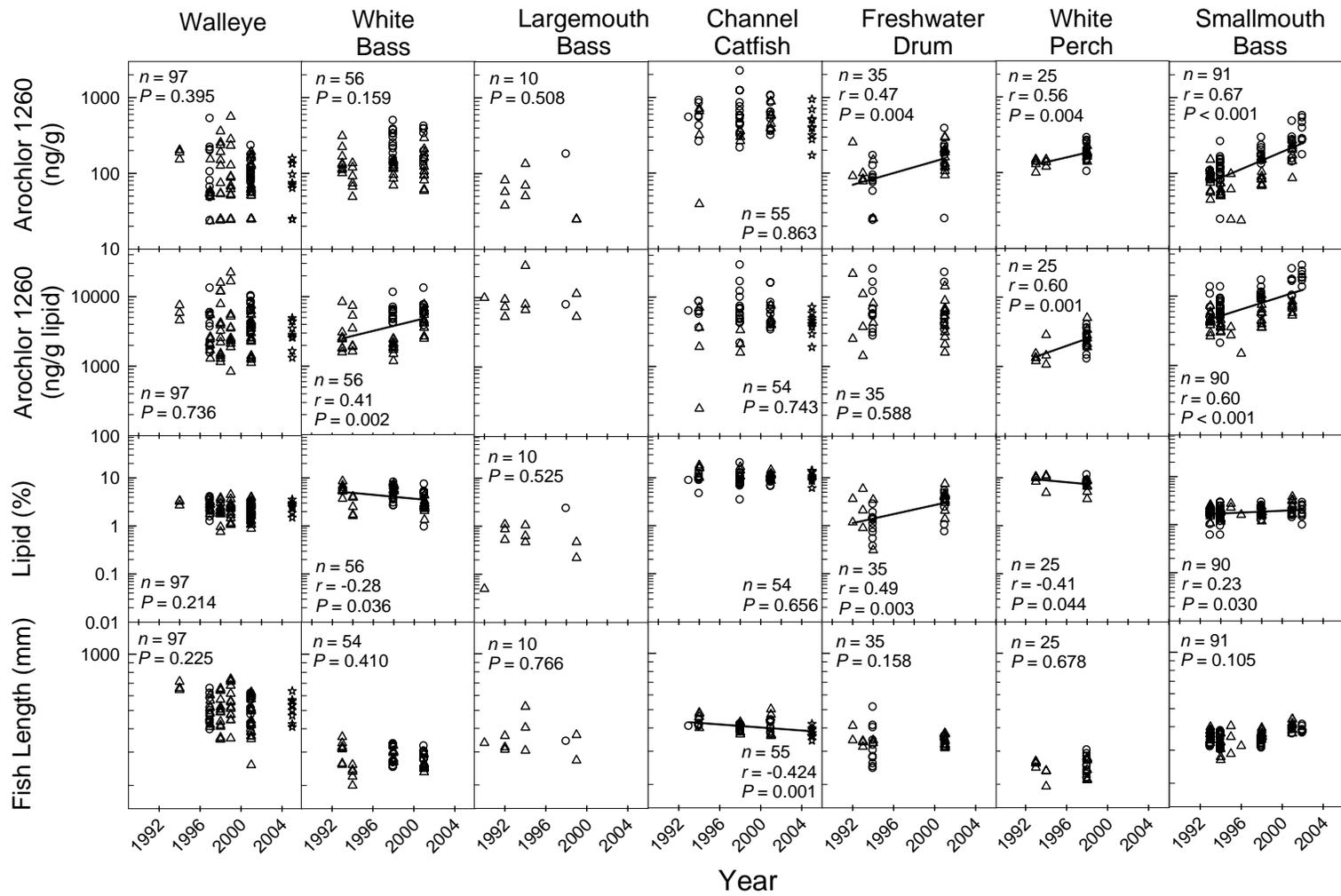


Figure 15.

## **CHAPTER 5**

# **THE ROLE OF DREISSENIID MUSSELS, SEDIMENT CHARACTERISTICS, AND ORGANIC POLLUTANTS IN STRUCTURING NEARSHORE BENTHIC MACROINVERTEBRATE COMMUNITIES IN LAKE ERIE**

### **ABSTRACT**

Benthic communities in Lake Erie are recovering from decades of excessive inputs of pollutants and nutrients. Commensurate with this recovery, the role of dreissenid mussels in structuring benthic macroinvertebrate communities is being explored. To assess their impact, we quantified sediment characteristics, PCB concentration, and macroinvertebrate densities at four harbors (Maumee, Sandusky, Grand, and Ashtabula) along the southern shore of Lake Erie during 2001 and 2002, sampling areas both inside and outside of harbors. We asked three questions: 1) do benthic macroinvertebrates vary between basins and areas inside and outside of harbors? 2) how do benthic habitats associate, if spatial differences are ignored? and 3), how do dreissenid mussels structure of benthic macroinvertebrate communities, compared with sediment characteristics and sediment contamination? We expected that degraded

benthic habitats would be more prevalent in the western versus central basin and higher inside versus outside harbors. As expected, areas inside harbors still suffer from organic and industrial pollution, compared with areas outside, as reflected by differences in relative oligochaete densities. Yet, we found little variation in benthic macroinvertebrate density (except oligochaetes and dreissenids) along basin-wide (100s of km) or harbor-wide scales (10s of km). Associations on small scales (< 1 km) appear driven by dreissenid mussels and their interactions with polychlorinated biphenyls (PCBs) and organic content of sediments. In contrast, physical characteristics of sediments did not explain macroinvertebrate density patterns. Whereas agricultural pollution appears to negatively affect benthic communities in the west basin, industrial pollution appears to impact benthos in the central basin. Because the influence of dreissenid mussels should increase with ongoing oligotrophication, we expect their influence to increase for the near future.

## **INTRODUCTION**

During the first half of the 20<sup>th</sup> century, water quality in Lake Erie declined as human populations increased. As the southernmost, shallowest, and most productive of the Laurentian Great Lakes, Lake Erie suffered intensely from eutrophication. Excessive anthropogenic inputs of nutrients over-stimulated primary production and caused organic material to accumulate (Makarewicz and Bertram 1991; Dolan 1993). Resultant high algal production, frequent harmful algal blooms, and widespread oxygen depletion in bottom waters led to the disappearance of sensitive benthic organisms (Carr and Hiltunen

1965; Makarewicz and Bertram 1991; Myers et al. 2000). In addition to nutrients, industrial contaminants, such as polychlorinated biphenyls (PCBs), and suspended sediments from agriculture accumulated in bottom sediments, further reducing the abundance and diversity of benthic organisms (Beeton 1961; Carr and Hiltunen 1965).

Since the 1970s, pollution control has improved water quality in Lake Erie. The Great Lakes Water Quality Act of 1972 imposed a limit of 1 mg/L total phosphorus on large municipalities and banned phosphorus use in detergents (Dolan 1993). Within 10 years, phosphorus loading by Canada and the U.S. into Lake Erie declined to mandated levels (Dolan 1993); spring water-column total phosphorus reached its goal around 1989, increasing hypolimnetic dissolved oxygen (Bertram 1993). After the 1977 PCB ban, lake-wide PCB concentrations in Lake Erie sediments declined about 70% between 1971 and 1997 (Painter et al. 2001). To a lesser degree, improved agricultural practices reduced sediment discharges (Richards and Baker 1993; Myers et al. 2000); suspended sediment input from the Maumee River decreased about 11.3% from 1970 to 1998 (Myers et al. 2000). These benefits have improved benthic habitats.

Improved water quality has benefited selected flora and fauna in Lake Erie. The most impressive change occurred in the western basin, shifting from a eutrophic to mesotrophic state (Makarewicz and Bertram 1991). As early as the 1980s, reductions in pelagic algal biomass and a shift toward intolerant phytoplankton and zooplankton occurred (Makarewicz and Bertram 1991; Makarewicz 1993). As a result, increased water clarity and oxygen in bottom waters allowed pollution-intolerant fishes to recover (Ludsin et al. 2001). Also, burrowing mayfly populations *Hexagenia* spp. have recovered, which were virtually eliminated in the 1950s, due to eutrophication and contaminated

sediments (Britt 1955). Since the early 1990s, improvements in bottom dissolved oxygen have allowed *Hexagenia* to recover throughout the western basin (Krieger et al. 1996; Madenjian et al. 1998). Clearly, benthic communities have started to improve.

Compared to open-water areas, recovery of benthic habitats near harbors has been slower and less dramatic. By the mid to late 1980s, macroinvertebrate communities near harbors shifted to species less tolerant of eutrophic conditions; yet, degraded conditions persist due to high levels of organic contaminants in enriched bottom sediments (Krieger and Ross 1993; Schloesser et al. 1995; Painter et al. 2001). Almost universally located at the mouths of large rivers, harbors overlap critical nursery habitat for river-spawned fishes, which prey on benthic macroinvertebrates; in Lake Erie, this includes fish species that are an important component of sport and commercial fisheries, including walleye *Sander vitreus* and yellow perch *Perca flavescens* (Mion et al. 1998; Tyson and Knight 2001). As such, benthic macroinvertebrate communities are important as bio-indicators of the returns on pollution-control investments (Bailey et al. 1995) and as prey for young sport and commercial fishes (Tyson and Knight 2001).

Benthic macroinvertebrate communities also have suffered from recent invasions of nonindigenous species (henceforth, exotic species). Initially collected in 1988, zebra mussels (*Dreissena polymorpha*) and quagga mussels (*D. bugensis*) were probably accidentally introduced via ship ballast water, spreading throughout Lake Erie and the Great Lakes basin within 2 years (Mills et al. 1993). Abundant zebra mussels reduce algae and seston by filter feeding, removing an estimated 7-30% of the total suspended matter in the western basin (Klerks et al. 1996). Because they alter nutrient dynamics,

contaminant fate, organic material deposition, and habitat complexity, dreissenid mussels influence benthic macroinvertebrate community structure (Botts et al. 1996; Ricciardi et al. 1997; Stewart et al. 1998a, 1998b).

How dreissenid mussels will affect the on-going recovery of benthic macroinvertebrate communities in Lake Erie is uncertain. Because they sequester contaminants and increase water clarity (Klerks et al. 1996), dreissenid mussels could increase rate of recovery. Conversely, they could hinder recovery by bio-concentrating contaminants in feces or pseudo-feces, which are ingested by macroinvertebrates (Bruner et al. 1994b). This is especially relevant at harbor sites in Lake Erie, which are still severely impacted by industrial pollutants and organic enrichment in sediments. Previous studies on macroinvertebrate communities in these areas have compared eutrophic periods to years just before the establishment of dreissenid mussels (Krieger 1984; Krieger and Ross 1993; Schloesser et al. 1995), but no studies have compared benthic communities post-dreissenid mussel establishment. Hence, we assessed benthic macroinvertebrate communities in the Ohio nearshore waters of Lake Erie post dreissenid mussel establishment.

We sought to disentangle the influence of pollutants, sediment characteristics, and dreissenid mussels in structuring benthic macroinvertebrate communities. To do this, we surveyed four harbors (Maumee, Sandusky, Grand, and Ashtabula) along the southern shore of Lake Erie during 2001 and 2002, sampling inside and outside of harbors. Using a combination of univariate, multivariate, and information-theoretic approaches, we addressed three questions: 1) do benthic macroinvertebrate communities vary between

western and central basins and at areas inside and outside of harbors? 2) ignoring spatial distinctions, how are benthic macroinvertebrates, sediment characteristics, and contaminants associated? and 3), how important are dreissenid mussels in structuring benthic macroinvertebrate communities, compared with structuring by sediment characteristics and sediment contamination?

## **METHODS**

### **Field Collection**

In this study, we quantified sediment characteristics, macroinvertebrate communities, and PCB concentrations (2001 only) at four sites in Lake Erie. We collected sediments according to standard procedures (OEPA 2001) during May through June 2001 and September 2002. From west to east, the two sites in the western basin were Maumee Harbor (Toledo, OH, USA) and Sandusky Harbor (Sandusky, OH, USA); the two sites in the central basin were Grand Harbor (Fairport, OH, USA) and Ashtabula Harbor (Ashtabula, OH, USA, 2001 only). At each site, we sampled inside and outside (but adjacent to) harbors, because past studies suggest that pollutants (and effects on biota) decline with distance from harbors (Carr and Hiltunen 1965; Krieger 1984; Krieger and Ross 1993). We selected sites at random, but re-randomized a location if the selected site contained >70% sand (OEPA 2001; sites were 3 – 16 m deep; Table 3). We used a stainless-steel Eckman dredge to collect 4 – 5 sediment grabs, packed homogenized

sediment into amber jars, and then transported the samples on ice to the laboratory, where they were stored at -20°C, pending analysis. All equipment and jars were pre-cleaned with hexane and acetone.

Sample Preparation for PCB Analysis for Sediments—Sediment PCB

concentrations were determined by AXYS Analytical Laboratory (Sidney, BC, Canada) using the High Resolution GC/Low Resolution Mass Spectrometry method (MLA-007). Briefly, 10 g of dried sediments were spiked with isotopically labeled surrogate standards, dried with sodium sulfate, and then Soxhlet extracted with dichloromethane. Extracts were separated on a Florisil column, concentrated, and received <sup>13</sup>C-labelled internal standards. When necessary, gel permeation and alumina column cleanup steps helped avoid matrix interferences. Extracts were analyzed on a GC equipped with a quadrupole mass spectrometer with a J&W DB-5 column (60 m long, 0.25 mm i.d., 0.10 µm film thickness) coupled directly to the mass spectrometer source, using a splitless/split injection sequence. Each sediment sample batch had a concurrent procedural blank, a spiked matrix sample, and a duplicate sample.

Quality assurance was monitored for sediment samples. Target concentrations were determined by isotope dilution or internal standard qualification methods using HP PROLAB software. Percent differences between calibration standards were < 20%; recovery rates ranged 70 and 130%. Detection limits were between 0.01 and 0.47 ng/g; procedural blanks were below detection limits. We calculated total PCBs as the sum of all congeners above detection limits, which represented the bulk of PCBs potentially available. In addition, we calculated the concentration of dioxin-like PCB congeners as the sum of PCBs 77, 81, 105+127, 118+106, 114, 123, 126, 156, 157, 167, 169, and 189

above detection limits (Van den Berg 1998). We statistically analyzed values as dry mass (ng/g) or standardized to carbon content (ng/g C).

Macroinvertebrates and Sediment Characteristics— We sampled sediments and macroinvertebrates during May through June 2001 and September 2002, using a stainless steel Eckman dredge sampler (8-10 grabs per site) or a Ponar dredge (5 grabs per site; 13% of sites), depending on substrate type (Ponar for larger sand and cobble). We immediately sieved samples (US Standard No. 30 mean, 0.541 mm) and stored invertebrates in 95% ethanol. In the laboratory, we identified macroinvertebrates as follows: *Hexagenia* spp., oligochaetes, chironomids, leeches, amphipods, dreissenid mussels, other bivalves, and gastropods. Small bivalves were difficult to distinguish between exotic *Corbicula* and native bivalves; therefore, we designate this group as ‘bivalves’ (not native bivalves).

We analyzed chemical and physical characteristics of sediments by first quantifying moisture and organic content of sediments (drying at 100°C until stable mass) in triplicate according to standard methods (2540 B and E; APHA 1998). After combustion at 550°C, we calculated percent organic content as mass lost upon ignition / dry mass  $\times$  100. We assessed sediment grain size in duplicate, according to methods in Folk (1980), estimating distribution of sand (50 to <2,000  $\mu$ m), silt (2 to <50  $\mu$ m), and clay (<2  $\mu$ m) via a sieve-pipette procedure using sodium oxalate. To achieve estimates within 10%, seven required a third run (16%), none required a fourth run, and two (4%) had sufficient sample mass for only one run. Total organic carbon was measured for each replicate using a Fisons NA 1500 Elemental Analyzer with acidification to remove carbonates (Penn State Agricultural Analytical Services Lab, University Park, PA).

## **Hypotheses and Statistical Analysis**

*Hypothesis 1*—We first asked how macroinvertebrates densities vary between basins: western (Maumee and Sandusky) and central basin (Grand and Ashtabula) and locations inside and outside harbors. Previous studies have found that macroinvertebrate communities differ between the western and central basins (Bailey et al. 1995) and between inside and outside harbors (Carr and Hiltunen 1965; Goodnight 1973; Krieger 1984; Krieger and Ross 1993). We compared 2001 densities of *Hexagenia*, amphipods, chironomids, and dreissenid mussels, in addition to relative oligochaete density. Because sediment contamination increases from the eastern to western basin in Lake Erie (Painter et al. 2001) and pollution typically is higher inside harbors versus outside harbors (Carr and Hiltunen 1965; Goodnight 1973; Krieger 1984), we expected densities of intolerant taxa (*Hexagenia*, amphipods, chironomids) to be higher and densities of tolerant taxa (oligochaetes) to be lower in the central versus the western basin and in areas outside versus inside harbors. We had no directional expectation for dreissenids.

Prior to analysis, we transformed densities ( $\log_{10} x+1$ ) to help normalize data and homogenize variance and arcsine-square-root-transformed proportional data, because these variances tend to associate with the mean for proportional data (Sokal and Rohlf 1995). We used a two-way analysis of variance ([ANOVA], unbalanced design; general linear model procedure [GLM]; [SAS 9.1; SAS Institute, Cary, NC, USA] with basin (western and central) and harbor (inside and outside) as main effects. Upon finding significant differences ( $\alpha = 0.05$ ), we used Tukey's post-hoc multiple comparisons.

*Hypothesis 2*—We used nonmetric multidimensional scaling (NMS) to determine how macroinvertebrates were associated with sediment characteristics, PCB

concentrations, and organic enrichment, independent of geographical distinctions. Often, patterns in macroinvertebrate communities are better described by ordination techniques than by spatial demarcations (Bailey et al. 1995; Kilgour et al. 2000).

As a nonparametric ordination technique, NMS has gained favor among ecologists (Ault and Johnson 1998; Bunnell et al. 2006) because it is well suited for non-normal and non-linear data at any distance scale, unlike other multivariate techniques, such as principal components analysis and canonical correspondence analysis (McCune and Mefford 1999). Using an iterative process, NMS minimizes the “stress” of a  $k$ -dimension configuration to determine synthetic multivariate dimensions that segregate data points (McCune and Mefford 1999). We used the Sørensen (Bray-Curtis) distance to calculate the dissimilarity matrix for means of each combination of site, location, and year. For these analyses, we used data from both sampling years. Because we did not return to the Ashtabula site in 2002, this yielded 14 site x harbor x year combinations.

Our main matrix in the NMS analysis was macroinvertebrate densities of *Hexagenia*, dreissenid mussels, chironomids, oligochaetes, bivalves (excluding dreissenids), amphipods, leeches, and gastropods. We excluded minor taxa (water mites, eggs, polychaetes, Trichoptera, and unidentifiable organisms), which represented <5% of the samples and occurred in just a few samples. Our second matrix consisted of environmental variables: sediment organic content, site depth, pH and temperature at the sediment interface, PCB concentration, Secchi disk visibility, and sediment size (% sand, clay, and silt).

To run the NMS analysis, we used PC-ORD software (MjM software Design, Glenenden Beach, OR) with the “slow and thorough” autopilot mode. This option

combines 40 runs from real data with 50 Monte Carlo runs of randomized data to select a solution that reduces stress more than chance ( $\alpha = 0.05$ , McCune and Mefford 1999). After finding specific multivariate dimensions, we correlated the ranks of axis scores to macroinvertebrate taxa and environmental variables with Kendall's  $\tau$  to determine which variables drove each dimension (Bunnell et al. 2006). Because we conducted 16 correlations (eight taxa and eight environmental variables) to each axis, we applied a Bonferroni correction ( $\alpha = 0.003$ ). To assign sites to cluster groups, we used Sørensen's distance matrix and flexible beta linkage with  $\beta = -0.25$  (McCune and Mefford 1999) and scaled the dendrogram by Wishart's objective function converted to percent information retained.

Hypothesis 3—Finally, we used the information-theoretic model selection approach (Burnham and Anderson 2002) to test how important dreissenid mussels were in structuring macroinvertebrate communities, compared with sediment characteristics and sediment contamination. Previous work provides *a priori* expectations. Variability in benthic community structure at the St. Louis Area of Concern (AOC) in Lake Superior was explained better by sediment physical features than by contaminant levels and least by organic enrichment (Breneman et al. 2000). Also, changes in benthic macroinvertebrate communities at the Muskegon Lake AOC in Lake Michigan resulted more from wastewater diversion than from dreissenid mussels (Carter et al. 2006). Therefore, we hypothesized that relative influence would rank sediment physical characteristics > industrial pollution > organic enrichment > dreissenid mussels. To test this, we used the dataset from hypothesis 1 to explain variation in each macroinvertebrate taxon. Rather than compare all variables (Tables 3 – 5), which can lead to spurious

correlations and excessively complex models, we tested only models derived from published findings.

We then created a set of *a priori* candidate models. First, we included dreissenid mussel density, given that they structure benthic macroinvertebrate communities by creating shell habitat and altering organic material deposition (Bruner et al. 1994b; Botts et al. 1996; Ricciardi et al. 1997; Thayer et al. 1997; Stewart et al. 1999; Beekey et al. 2004). Second, we used sediment PCB concentration to represent industrial pollution, because sediment PCB concentrations at many Lake Erie sites still exceed thresholds for deleterious effects (Painter et al. 2001). To abide by parsimony in candidate model selection, we used only total PCB concentration (ng/g dry mass) because all PCB measurements were correlated (Table 5; all  $r > 0.75$ , all  $P < 0.05$ ). Third, sediment organic content represented organic enrichment, which affects diversity and abundance of nearshore benthic macroinvertebrates (Krieger and Ross 1993; Thayer et al. 1997). Percent organic material was sampled both years and correlated with organic carbon ( $r = 0.86$ ,  $P < 0.001$ ,  $n = 24$ ). Fourth, we included site depth, because macroinvertebrate communities differ greatly between shallow and deep sites (Kilgour et al. 2000). Fifth, we selected percent silt from our size fractions, because it correlates with chironomid density in central basin Lake Erie (Krieger and Ross 1993). We included it for all taxa, assuming that the dearth of published relationships arises from excluding this time-consuming task, rather than lack of biological association.

We used the model selection approach of Burnham and Anderson (1998) for all possible combinations of zero to three model terms, in addition to the null model (intercept without any explanatory variables) and the global model that contained all

terms. We chose a limit of three model terms to produce a parsimonious model that would allow fathomable ecological inference. Using the least squares case, we calculated Akaike's information criterion, corrected for small-sample bias ( $AIC_c$ ), from estimated residuals from each candidate model, because our ratio of observations to parameters was  $> 40$  (Burnham and Anderson 1998). We calculated the difference between the  $AIC_c$  for each model  $i$  and the "best" model in the set (smallest  $AIC_c$  value) to calculate  $\Delta_i$  and the Akaike weight ( $w_i$ ) for each model. A model with  $\Delta_i < 2$  and large  $w_i$  is considered one of the best approximating models among the set of models considered (Burnham and Anderson 1998).

## RESULTS

*Hypothesis 1*—Contrary to our expectations, benthic macroinvertebrates communities densities did not differ strongly between basins or harbor locations. *Hexagenia* densities did not differ between basins or harbor locations (two-way ANOVA, basin  $df = 1, 20$ , harbor  $df = 1, 20$ , and site x harbor interaction  $df = 1, 20$ , Figure 16A). Whereas chironomid density did not differ spatially (Figure 16B), dreissenid mussel density (Figure 16C) and relative oligochaete density did (Figure 17A). Dreissenid mussels were more prevalent in areas outside of western basin harbors, especially at Maumee (two-way ANOVA, basin  $df = 1, 20$ , harbor  $df = 1, 20$ , and site x harbor interaction  $df = 1, 20$ , Figure 16C). The area outside Maumee was unique, given that it was shallowest among all outside harbor locations (Table 3). In general, the central basin and areas inside harbors had higher proportions of oligochaetes than the western basin

and areas outside of harbors (two-way ANOVA, basin  $df = 1, 20$ , harbor  $df = 1, 20$ , and site x harbor interaction  $df = 1, 20$ , Figure 17A). Although we expected the high densities of oligochaetes inside harbors, the greater prevalence of oligochaetes in the central versus the western basin ran counter to our hypothesis. Finally, amphipod and total macroinvertebrate densities did not differ spatially (Figure 17B-C). Other density estimates are provided in Table 6.

Hypothesis 2—Benthic macroinvertebrates were associated along two ordination dimensions. When we used the 2001 dataset that included PCB data, a reliable one-dimensional ordination occurred in 3 of 6 NMS runs; even when a one-dimensional ordination was found, PCBs did not influence that axis ( $P > 0.5$ ). This likely arose from adding variables while decreasing sample size to  $n=8$ , which resulted in weakly structured data. Therefore, the remaining NMS results include both years and exclude PCB data.

From the NMS analysis, we documented a two-dimensional representation of our sites. Together these two axes explained 91% of the variance in the data, determined by the coefficients of determination for the correlations between ordination distances and the original  $n$ -dimensional space. We do not report variance explained by each axis because, unlike the variance explained by the combined axes, variance explained by each axis changed with multiple runs of the model. We trimmed the dendrogram to three groups, retaining about 50% of the information (Figure 18) discovering that pH was related positively to axis 1 and both water temperature and bivalve density (excluding dreissenid mussels) related negatively to axis 1 (Kendall's  $\tau$ ;  $\alpha < 0.003$ , Figure 19). Along axis 2, densities of dreissenid mussels, *Hexagenia*, amphipods, and snails related positively

(Kendall's  $\tau$ ;  $\alpha < 0.003$ , Figure 19). These findings were contrary to our expectations that sites would separate along conditions associated with harbor areas. Although negative values along axis 1 could aptly describe harbor conditions (Figure 19), inside and outside harbor sites did not separate along either axis.

Of the three cluster groups, to which we arbitrarily assigned cluster numbers, two groups separated from the majority of sites. Cluster 1 contained the shallow area outside of Maumee Harbor that were associated with high densities of dreissenids, *Hexagenia*, amphipods, and snails and these associations were consistent between sampling years (Figure 19). Cluster 2 contained areas inside and outside of Grand River Harbor, as well as areas outside Sandusky Harbor in 2002, that were associated with lower densities of dreissenid mussels, *Hexagenia*, amphipods, and snails, low pH, and high bivalve density (excluding dreissenids) and water temperature (Figure 19). This association was consistent between years at Grand River. Cluster 3 contains the remaining site x location x year combinations, which were weakly characterized by our ordination, given that they did not spread out along either axis (Figure 19).

Hypothesis 3—The relative rankings of factors that influenced benthic community structure ran counter to our expectations. Dreissenid mussel density was the most important factor structuring benthic macroinvertebrate taxa for oligochaete and amphipod densities (Tables 6-9). Organic enrichment and PCB concentrations in sediments explained variation only when interacting with dreissenid mussel density. Sediment characteristics had the least influence and did not explain variation for any taxon. For relative oligochaete density, only the model including dreissenid mussel density and the

interaction of dreissenids and organic enrichment of sediments (DRM and DRM x ORG interaction) was found to explain variation in density (Table 8). Also, for amphipod density, only one model that included dreissenid mussel density and the interaction of dreissenids and PCB concentration (DRM and PCB x DRM interaction) effectively explained variation (Table 9).

None of our linear models were useful to explain variation in densities of *Hexagenia*, chironomids, and dreissenid mussels, as indicated by the high relative ranking of the global and null (intercept only) model. The null model ranked highest among the model set to explain variance in *Hexagenia* density (Table 6). For chironomid density, the global model (which contained all terms) ranked highest among the model set (Table 7). Density of dreissenid mussels was explained best by the global and null models (Table 10).

## DISCUSSION

As oligotrophication and control of source inputs of chemical contaminants continue, benthic communities will be increasingly structured by dreissenid mussels and other exotic species. Contrary to previous studies, we found little support for strong segregation of benthic macroinvertebrates along basin-wide (100s of km) or harbor-wide scales (10s of km), except for relative density of oligochaetes. Instead, benthic macroinvertebrate taxa appear to be closely associated on smaller scales (< 1 km). Ultimately, dreissenid mussels appear to be driving these associations, along with

dreissenid mussel interactions with PCBs and organic content of sediments; the relative influence on benthic macroinvertebrate communities was dreissenid mussels > industrial pollution = organic enrichment > sediment physical characteristics. This ran counter to our expectation that physical characteristics would drive benthic macroinvertebrate communities (per Breneman et al. 2000, Carter et al. 2006).

*Recovery of Benthic Communities*—Compared with the past 40 years, slow recovery of benthic macroinvertebrate communities appears to be continuing at these nearshore areas. Despite basin-wide reductions in hypoxic bottom waters, leading to benthic organism recovery (Ludsin et al. 2001; Krieger et al. 1996; Madenjian et al. 1998), seasonal hypoxia still occurs in the central basin (“the dead zone”) and may be expanding (Wilhelm et al. 2006). Goodnight (1973) suggested that the relative abundance of oligochaetes was an effective surrogate measure of organic enrichment or industrial pollution: <60% indicates “good conditions”, between 60% and 80% indicates “doubtful conditions”, and >80% indicates a high degree of either organic enrichment or industrial pollution. In 1961, Maumee Harbor (comprising areas both inside and outside harbors in our study) averaged 90% oligochaetes, while the open-lake section of the western basin averaged 42% oligochaetes (Carr and Hiltunen 1965). In 1978 and 1979, at five central basin sites, including Grand and Ashtabula Harbors, harbor locations averaged 91% and open waters averaged 49% oligochaetes (Krieger 1984). In 1989, Cleveland Harbor (Cleveland, OH) in the central basin of Lake Erie, relative oligochaete density was 86% inside the harbors and 30% in the open water (Krieger and Ross 1993). Although in our study Sandusky Harbor averaged slightly lower than the other three harbors, mean relative oligochaete density across all sites was 64% inside harbors and

28% outside harbors, corresponding to doubtful and good conditions, respectfully (Goodnight 1973). Based on this index, our benthic communities appear to have improved significantly during the decade since the 1989 study (Krieger and Ross 1993).

Harbor areas still suffer from organic and industrial pollution. In our study, areas inside harbors contained sediments with higher organic content and relative oligochaete densities than areas outside of harbors, especially in the agriculture-dominated western basin (Myers et al. 2000). Although this pattern is relatively consistent, the underlying reason for it differs between basins. Despite consistently high relative oligochaete densities in all harbors, organic enrichment was higher and total PCBs were lower in western basin harbors versus central basin harbors. In contrast, relative oligochaete densities in the areas outside of the central basin harbors were higher than their western basin counterparts. While organic content in outside harbor sediments was similar between basins, sediments outside central basin harbors had higher total PCB concentrations than outside of the western basin harbors. We infer that agricultural pollution (i.e., organic enrichment of sediments) appears to be hampering recovery of benthic communities in the western basin, while industrial pollution (i.e., PCBs) is slowing the rate of recovery for central basin communities.

The utility of using relative oligochaete density as a surrogate measure of industrial and organic pollution may diminish over time. In general, as nutrient inputs decrease, the contribution of benthic primary production to overall system productivity increases relative to other energy sources (Vadeboncoeur et al. 2003). Therefore, we expect the nonlinear influence of dreissenid mussels on relative oligochaete density (i.e.,

dreissenid x organic material interaction) to increase through time. Future studies should use this index with caution.

*Hexagenia* appears to be recovering in our nearshore areas in both basins. Although recovery of *Hexagenia* has been limited to the western basin of Lake Erie (Krieger et al. 1996; Madenjian et al. 1998), recovery also should occur in the central basin. Sediment cores suggest that *Hexagenia* were once abundant in the central basin nearshore (Reynoldson and Hamilton 1993). Wright (1995) posited that sites with  $>100$  *Hexagenia*/m<sup>2</sup> and  $<1000$  oligochaetes/ m<sup>2</sup> (primarily Tubificidae) indicate low levels of pollution,  $<100$  *Hexagenia*/m<sup>2</sup> and between 1,000 and 5,000 oligochaetes/ m<sup>2</sup> indicate moderate pollution, and  $<100$  *Hexagenia*/m<sup>2</sup> and  $>5000$  oligochaetes/ m<sup>2</sup> indicate heavy pollution. Based on this index (Wright 1995), outside Maumee Harbor had the lowest level of pollution and inside Grand River Harbor had the highest level of pollution. These findings supported the results from NMS ordination (nonmetric multidimensional scaling). The lowest levels of pollution coincided with cluster 1 and the highest levels of pollution coincided with cluster 2. Although shallow locations, outside Maumee Harbor and (cluster 1) and inside Grand Harbor (cluster 2), separated from the majority of locations (cluster 3), site depth did not drive either ordination axis.

*Dreissenid Mussel Influence on Recovering Benthic Communities*—Dreissenid mussels influence recovering benthic macroinvertebrate communities at our nearshore sites. Not only did dreissenid mussels drive axis 2 in the NMS analysis, they were the most important factor structuring our benthic macroinvertebrate taxa during model selection, explaining variation in all of our taxa. This results runs counter to our expectation that physical characteristics would be most important and dreissenid mussels

would be least important drivers of benthic communities (per Breneman et al. 2000, Carter et al. 2006). Instead, for our sites, the relative influence on benthic macroinvertebrate communities ranked dreissenid mussels > industrial pollution = organic enrichment > sediment physical characteristics.

The likely mechanisms for dreissenid mussel influence in our study was via increases in particulate organic matter by depositing feces or pseudofeces, creation of shell habitat, and contaminant transfer via feces or pseudofeces (Bruner et al. 1994b; Stewart 1998a, 1998b). The clearest responses in our study were for relative oligochaete density (DRM and DRM x ORG interaction) and amphipod density (DRM and PCB x DRM interaction), suggesting that organic matter and PCBs likely were re-routed by dreissenids, as found by others (Bruner et al. 1994b; Thayer et al., 1997; Botts et al. 1996; Beeky et al. 2004). To a lesser degree, *Hexagenia* density was explained by dreissenid mussels. Both genera increased along the same NMS axis; however, dreissenid mussels explained variation to a similar degree as the null model. This association may be driven by additive bioturbation and nutrient recycling by both organisms (Bachteram et al. 2005; Conroy et al. 2005). Unlike other studies (Botts et al. 1996; Beeky et al. 2004, the influence of dreissenid mussels on chironomid density was negligible. Also, contrary to past studies (Krieger and Ross 1993; Kilgour 2000), sediment physical characteristics did not influence macroinvertebrate communities. Thus, for nearshore areas (i.e., <10-m depth), dreissenid mussels likely will continue to exert influence on the benthic macroinvertebrate community.

*In Conclusion*— Through time, recovery of benthic communities will become increasingly difficult to assess with current rapid bioassessment indices. Dreissenids can be anticipated to become a sentinel species of contaminant bioavailability (Cope et al. 1999). We suggest that dreissenid mussels also be used to assess benthic macroinvertebrate communities, given that they influenced the densities of all of our taxa. However, Botts et al. (1996) points out that living and dead shells of dreissenids drive different responses that are taxa-specific. Future work could calibrate such an index that uses both living and dead dreissenid mussels.

Clearly, a reduction in environmental contaminants in Lake Erie is a positive return on the past 30 years of pollution control; however we expect that future improvements to biota will continue. However, discrete spatial patterns in benthic communities and the utility of simple biological indices (i.e., relative oligochaete density) to predict organic and industrial pollution may decline. Through time, the relative influence of dreissenid mussels on benthic communities will exceed that of sediment contamination. In other words, the effects of chemical pollution will lessen with reductions in source input and the increasing ecological effects of biological pollution (i.e., exotic species).

Site	Location	Sample	Latitude	Longitude	Depth (m)
<b>Maumee</b>	Inside	1 <sup>†</sup>	41° 42.042 N	-83° 27.686 W	3.7
		2 <sup>†</sup>	41° 41.926 N	-83° 28.090 W	2.9
		3 <sup>†</sup>	41° 42.532 N	-83° 26.145 W	4.7
		4 <sup>‡</sup>	41° 42.532 N	-83° 27.750 W	2.1
	Outside	1 <sup>†</sup>	41° 42.158 N	-83° 23.637 W	2.3
		2 <sup>†</sup>	41° 42.900 N	-83° 23.888 W	2.8
3 <sup>†</sup>		41° 43.410 N	-83° 23.627 W	3.0	
<b>Sandusky</b>	Inside	1 <sup>†</sup>	41° 27.710 N	-82° 44.365 W	2.4
		2 <sup>†</sup>	41° 28.136 N	-82° 45.966 W	2.6
		3 <sup>†</sup>	41° 29.351 N	-82° 47.210 W	2.3
		4 <sup>†</sup>	41° 29.242 N	-82° 45.380 W	2.1
	Outside	1 <sup>†</sup>	41° 29.120 N	-82° 39.126 W	7.8
		2 <sup>†</sup>	41° 28.653 N	-82° 39.100 W	7.7
3 <sup>†</sup>		41° 27.311 N	-82° 37.031 W	6.7	
<b>Grand</b>	Inside	1 <sup>†</sup>	41° 45.881 N	-81° 16.551 W	5.6
		2 <sup>†</sup>	41° 46.010 N	-81° 16.695 W	6.4
		3 <sup>†</sup>	41° 45.949 N	-81° 16.905 W	4.6
	Outside	1 <sup>†</sup>	41° 48.284 N	-81° 17.525 W	14.8
		2 <sup>†</sup>	41° 47.883 N	-81° 16.869 W	13.9
		3 <sup>†</sup>	41° 48.165 N	-81° 16.937 W	14.9
<b>Ashtabula</b>	Inside	1 <sup>§</sup>	41° 55.061 N	-80° 47.331 W	4.9
		2 <sup>§</sup>	41° 54.950 N	-80° 47.041 W	4.3
		3 <sup>§</sup>	41° 54.691 N	-80° 47.562 W	5.5
	Outside	1 <sup>§</sup>	41° 55.111 N	-80° 48.801 W	12.2
		2 <sup>§</sup>	41° 55.781 N	-80° 47.141 W	13.1
		3 <sup>§</sup>	41° 55.901 N	-80° 45.701 W	14.3

Table 3. Characteristics of sediment sampling locations during May through June 2001 at Maumee, Sandusky, Fairport, and Ashtabula Harbors, Lake Erie, Ohio. Locations were either within the harbor proper (Harbor) or adjacent to the harbor (Outside).

Samples were coded according to years: <sup>†</sup>Samples collected during both years, <sup>‡</sup>Samples collected during 2002 only, and <sup>§</sup>Samples collected during 2001 only.

	Maumee		Sandusky		Grand		Ashtabula	
	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside
Gastropods (no./m <sup>3</sup> )	1.8 (1.8)	191.7 (45.6)	233.9 (33.9)	7.2 (5.2)	0.0 (0.0)	161.5 (91.5)	7.2 (4.7)	48.4 (26.5)
Leeches (no./m <sup>3</sup> )	40.3 (12.4)	0.0 (0.0)	43.1 (0.0)	47.4 (20.3)	2.4 (2.4)	53.5 (18.8)	11.6 (6.3)	26.9 (15.5)
Other Bivalves (no./m <sup>3</sup> )	146.1 (90.3)	11.7 (11.7)	28.7 (14.4)	200.9 (87.3)	126.8 (67.4)	209.9 (120.0)	7.2 (4.7)	48.4 (26.5)
Oligochaetes (no./m <sup>3</sup> )	3,775.5 (1,323.6)	69.7 (39.6)	892.7 (301.6)	284.2 (73.6)	4,271.5 (2,374.0)	1,954.4 (695.2)	2,329.7 (1,059.1)	611.7 (400.0)

Table 4. Densities of other macroinvertebrate taxa at four Lake Erie sites (from west to east): Maumee (Maumee R. Harbor), Sandusky (Sandusky R. Harbor), Grand (Grand R. Harbor), and Ashtabula (Ashtabula R. Harbor) sampled during 2001. All values were the mean of three replicates and parenthetical values are standard error. Other bivalves excluded dreissenid mussels.

	Maumee		Sandusky		Grand		Ashtabula	
	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside
Water Content (%)	47.0 (2.3)	34.2 (2.5)	44.0 (0.7)	34.9 (0.5)	34.8 (2.6)	40.9 (4.2)	33.2 (2.1)	32.5 (2.8)
Total PCB (ng/g)	48.3 (8.0)	68.4 (15.4)	40.8 (6.4)	73.0 (11.0)	58.9 (16.3)	106.4 (9.3)	103.9 (32.5)	152.4 (53.9)
Total PCB (ng/g C)	1,867 (257)	5,404 (1,747)	1,427 (56)	4,961 (922)	5,212 (1,976)	5,369 (387)	7,149 (1,109)	11,536 (2,026)
Dioxinlike PCBs (ng/g)	2.4 (0.5)	3.5 (0.8)	3.1 (0.3)	5.3 (0.7)	3.0 (0.9)	6.8 (0.9)	4.7 (1.2)	9.2 (3.6)
Dioxinlike PCB (ng/g C)	91.7 (15.3)	276.8 (91.1)	110.4 (7.8)	356.9 (62.3)	281.6 (115.7)	344.2 (35.1)	325.6 (34.9)	688.2 (147.6)
pH	8.6 (0.1)	9.0 (0.2)	8.9 (0.2)	9.0 (0.1)	8.8 (0.1)	9.0 (0.1)	8.7 (0.2)	8.9 (0.1)
Depth (m)	3.3 (0.1)	2.6 (0.2)	2.5 (0.1)	7.6 (0.5)	5.5 (0.5)	15.3 (0.5)	4.9 (0.4)	13.2 (0.6)
Secchi Depth (cm)	40.0 (2.9)	83.3 (33.3)	76.7 (26.0)	185.0 (28.4)	136.7 (12.0)	361.7 (21.7)	171.7 (30.9)	325.0 (400.0)
Water temperature (°C)	16.9 (0.2)	16.9 (0.6)	17.9 (0.4)	13.5 (0.3)	13.1 (0.4)	12.2 (0.1)	13.3 (0.2)	12.0 (0.4)
% Carbon	2.6 (0.1)	1.4 (0.1)	2.9 (0.4)	1.5 (0.1)	1.2 (0.2)	2.0 (0.1)	1.4 (0.2)	1.2 (0.3)
% Sand	6.6 (2.7)	27.8 (17.0)	15.8 (6.1)	14.5 (8.3)	31.8 (10.1)	18.8 (12.3)	7.8 (1.7)	21.0 (8.3)
% Clay	55.2 (9.4)	31.0 (12.0)	48.4 (5.7)	28.4 (5.7)	24.1 (2.9)	34.1 (3.2)	30.2 (1.0)	28.8 (7.9)
% Silt	27.3 (12.6)	41.2 (11.6)	34.7 (3.6)	57.1 (9.3)	44.1 (7.3)	49.5 (9.5)	62.0 (1.0)	50.2 (3.7)

Table 5— Sediment characteristics at four Lake Erie sites (from west to east): Maumee (Maumee R. Harbor), Sandusky (Sandusky R. Harbor), Grand (Grand R. Harbor), and Ashtabula (Ashtabula R. Harbor) sampled during 2001. All sediment measures were expressed on a dry-mass basis. All values were the mean of three replicates and parenthetical values are standard error. Water temperature was measured at the sediment-water interface.

*Hexagenia*

Model Rank	Model Terms	K	$r^2$	$\Delta i$	$w_i$
1	NULL	2	0.000	0.00	0.074
2	DRM	3	0.084	0.52	0.057
3	PCB, ORG	4	0.173	0.97	0.046
4	PCB, PCB*DRM	4	0.172	1.00	0.045
5	PCB	3	0.065	1.02	0.045
6	ORG	3	0.062	1.08	0.043
7	SLT, ORG*SLT	4	0.165	1.21	0.041
8	PCB, DRM	4	0.161	1.32	0.038
9	ORG, PCB*ORG	4	0.155	1.48	0.035
10	DRM, PCB*DRM	4	0.143	1.84	0.030

Table 6. Summary of *a priori* regression models to explain variance in *Hexagenia* densities collected in 2001. Model terms are the intercept as the intercept (NULL), dreissenid mussel density (DRM), site depth (DEP), percent silt in sediments (SLT), percent organic content in sediments (ORG), and total PCB concentration (ng/g dry mass) in sediments (PCB). Column terms are the number of slope parameters plus the error and intercept (K), the difference between each model and the model with the minimum AICc value ( $\Delta i$ ), the relative “weight” of evidence for each model ( $w_i$ ), and the proportion of variance explained by each model ( $r^2$ ). A model with  $\Delta i < 2$  and large  $w_i$  is considered one of the best approximating models among the set of models considered (Burnham and Anderson 1998).

Chironomid

Model Rank	Model Terms	K	$r^2$	$\Delta i$	$w_i$
1	DRM, ORG, DEP, SLT, PCB, DRM*AORG*DEP*SLT*PCB	8	0.627	0.00	0.164
2	ORG, DEP, PCB	5	0.331	1.78	0.067
3	ORG, ORG*DEP	4	0.227	1.99	0.061
4	DEP, ORG*DEP	4	0.220	2.20	0.055
5	ORG, DEP	4	0.215	2.36	0.050
6	INT	2	0.000	2.65	0.044
7	PCB, DEP	4	0.192	3.05	0.036
8	DEP, PCB*DEP	4	0.185	3.28	0.032
9	ORG	3	0.075	3.41	0.030
10	ORG, DEP, SLT	5	0.280	3.53	0.028

Table 7. Summary of *a priori* regression models to explain variance in chironomid densities collected in 2001. Model terms are the intercept as the intercept (NULL), dreissenid mussel density (DRM), site depth (DEP), percent silt in sediments (SLT), percent organic content in sediments (ORG), and total PCB concentration (ng/g dry mass) in sediments (PCB). Column terms are the number of slope parameters plus the error and intercept (K), the difference between each model and the model with the minimum AICc value ( $\Delta i$ ), the relative “weight” of evidence for each model ( $w_i$ ), and the proportion of variance explained by each model ( $r^2$ ). A model with  $\Delta i < 2$  and large  $w_i$  is considered one of the best approximating models among the set of models considered (Burnham and Anderson 1998).

Relative oligochaete density

Model Rank	Model Terms	K	$r^2$	$\Delta i$	$w_i$
1	DRM, DRM*ORG	4	0.51	0.00	0.40
2	DRM	3	0.38	2.52	0.11
3	DRM, ORG, DRM*ORG	5	0.51	3.19	0.08
4	DRM, ORG	4	0.42	3.86	0.06
5	DRM, DEP	4	0.41	4.51	0.04
6	DRM, SLT	4	0.41	4.54	0.04
7	DRM, DRM*SLT	4	0.39	5.05	0.03
8	DRM, PCB*DRM	4	0.39	5.37	0.03
9	PCB, PCB*DRM	4	0.38	5.40	0.03
10	PCB, DRM	4	0.38	5.42	0.03

Table 8. Summary of *a priori* regression models to explain variance in relative oligochaete density ( $[\text{oligochaetes} / \text{m}^2] / [\text{total macroinvertebrates} / \text{m}^2]$ ) collected in 2001. Model terms are the intercept as the intercept (NULL), dreissenid mussel density (DRM), site depth (DEP), percent silt in sediments (SLT), percent organic content in sediments (ORG), and total PCB concentration (ng/g dry mass) in sediments (PCB). Column terms are the number of slope parameters plus the error and intercept (K), the difference between each model and the model with the minimum AICc value ( $\Delta i$ ), the relative “weight” of evidence for each model ( $w_i$ ), and the proportion of variance explained by each model ( $r^2$ ). A model with  $\Delta i < 2$  and large  $w_i$  is considered one of the best approximating models among the set of models considered (Burnham and Anderson 1998).

## Amphipod

Model Rank	Model Terms	K	$r^2$	$\Delta i$	$w_i$
1	DRM, PCB*DRM	4	0.586	0.00	0.607
2	PCB, DRM, PCB*DRM	5	0.587	3.21	0.122
3	DRM	3	0.425	4.99	0.050
4	DRM, DRM*SLT	4	0.475	5.73	0.035
5	PCB, DRM	4	0.459	6.44	0.024
6	DRM, DRM*ORG	4	0.455	6.62	0.022
7	ORG, DRM*ORG	4	0.455	6.63	0.022
8	DRM, SLT	4	0.455	6.64	0.022
9	DRM, DEP	4	0.429	7.75	0.013
10	DRM, ORG	4	0.425	7.90	0.012

Table 9. Summary of *a priori* regression models to explain variance in amphipod densities collected in 2001. Model terms are the intercept as the intercept (NULL), dreissenid mussel density (DRM), site depth (DEP), percent silt in sediments (SLT), percent organic content in sediments (ORG), and total PCB concentration (ng/g dry mass) in sediments (PCB). Column terms are the number of slope parameters plus the error and intercept (K), the difference between each model and the model with the minimum AICc value ( $\Delta i$ ), the relative “weight” of evidence for each model ( $w_i$ ), and the proportion of variance explained by each model ( $r^2$ ). A model with  $\Delta i < 2$  and large  $w_i$  is considered one of the best approximating models among the set of models considered (Burnham and Anderson 1998).

Dreissenid mussel

Model Rank	Model Terms	K	$r^2$	$\Delta i$	$w_i$
1	ORG, DEP, SLT, PCB, AORG*DEP*SLT*PCB	7	0.522	0.00	0.212
2	NULL	2	0.000	1.28	0.112
3	PCB, PCB*DEP	4	0.183	1.96	0.080
4	PCB, SLT, PCB*SLT	5	0.274	2.34	0.066
5	DEP	3	0.043	2.85	0.051
6	ORG	3	0.026	3.27	0.041
7	SLT	3	0.022	3.38	0.039
8	SLT, DEP*SLT	4	0.128	3.53	0.036
9	PCB	3	0.007	3.73	0.033
10	PCB, DEP	4	0.112	3.95	0.029

Table 10. Summary of *a priori* regression models to explain variance in dreissenid mussel densities collected in 2001. Model terms are the intercept (NULL), site depth (DEP), percent silt in sediments (SLT), percent organic content in sediments (ORG), and total PCB concentration (ng/g dry mass) in sediments (PCB). Column terms are the number of slope parameters plus the error and intercept (K), the difference between each model and the model with the minimum AICc value ( $\Delta i$ ), the relative “weight” of evidence for each model ( $w_i$ ), and the proportion of variance explained by each model ( $r^2$ ). A model with  $\Delta i < 2$  and large  $w_i$  is considered one of the best approximating models among the set of models considered (Burnham and Anderson 1998).

Figure 16. Mean densities ( $\pm 1$  standard error) of benthic macroinvertebrates collected during 2001 at four Lake Erie sites (from west to east): Maumee (Maumee R. Harbor), Sandusky (Sandusky R. Harbor), Grand (Grand R. Harbor), and Ashtabula (Ashtabula R. Harbor). All values are the mean of three replicates. Panels are as follows: Panel A: *Hexagenia* density, Panel B: chironomid density, and Panel C: dreissenid mussel density. Basins or harbor locations that share the same underline did not differ (two-way ANOVA, Tukey's post-hoc test,  $P > 0.05$ ). Note that y-axes differ.

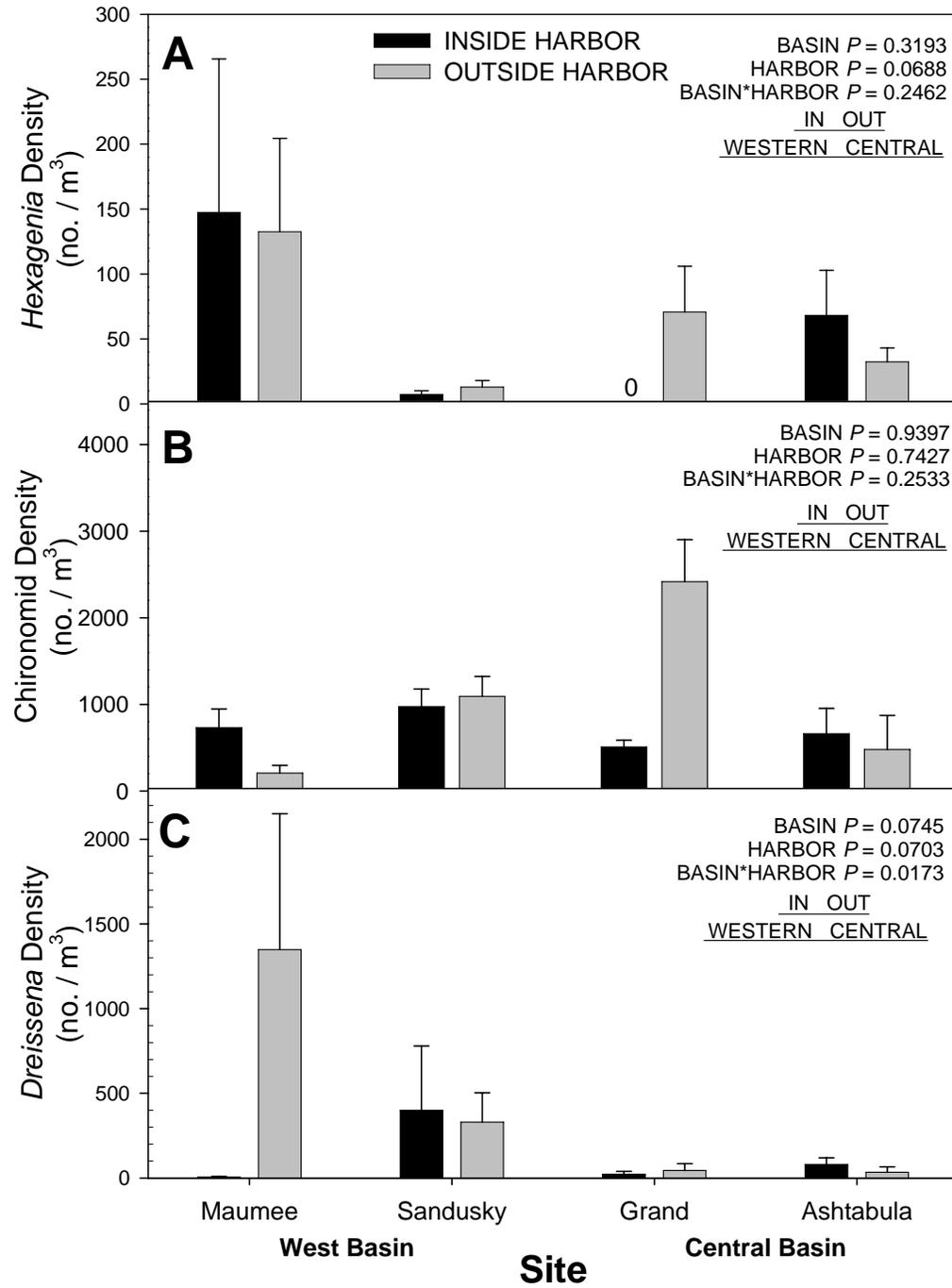


Figure 16.

Figure 17. Mean densities ( $\pm 1$  standard error) of benthic macroinvertebrates collected during 2001 at four Lake Erie sites (from west to east): Maumee (Maumee R. Harbor), Sandusky (Sandusky R. Harbor), Grand (Grand R. Harbor), and Ashtabula (Ashtabula R. Harbor). All values are the mean of three replicates. Panels are as follows: Panel A: Percent contribution of oligochaetes to total macroinvertebrate density (density of oligochaetes / total macroinvertebrate density), Panel B: amphipod density, and Panel C: total macroinvertebrate density. Basins or harbor locations that share the same underline did not differ (two-way ANOVA, Tukey's post-hoc test,  $P > 0.05$ ). Note that y-axes differ.

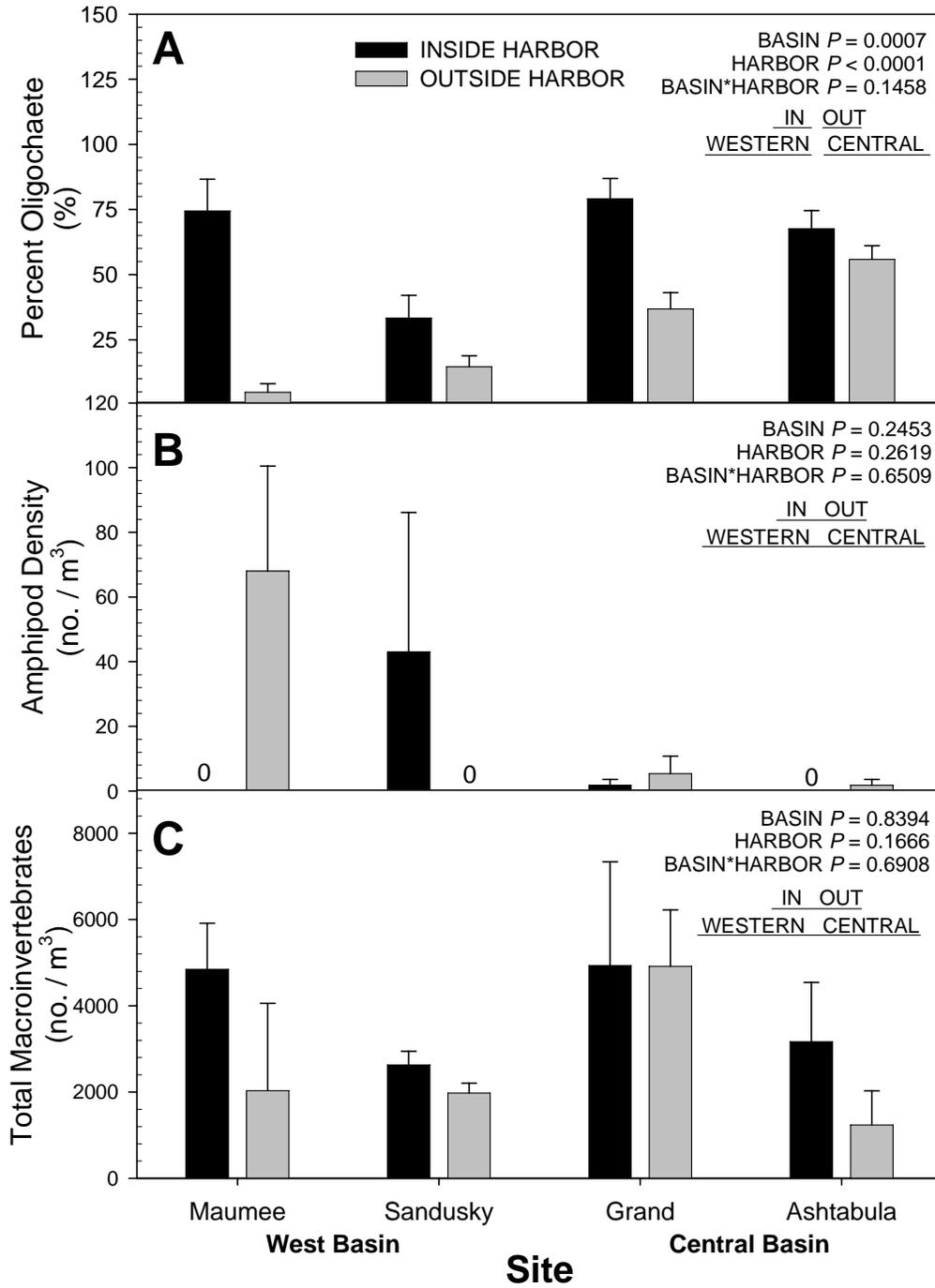


Figure 17.

Figure 18. Cluster analysis of site means sampled during 2001 and 2002 at four Lake Erie sites (from west to east): Maumee R. Harbor, Sandusky R. Harbor, Grand R. Harbor, and Ashtabula R. Harbor. The site codes are the site (MH=Maumee inside harbor, MO=Maumee outside harbor, SH=Sandusky inside harbor, SO=Sandusky outside harbor, GH=Grand inside harbor, GO=Grand outside harbor, AH=Ashtabula inside harbor, AO=Ashtabula outside harbor), followed by the year designation (01=2001 and 02=2002). This analysis used Sørensen's distance matrix and flexible beta linkage where  $\beta = -0.25$ . The dendrogram was scaled to Wishart's objective function converted to percent of information retained.

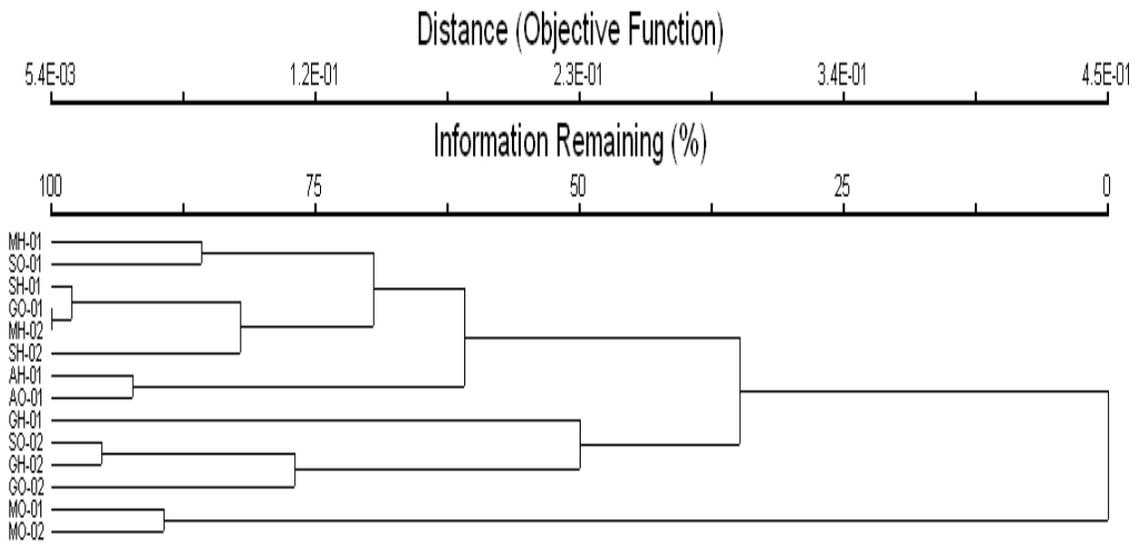


Figure 18.

Figure 19. Nonmetric multidimensional scaling (NMS) ordination of mean macroinvertebrate density and environmental variables sampled in 2001 and 2002 at Lake Erie nearshore sites. Coding indicates site and location (MH=Maumee Harbor, MO=Maumee outside harbor, SH=Sandusky Harbor, SO=Sandusky outside harbor, GH=Grand Harbor, GO=Grand outside harbor, AH=Ashtabula Harbor, AO=Ashtabula outside harbor), followed by the year sampled (01=2001 and 02=2002). Polygons encircle arbitrarily numbered clusters generated from Sørensen's distance matrix and flexible beta linkages where  $\beta = -0.25$ . Variables along each axis indicate the relationship between each point and axis scores (Kendall's  $\tau$ ;  $\alpha = 0.003$ ). Note: the designation bivalve excluded dreissenid mussels.

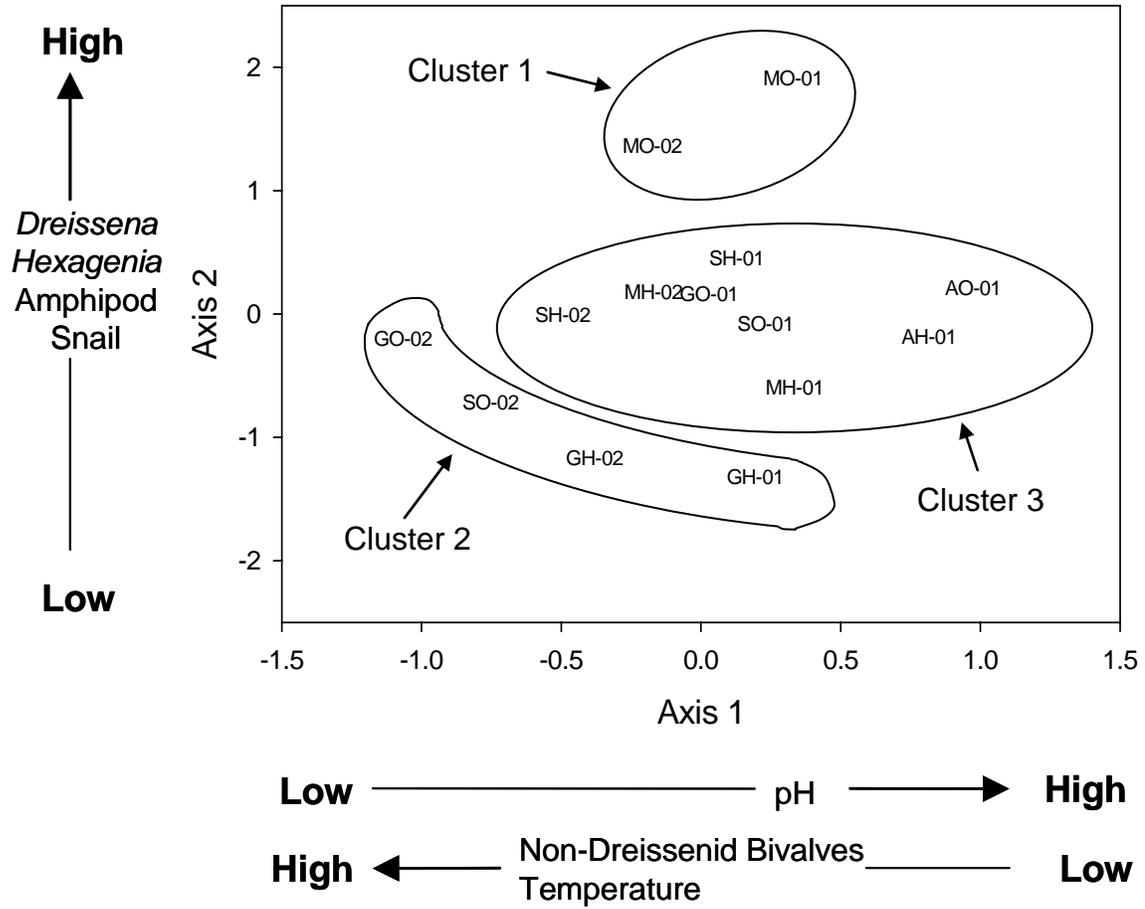


Figure 19.

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## **APPENDIX**

### **PCB UPTAKE AND DEPURATION BY SMALLMOUTH BASS FEEDING ON EXOTIC ROUND GOBY PREY**

#### **OBJECTIVE**

To experimental quantify uptake and depuration rates of smallmouth bass fed PCB-spiked round gobies.

#### **METHODS**

We collected experimental smallmouth bass during November 2002 by electrofishing. Rather than use fish directly from Lake Erie, we sampled fish from local reservoirs that likely had lower initial PCB body burdens in smallmouth bass: Griggs Reservoir, Piedmont, and Alum Creek Reservoir. Other sampling in these reservoirs documents their low PCB contamination, relative to Lake Erie (personal communication, Dennis Mishne, Ohio Environmental Protection Agency). To reduce mortality, we

transported them with aeration and methane tricainesulfonate (MS-222). At the laboratory, we assigned each fish at random to either individual aquaria (38-95 L volume, depending on fish size) within a walk-in environmental chamber or compartments in a 400-gallon recirculation system. We ensured stable water temperatures (19-21°C), aeration, activated carbon filters, a 14:10 light:dark photoperiod, and water exchange with dechlorinated city water (at least every 48 h). We monitored pH, nitrates, ammonia, hardness, and alkalinity (Freshwater Aquaculture Test Kit, LaMotte Co.), in addition to oxygen and temperature (YSI Model 57 oxygen meter) at least once per 72 to 96 h.

We needed the 9 months between capture and the start of the experiment to feed-train smallmouth bass to eat dead minnows and eliminate their initial PCB body residues. Beginning about 200 d before the experiment, we started feeding experimental smallmouth bass fathead minnows *Pimephales promelas* (R & R Bait, Columbus, OH, USA). At first, we fed experimental smallmouth bass fathead minnows at 2% of their body mass/d. Through time, we switched live with dead fathead minnows (our attempts to use trout chow were unsuccessful). We selected only those fish that fed on dead fish daily for use in the experiment.

The uptake experiment began on 12 September 2003 (Day 1). During the uptake period (days 1 to 30), we fed experimental smallmouth bass PCB-spiked round gobies (see below); however, during the clearance period we used fathead minnows, because of the lack of uncontaminated round gobies. Before the experiment, fish were measured for length (mm TL) and mass (g). We used the Wisconsin bioenergetics model software (Hanson et al. 1997), using the subadult and adult smallmouth bass model (Whitledge et al. 2003), caloric densities for round gobies (unpublished data) and fathead minnows

(Gill and Weatherley 1984 for *P. notatus*) to estimate maintenance rations for experimental smallmouth bass (i.e., zero weight change). As such, we fed experimental smallmouth bass round gobies at a rate of  $1.7 \pm 0.1$  % of their body mass/d during the uptake period and fathead minnow at a rate of  $1.2 \pm 0.1$  % of their body mass/d during the clearance phase. During the experiment, we maintained temperatures at  $20.5 \pm 0.1^\circ\text{C}$  (range:  $19.5 - 21.2^\circ\text{C}$ ).

We fed PCB-spiked round gobies to experimental smallmouth bass during a 30-d uptake period. These round gobies were collected by trawling in the central basin of Lake Erie (mainly off Chagrin and Perry, OH, USA, at 10-15 m depth), and then frozen until injection. Into each thawed round goby, we injected 50-100  $\mu\text{L}$  of Arochlor 1254 (AccuStandard Inc., New Haven, CT) at a concentration of 250 ng/g (in vegetable oil) of per g of round goby directly into multiple locations in dorsal muscle tissue (to prevent leakage), and then re-froze daily rations individually. Our expectation was that these round gobies have low PCB body burdens, relative to those found near point-sources of PCBs. By adding a standard amount of Arochlor 1254, we hoped to homogenize PCB concentration and congener pattern among round gobies at a concentration that matched field levels. For similar sites to ours, round gobies range from 118 to 256 ng/g (Kwon et al. 2006); however, in Michigan tributaries of the Great Lakes, labeled as Areas of Concern by the International Joint Commission, round gobies range from 81 to 4,710 ng/g total PCB (Hanari et al 2004).

We selected fish for sacrifice at random. During the uptake period, we sampled fish on days 0, 10, 20, and 30 (3 fish/d), 24 h after their last feeding to allow for clearance of food. During the clearance period, we sacrificed fish on days 45, 75, and 115 (3

fish/d). For each fish, we measured length (nearest 0.1 mm TL) and wet mass (nearest 0.1 g), removed stomach contents, and extracted sagittal otoliths for age estimation. Then, fish were frozen pending analysis. We analyzed fish according to established procedures in

We calculated trophic transfer efficiency ( $\gamma$ ) for each smallmouth bass as in Madenjian et al. (2000):  $(\Delta \text{ PCB body burden}) / (\text{amount of PCBs ingested})$ , where  $\Delta$  PCB body burden where is the increase in the PCB body burden of smallmouth bass during the experiment (in ng of PCB) and the amount of PCBs ingested represents the weight of PCBs in the food eaten by experimental smallmouth bass during the course of the experiment (in ng of PCB). Increase in body burden was calculated as in Madenjian et al. 2000):  $\Delta \text{ PCB body burden} = ([\text{PCB}_f] \times W_f) - ([\text{PCB}_i] \times W_i)$ , where  $[\text{PCB}_f]$  represents the PCB concentration at the end of the experiment (in ng/g wet mass),  $W_f$  is the final weight at the end of the experiment (g wet mass),  $[\text{PCB}_i]$  is the mean PCB concentration (ng/g wet mass) in experimental smallmouth bass at the start of the experiment, and  $W_i$  is the starting mass of the experimental smallmouth bass (g wet mass). We used the mean value of day 0 fish as  $W_i$  for all fish. Because weighing fish severely disrupted their regularity in eating dead fish, we calculated  $W_i$  with the previously mentioned Wisconsin smallmouth bass bioenergetics model (Hanson et al. 1997; Whitley et al. 2003).

Examining the data revealed that depuration was negligible in our experiments (Peter Landrum, personal communication,). Therefore, we calculated assimilation efficiency (AE) based a simplification of Kukkonen and Landrum (1995)

as:  $AE = [PCB_f] / (Fr \times C_{food} \times T)$ , where  $Fr$  is daily feeding rate (g food / g fish / d),  $C_{food}$  is the PCB concentration (ng/g) in spiked round gobies fed to experimental smallmouth bass, and  $T$  is the duration of uptake (d).

## RESULTS AND DISCUSSION

Our procedure to PCB-spike field-collected round gobies was successful in approximating the lower range of PCB concentrations found in Lake Erie round gobies. Compared with Kwon et al. (2006), who found total PCBs of 118-256 ng/g in round gobies, our mean value of 130.4 ng/g was realistic (Figure 1A-B). Injecting PCBs via a vegetable oil carrier did not appear to result in appreciable change in lipid content of PCB-spiked round gobies, compared with field-caught round gobies (Figure 1C).

During the experiment, total PCB concentrations increased during the uptake phase, and then started to stabilize during the depuration phase (Figure 2A-C). However, it appears that there was no clear depuration of PCBs during the second half of the experiment. The apparent decrease in PCB body burden (Figure 2B) was driven by the smaller sizes of smallmouth bass during the depuration phase (Figure 3); the apparent decrease in lipid-normalized PCB concentration (Figure 2C) likely was driven by increases in lipid content during the experiment (Figure 4).

It appears that our underestimation of the time for PCB clearance and the size bias introduced by our randomization procedure doomed this experiment. Apparently, 200 d was insufficient to reduce PCB residues in our field-collected smallmouth bass to negligible levels, relative to the small increases in PCB concentrations during our uptake

phase of the experiment (Peter Landrum, personal communication). Although low, the non-zero concentrations of PCB residues in fathead minnows likely would necessitate an even longer period (Figure 1). More importantly, it appears that our randomization of fish order resulted in larger fish during the uptake phase (especially days 20, 20 and 30; Figure 4). As a result, our estimates of trophic transfer efficiency (Madenjian et al. 2000) and assimilation efficiency (Kukkonen and Landrum 1995) were all well above 100% (Table 1).

We suggest post-hoc amendments to the experimental design that could yield meaningful results. Instead of randomization, a stratified design may have produced interpretable results, selecting one small, one medium, and one large fish for sacrifice during each sampling day of the experiment. Also, increasing feeding rate and sample size could off-set initial variation in PCB residues in experimental fish. The use of cultured juvenile fish was not an option, because we wanted uptake and elimination rates of adult smallmouth bass.

Day	Source Lake	TL Start	TL End	Mass Start	Mass End	% Lipid End	[PCB] ng/g	Food g	[PCB] food ng/g	$\gamma$ %	AE %
0	Alum	231	231	151.8	151.8	2.5	29.6	0.0	130.4	216	390
0	Griggs	289	289	269.5	269.5	2.6	31.5	0.0	130.4	285	570
0	Griggs	204	204	75.4	75.4	1.8	35.6	0.0	130.4	289	468
10	Griggs	258	264	211.6	209.2	3.3	74.1	30.8	130.4	175	270
10	Griggs	284	285	310.6	311.6	2.8	79.9	40.1	130.4	266	390
10	Griggs	257	300	205.8	202.8	3.8	87.8	29.6	130.4	85	190
20	Griggs	279	288	240.8	237.2	4.0	95.9	65.6	130.4	148	231
20	Alum	363	365	601.2	614.4	3.8	94.7	112.0	130.4	105	159
20	Alum	218	226	131.5	117.9	3.2	72.0	38.3	130.4	122	202
30	Griggs	278	275	292.1	283.0	3.8	98.8	95.9	130.4	.	.
30	Griggs	290	283	247.0	249.1	3.3	92.5	110.4	130.4	.	.
30	Alum	257	238	219.0	205.0	5.7	96.3	79.9	130.4	.	.
45	Alum	215	230	136.0	136.0	3.7	81.2	57.2	130.4	.	.
45	Alum	238	234	150.2	150.2	3.8	86.3	68.8	130.4	.	.
45	Alum	202	177	214.0	214.0	3.8	114.2	57.5	130.4	.	.
75	Piedmont	226	234	142.0	142.0	6.6	84.9	64.1	130.4	.	.
75	Griggs	250	259	201.0	201.0	5.4	111.1	82.1	130.4	.	.
75	Alum	225	225	127.0	127.0	5.7	94.7	62.4	130.4	.	.
115	Piedmont	256	280	231.0	231.0	4.9	99.8	84.7	130.4	.	.
115	Piedmont	255	246	145.0	145.0	4.7	83.7	72.6	130.4	.	.
115	Alum	232	231	146.0	146.0	6.4	97.7	64.0	130.4	.	.

Table 11. Summary table of a laboratory experiment with a 30-d uptake period, followed by an 85-d depuration period. The table includes is the day of experiment when the fish was killed (Day), the lake from which each fish was collected (Source Lake), starting total length in mm (TL Start), final mm total length (TL End), estimated mass in g at day 0 (Mass Start), final mass in g (Mass End), final wet lipid concentration (% lipid), final total PCB concentration in ng/g wet mass ([PCB]), total amount of food fed during the experiment (Food), mean PCB concentration in spiked-round goby fed to experimental smallmouth bass ([PCB] food), trophic transfer efficiency according to Madenjian et al. (2000;  $\gamma$ ), and assimilation efficiency according to Kukkonen and Landrum (1995; AE).

Figure 20. Summary data for a 30-d uptake experiment, followed by an 85-d depuration period. During the uptake period, we fed smallmouth bass field-collected round gobies ('clean') that had been spiked with 250 ng/g of Arochlor 1254 ('spiked'). During the 85-d clearance period, smallmouth bass were fed fathead minnows ('FHM'). Data are showed as total PCB concentration (top panel), lipid-normalized PCB concentration (middle panel), and percent lipids (bottom panel). All values are expressed on a wet-mass basis. Error bars depict one standard error of the mean.

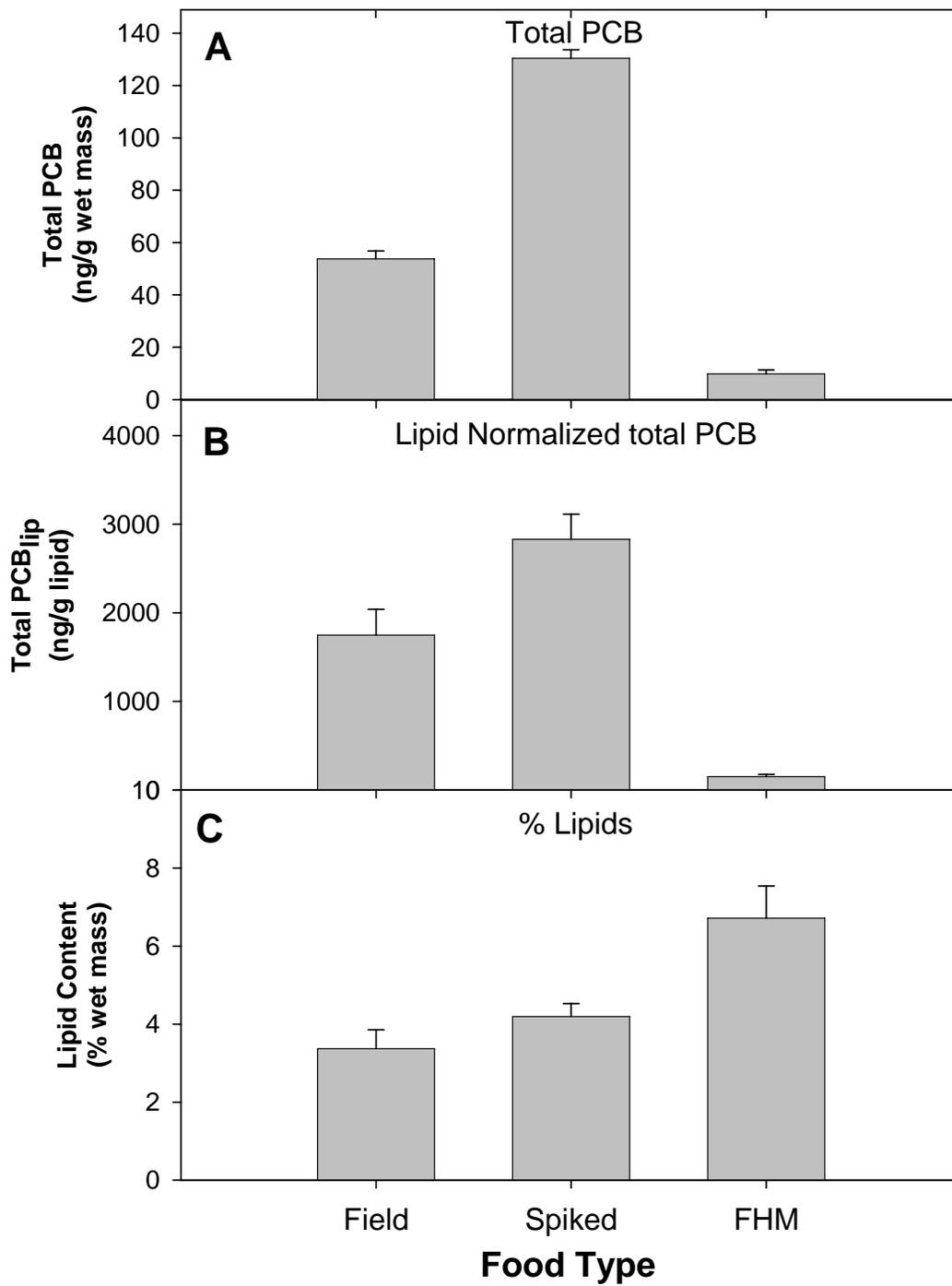


Figure 20.

Figure 21. Summary PCB data for experimental smallmouth bass in a 30-d uptake experiment, followed by an 85-d depuration period. PCB concentrations are expressed as total PCB concentration (top panel; ng/g wet mass), total body burden (middle panel; ng/g PCB x g fish), and lipid-normalized PCB concentration (bottom panel; ng/g lipid). All values are expressed on a wet-mass basis. The dashed vertical line demarcates the uptake and clearance periods. Error bars depict one standard error of the mean.

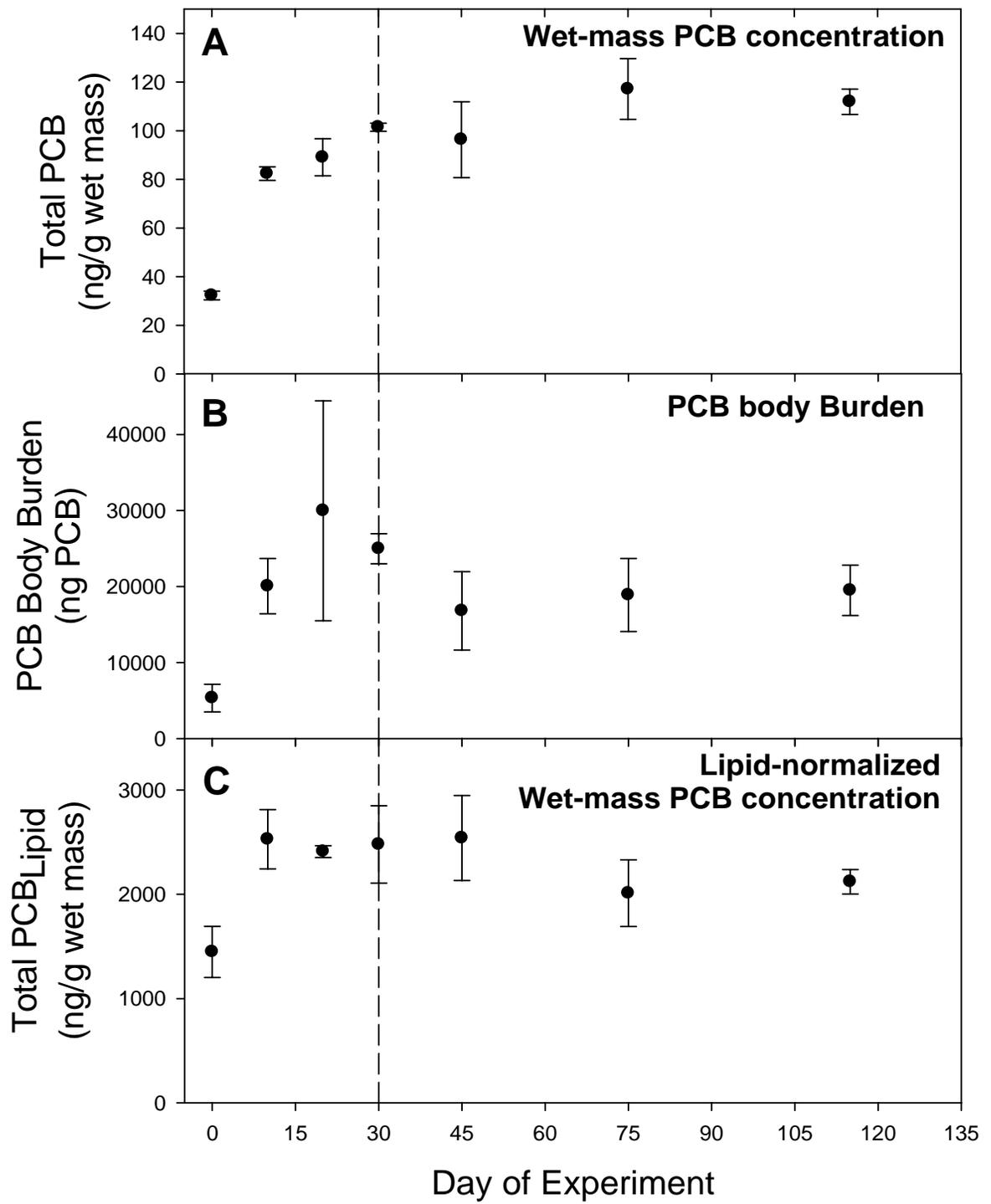


Figure 21.

Figure 22. Starting sizes of experimental smallmouth bass in a 30-d uptake experiment, followed by an 85-d depuration period. Fish size is expressed as starting mm total length (top panel) and starting g wet mass (bottom panel). The dashed vertical line demarcates the uptake and clearance periods. Error bars depict one standard error of the mean.

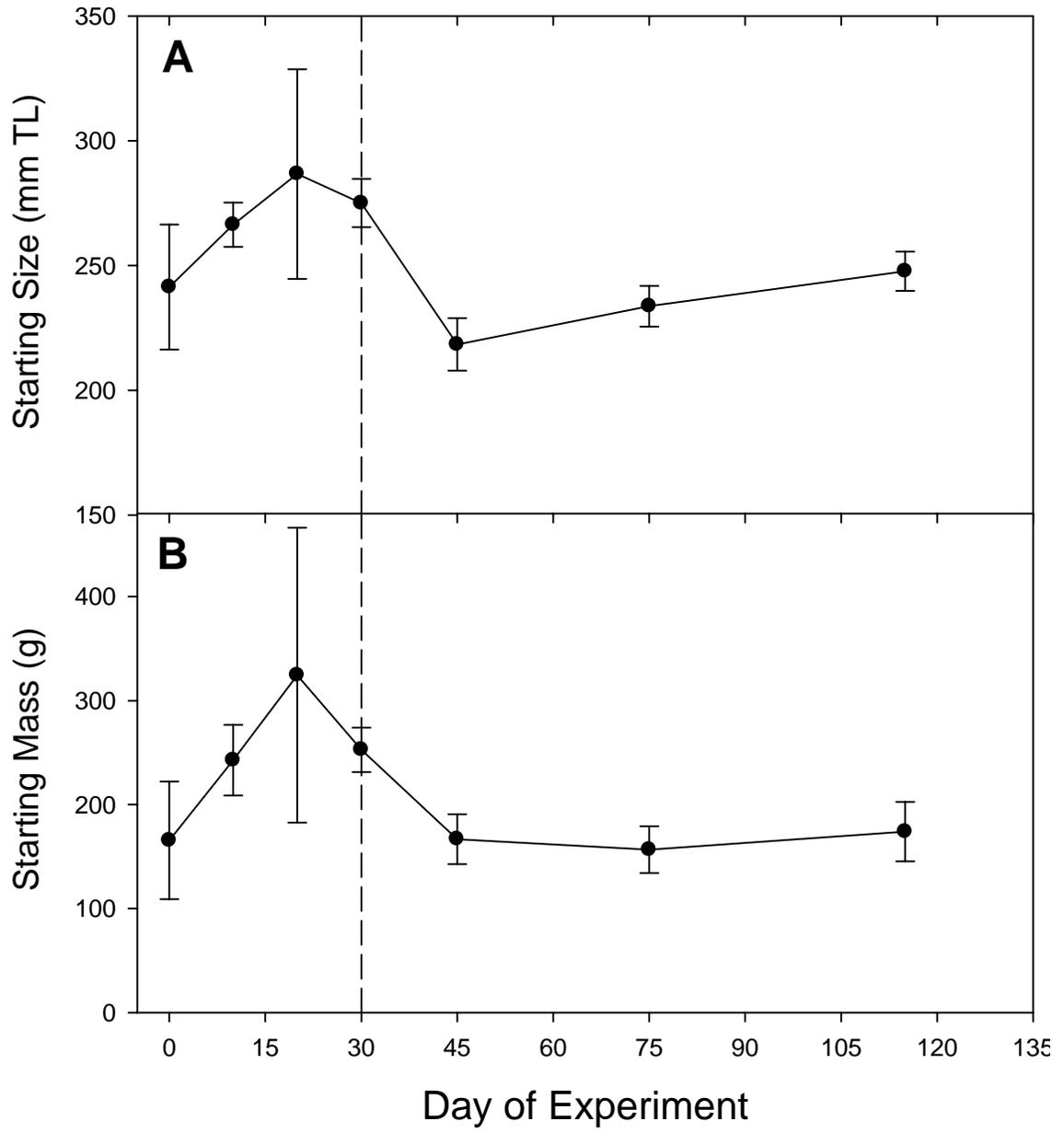


Figure 22.

Figure 23. Growth and lipid change in experimental smallmouth bass during a 30-d uptake experiment, followed by an 85-d depuration period. Changes are expressed as percent lipids (top panel), change in lipids from Day 0 (middle panel), and change in wet mass (bottom panel). All values are expressed on a wet-mass basis. The dashed vertical line demarcates the uptake and clearance periods. Error bars depict one standard error of the mean.

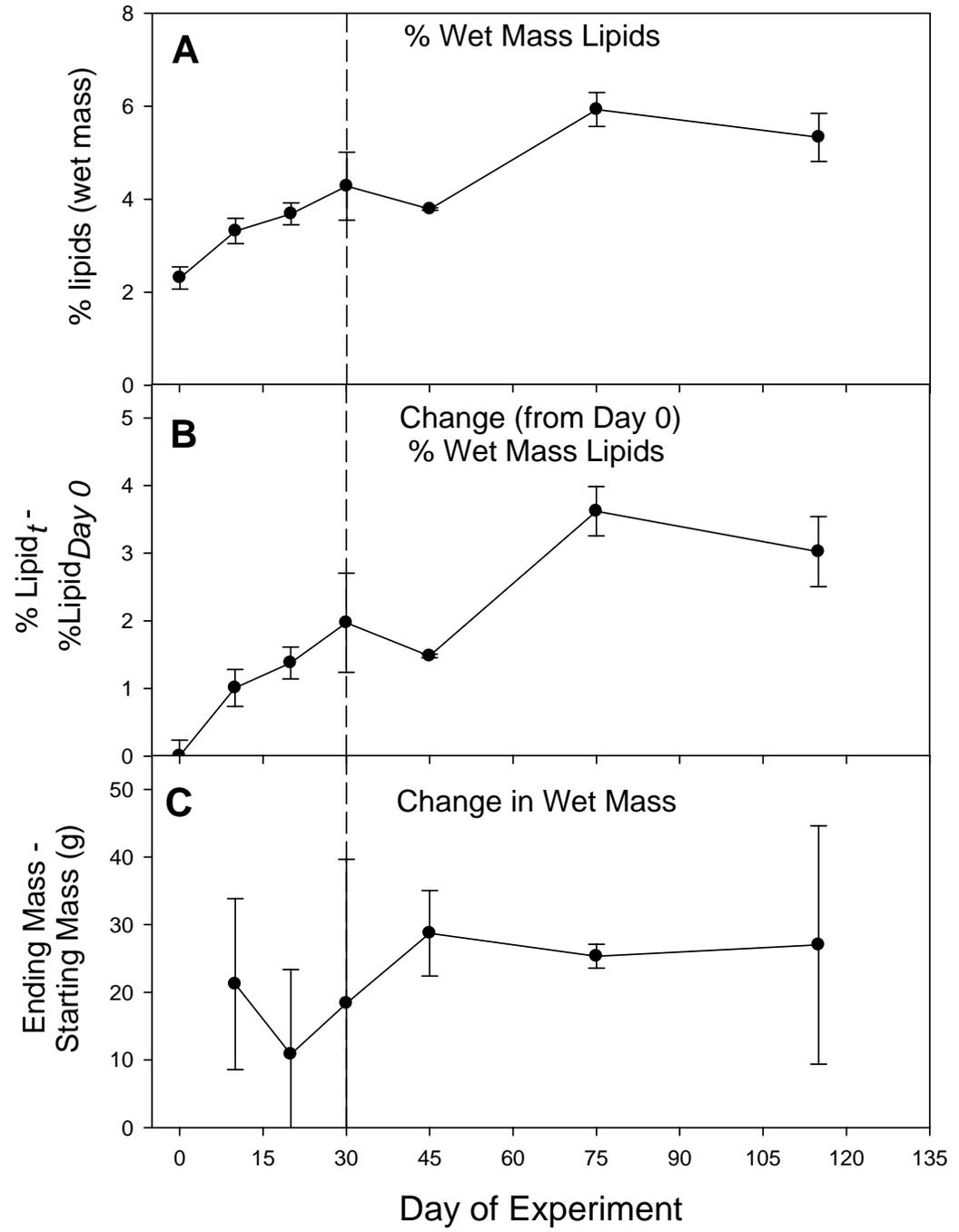


Figure 23.