

**FOOD WEB AND FEEDING INFLUENCES
ON PCB BIOAVAILABILITY**

FINAL REPORT

LAKE ERIE PROTECTION FUND

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Project Abstract

Understanding how exotic organisms influence native food webs is paramount to managing the Lake Erie fishery. We assessed this by combining a field study (2000-2002) at four sites in western (Maumee and Sandusky harbors) and central (Grand and Ashtabula harbors) Lake Erie with historical fish tissue data (1990-2005) and a laboratory bioassay experiment. We demonstrated biomagnification of polychlorinated biphenyls (PCBs) by an exotic species component (comprised of round goby *Neogobius melanostomus* and dreissenid mussels *Dreissena* spp.) to native smallmouth bass *Micropterus dolomieu* and largemouth bass *Micropterus salmoides*. Both PCB concentration and average chlorination increased with trophic level similarly at all our sites, despite differences in sediment PCB levels. Historical data revealed that Arochlor 1260 residues in benthic piscivores and molluscivores, which are likely to consume exotic species increased through time, whereas pelagic piscivores and benthic omnivores did not. To assess how dreissenid mussels affect benthic macroinvertebrate communities, we quantified sediment characteristics, PCB concentration in sediments, and macroinvertebrate densities, sampling location inside and outside of harbors. Although recovery was apparent, benthic communities inside harbors still suffered from organic and industrial pollution, compared with areas outside; however, benthic macroinvertebrates varied little between basins. Rather, dreissenid mussels appeared to drive community composition at the local scale. Contrary to expectations, sediment physical characteristics did not explain variation in macroinvertebrate density. To assess how feeding differences among benthic macroinvertebrates affects PCB transfer, we conducted a laboratory bioassay experiment, spiking sediments from Maumee, Sandusky, and Grand harbors with ^{14}C labeled 2,2',4,4',5,5'

hexachlorobiphenyl (HCBP). We quantified uptake rates and bioaccumulation factors over 48 h. Across all sites, uptake rates ranked *C. riparius* > *L. variegatus* = *H. azteca*. For bioaccumulation factors, organisms ranked *L. variegatus* > *C. riparius* > *H. azteca*. These differences can be explained by species-specific feeding habits and location within sediments. Although we found differences in uptake rates between locations inside and outside of Maumee and Grand, they were not related to sediment organic content. Overall, because round gobies consume benthic invertebrates, they can link PCBs in benthic sediments to upper trophic levels. However, the degree to which round gobies link benthic and pelagic food webs depends on feeding habits of prey in the trophic level below, as well as piscivores in the trophic level above.

Executive Summary

We describe research that quantifies how native and non-native (henceforth exotic) benthic organisms influence community and ecosystem processes in Lake Erie. As aquatic ecosystems recover from years of excessive inputs of nutrients and industrial pollution, the influence of benthic food webs on the overall ecosystem is predicted to increase. We assessed this hypothesis with a combination of field studies and laboratory experiments.

By combining a field study with historical data, we demonstrated biomagnification of polychlorinated biphenyls (PCBs) in a Lake Erie food chain by an exotic species component (comprised of round goby *Neogobius melanostomus* and dreissenid mussels *Dreissena* spp.) to native terminal predators, namely smallmouth bass *Micropterus dolomieu* and largemouth bass *Micropterus salmoides* (Chapter 1). In the field study during 2000, 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, PCB biomagnification was more pronounced in the central than the western basin. Historical data (1990-2005) revealed that benthic piscivores and molluscivores that consumed exotic species had increasing Arochlor 1260 (the only Arochlor mixture that met all of our data inclusion criteria) 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 biomagnification was consistent across fish size and life stage, location, and time.

Recovering benthic macroinvertebrate communities in Lake Erie appear influenced by dreissenid mussels and dreissenid mussel interactions with PCBs and organic content of sediments (Chapter 2). To assess the role of dreissenid mussels in structuring benthic macroinvertebrate communities, 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 benthic macroinvertebrate communities, compared with sediment characteristics and sediment contamination? Although recovery was apparent, areas inside harbors still suffered 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 at 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 have negatively affected benthic communities in the west basin, industrial pollution appears to have influenced benthos in the central basin.

Bioassays using spiked sediments were performed to determine how feeding behavior and sediment location influenced 2,2',4,4',5,5' hexachlorobiphenyl (HCBP) uptake (Chapter 3). We spiked sediments from locations inside and outside at the Maumee, Sandusky, and Grand sites with ¹⁴C labeled HCBP. We placed three organisms with different feeding strategies,

Lumbriculus variegatus, *Chironomus riparius*, and *Hyaella azteca*, in the spiked sediments. We determined uptake rates (ks) and bioaccumulation factors (BAFs) for each organism in sediments from each site for 48 h. *C. riparius* had significantly higher uptake rates than *L. variegatus* and *H. azteca* when sediments from all locations were taken into consideration; *L. variegatus* and *H. azteca* did not differ significantly. At all locations, *L. variegatus* had the highest BAFs. *C. riparius* consistently had intermediate BAFs, whereas *H. azteca* had the lowest BAFs for all sediments. *C. riparius* had the highest uptake rates because of constant, nonselective feeding and infaunal behavior. *L. variegatus* may have had lower uptake rates because of selective feeding on fine sediment with high organic carbon content and an avoidance response to the other organisms. *H. azteca* may have had lower uptake rates because of epibenthic behavior and an avoidance response that led them to spend a disproportionate amount of time in the water column. *L. variegatus* had the highest BAFs likely owing to their inability to eliminate HCBP relative to the other organisms. While differences were found between uptake rates at locations inside and outside harbor at Maumee and Grand, no pattern could be established with sediment total organic content. In contrast, no differences occurred between inside and outside harbor locations at Sandusky in the western basin.

Overall, we conclude that nutrient and contaminant inputs into Lake Erie continue to decline, but we expect that the importance of benthic transfer pathways and biotic interactions to increase. As a result, differences in feeding habits of benthic invertebrates and proliferation of exotic species are important in determining the bioavailability of PCBs sequestered in sediments. Because round gobies consume benthic invertebrates, they can link PCBs in benthic sediments to upper trophic levels. However, the degree to which round gobies link benthic and pelagic food

webs depends on feeding habits of prey in the trophic level below, as well as piscivores in the trophic level above.

Products Supported by or Associated with This Project

Graduate students at Ohio State University supported by this project:

- Gene Wook Kim. 2007. PhD Dissertation (Department of Evolution, Ecology, and Organismal Biology). Trophic transfer of energy and polychlorinated biphenyls by native and exotic fish in Lake Erie. 184 pages.
- Lynne Michelle Martin. 2005. MS Thesis (Department of Entomology). Determination of polychlorinated biphenyl levels in Cyprinidae and a trophic level assessment of potential biomagnification of polychlorinated biphenyls in *Chelydra serpentina* from the Lake Erie region. 118 pages.
- James Matthew Lawrence. 2004. MS Thesis (Department of Entomology). Bioaccumulation of sediment-associated 2,2',4,4',5,5' hexachlorobiphenyl by *Chironomus riparius*, *Lumbriculus variegatus*, and *Hyalella azteca*. 71 pages.

Publications supported by or in association with this project:

- 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.
- Kim, G.W., T-D Kwon, J.R. Flanary, R.A. Stein, E.A. Marschall, and S.W. Fisher. *In preparation*. Exotic species influence biomagnification of polychlorinated biphenyls in a Great Lakes benthic food web. (29 page of text, 2 tables, and 7 figures)
- Kim, G.W., S.W. Fisher, R.A. Stein, and E.A. Marschall. *In preparation*. The role of dreissenid mussels, sediment characteristics, and organic pollutants in structuring nearshore benthic macroinvertebrate communities in Lake Erie. (20 pages of text, 8 tables, 4 figures)
- Kim, G.W., M.R. Gearhiser, C.T. Knight, E.A. Marschall, S.W. Fisher, and R.A. Stein. *In Review at Canadian Journal of Fisheries and Aquatic Sciences*. Selective predation by smallmouth bass on exotic round gobies over historical Lake Erie prey: comparative results from laboratory- and field-based estimates.
- Kim, G.W., A.P. Wintzer, T.K. Menker, R.A. Stein, J.M. Dettmers, and D.R. DeVries. *Under revision at editor's request at Canadian Journal of Fisheries and Aquatic Sciences*. Benthic-pelagic habitat coupling by omnivorous gizzard shad along a detritus-quality gradient: a multi-scale study.

Conference presentations supported by or in association with this project:

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- Kim, G.W., A.N. Patel, T.K. Menker, J.M. Dettmers, R.A. Wright, D.R. DeVries, and R.A. Stein. 2004. Detritus quality and fish density influence gizzard shad growth and survival. Poster presentation at the 44th Ohio Fish and Wildlife Conference, Columbus, Ohio, 6 February 2004.
- Kim, G.W., T-D Kwon, M.R. Gearhiser, E.A. Marschall, S.W. Fisher, and R.A. Stein. 2003. PCB Biomagnification in the zebra mussel - round goby - smallmouth bass food chain in Lake Erie. Platform presentation at the 133rd Annual Meeting of the American Fisheries Society, Québec City, Québec, Canada, 10-14 August 2003.
- Kim, G.W., A.N. Patel, T.K. Menker, J.M. Dettmers, R.A. Wright, D.R. DeVries, and R.A. Stein. 2002. Detritus quality and fish density influence gizzard shad growth and survival. Poster presentation at the 132nd Annual Meeting of the American Fisheries Society, Baltimore, MD, 18-22 August 2002.
- Kim, G.W., M.R. Gearhiser, E.A. Marschall, C. Knight, S.W. Fisher, and R.A. Stein. 2002. Comparing laboratory and field estimates of predation by smallmouth bass on round goby, emerald shiner, and crayfish. Platform presentation at the 132nd Annual Meeting of the American Fisheries Society, Baltimore, MD, 18-22 August 2002.
- Kim, G.W., M. R. Gearhiser, C.T. Knight, E. A. Marschall, S. W. Fisher, and R. A. Stein. 2002. Selective predation by smallmouth bass on round goby, emerald shiner, and crayfish. Platform presentation at the 45th Annual Meeting of the International Association for Great Lakes Research, Winnipeg, Manitoba, 2-6 June 2002.
- Kim, G.W., E. A. Marschall, S.W. Fisher, and R.A. Stein. 2002. Lake Erie benthic food webs: effect of exotic species on energy and PCB flow. Invited platform presentation at the Ohio Division of Wildlife Annual Research Review Meeting, Columbus, Ohio, 14-15 February 2002.

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- Best Fisheries Poster Award. The 2004 Annual Ohio Fish and Wildlife Conference, Columbus, Ohio, 6 February 2004.
- IAGLR/Hydrolab 2002 Best Student Presentation Award. The 45th Annual Meeting of the International Association for Great Lakes Research, Winnipeg, Manitoba, 2-6 June 2002.
- EEOB Departmental “Darwin Award”. Best poster (tied) presented by an EEOB graduate student during 2002. The Ohio State University Department of Evolution, Ecology, and Organismal Biology.
- AFS Best Student Poster Award. The 132nd National Meeting of the American Fisheries Society, Baltimore, MD, 18-22 August 2002.

Media and press associated with this project:

- Radio Interview, titled “Lake Erie invaders pass harmful agents up food chain”. Interviewed by Carolyn Gramling (WOSU Science Reporter, AAAS Mass Media Fellow) about Gene Kim’s dissertation research. Aired 10/22/03 on WOSU 820 AM, Columbus, OH.
http://www.publicbroadcasting.net/wosu/news.newsmain?action=article&ARTICLE_ID=560065
- Radio Interview, titled “Invasives altering Great Lakes food web”. Interviewed by Carolyn Gramling (Great Lakes Radio Consortium) about Gene Kim’s dissertation research. Aired 12/15/03 on “The Environment Report” by the Great Lakes Radio Consortium.
http://www.gllrc.org/story.php3?story_id=2123

Chapter 1

Exotic species influence biomagnification of polychlorinated biphenyls in a Great Lakes benthic food web

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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. 2005). 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 μ m 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 H₂; and makeup gas N₂.

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 ¹³C-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 μm 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 $28 \pm 4\%$ 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 1A). 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 1B). 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 1C). In the western basin, total PCB_{carbon} concentrations averaged 3.2 times higher at locations outside of harbors versus inside (Figure 1C; 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 ± 4 mm TL and 9.5 ± 1.2 g wet mass. Largemouth bass size did not differ among sites (TL ANOVA $df = 2, 9$, $P = 0.108$), averaging 269 ± 9 mm TL and 303.0 ± 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 ± 8 mm TL and 289.8 ± 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 2A). 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 ± 0.1 , 3.1 ± 0.4 , 4.2 ± 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 2A). 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 2A).

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 ± 1.4 , 78.1 ± 5.7 , 256.7 ± 26.1 , and 352.3 ± 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 2B). 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 2C).

When biota were considered together, total lipids explained 47% of variation in PCB concentration (Figure 3). 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 ± 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 4A-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 4A-D). This pattern was similar for all species, despite differences in the magnitude of BSAF values (Figure 4A-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 5A-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 ≥ 1 for nearly all congeners, despite higher values and variability in western basin smallmouth bass (Figure 5B and 5E). Compared between round gobies and their dreissenid prey, TTF_{lip} was generally higher for central versus western basin round gobies (Figure 5C and 5F); 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 5C and 5F).

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 (Figure 6). 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 6) 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 7). First, in walleye and white bass, Arochlor 1260 concentrations did not change greatly over time (Figure 7); 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 7). Third, in freshwater drum, only wet-mass Arochlor 1260 and lipid levels increased over time (Figure 7). Fourth, in white perch and smallmouth bass, both wet mass and lipid normalized Arochlor 1260 values increased over time (Figure 7). 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 whit

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 re-construct estimates to match those 24 PCB congeners, our samples averaged 34.6 ± 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. 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. 1994). 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 life 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 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 (Mayura 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. 2005). 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.

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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 _{carbon} (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 _{carbon} (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 Legend

Figure 1. 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 ± 1 standard error.

Figure 2. 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 ± 1 standard error.

Figure 3. 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 4. 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 5. 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 6. 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 7. 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.

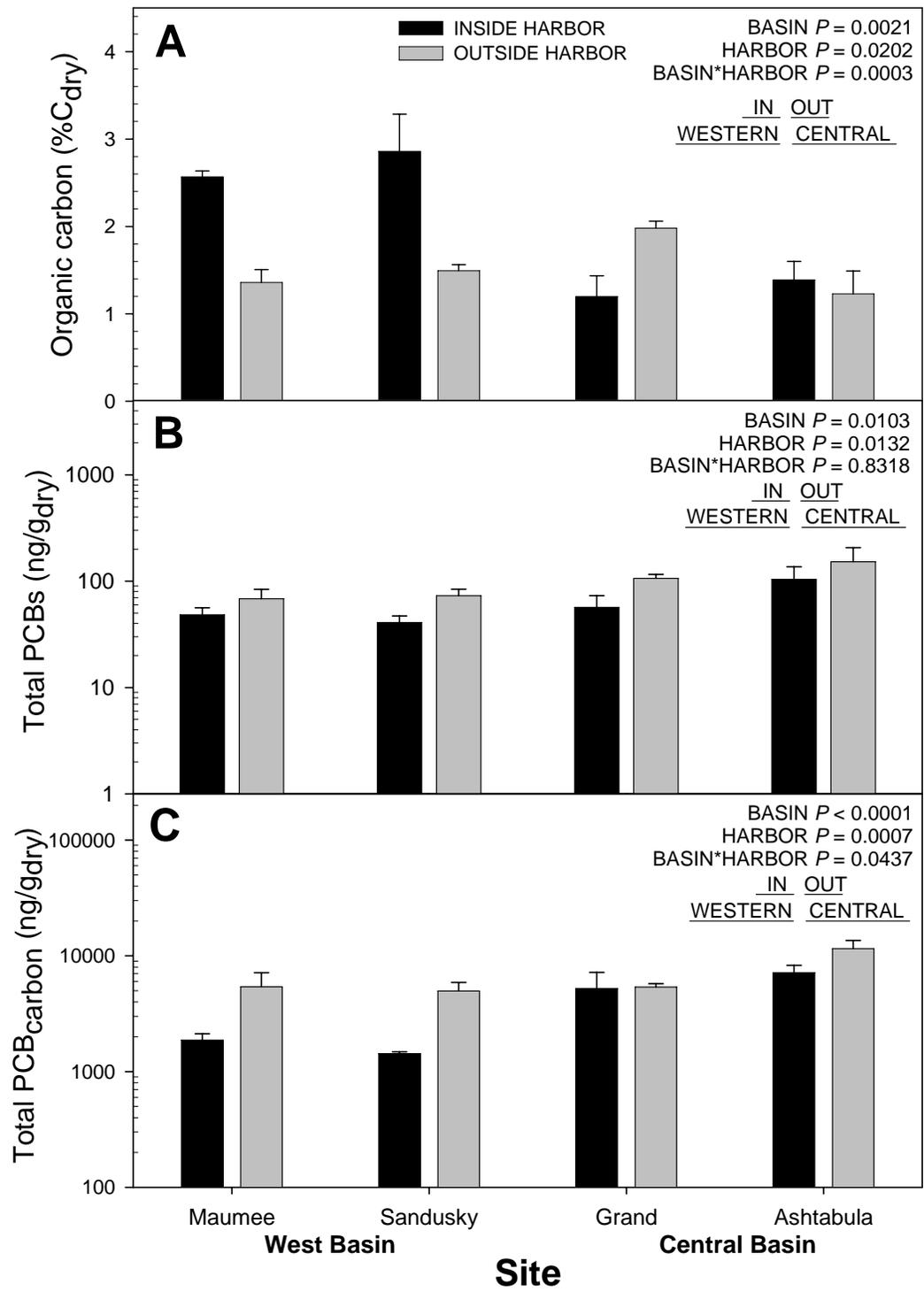


Figure 1.

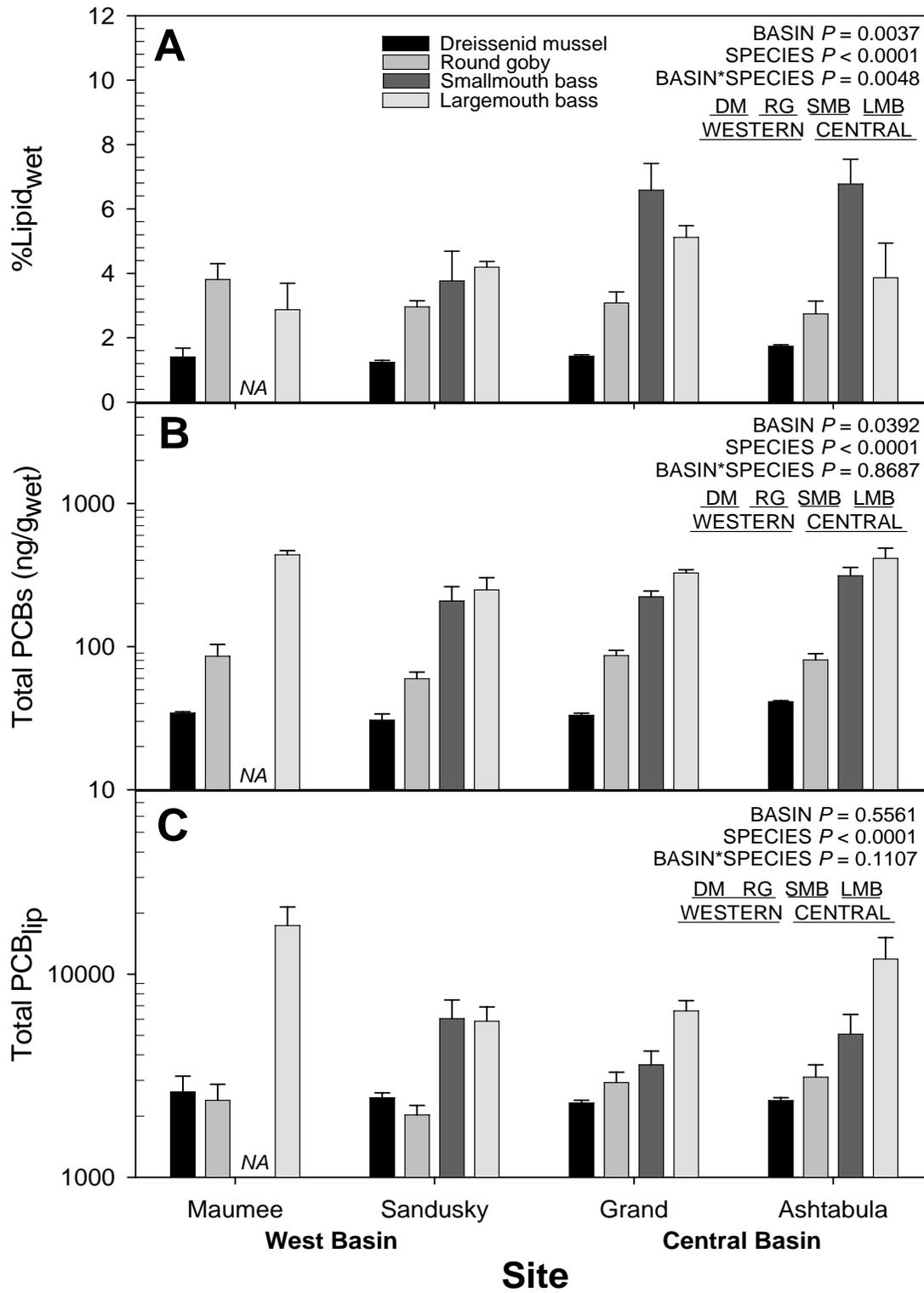


Figure 2.

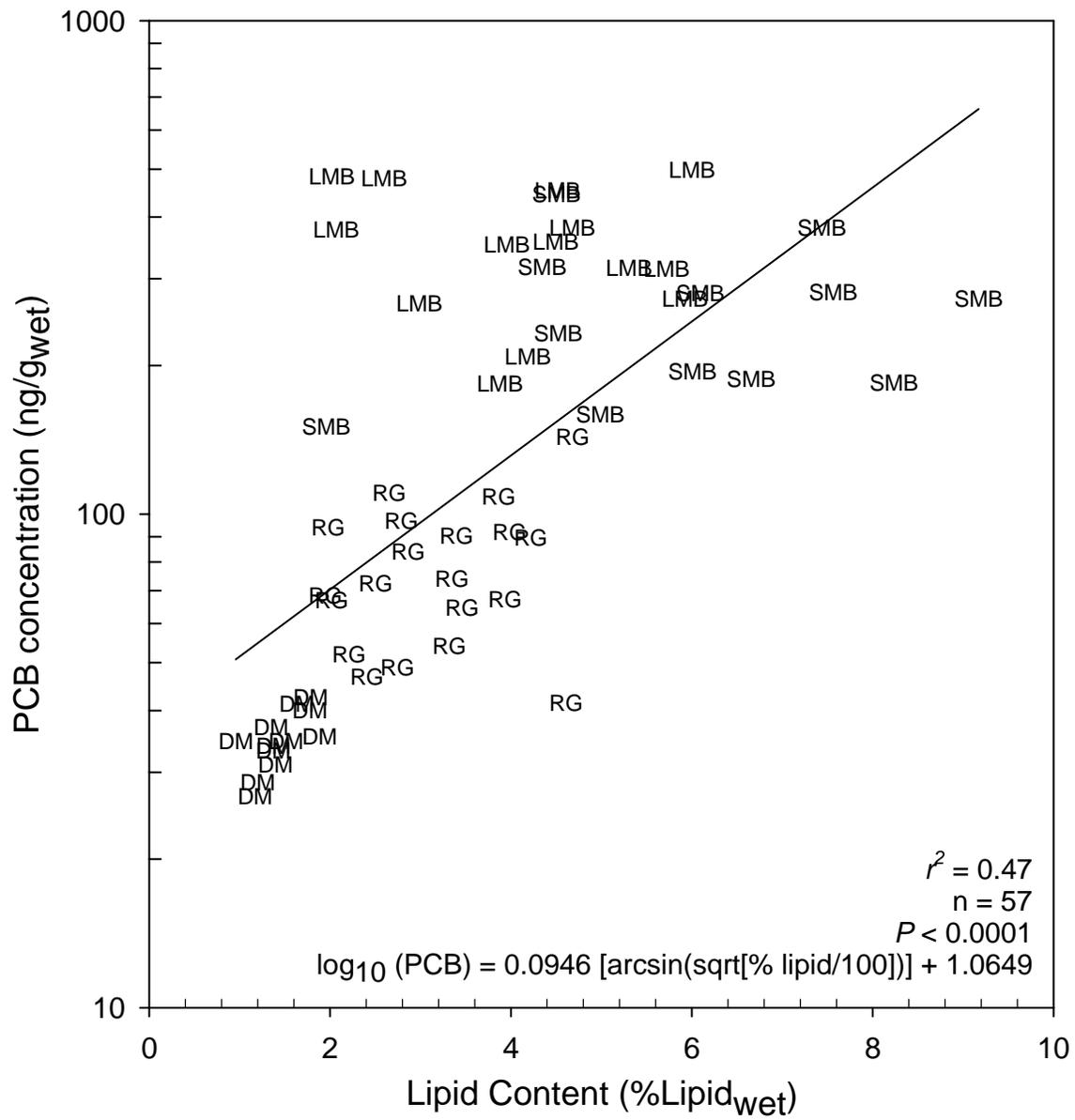


Figure 3.

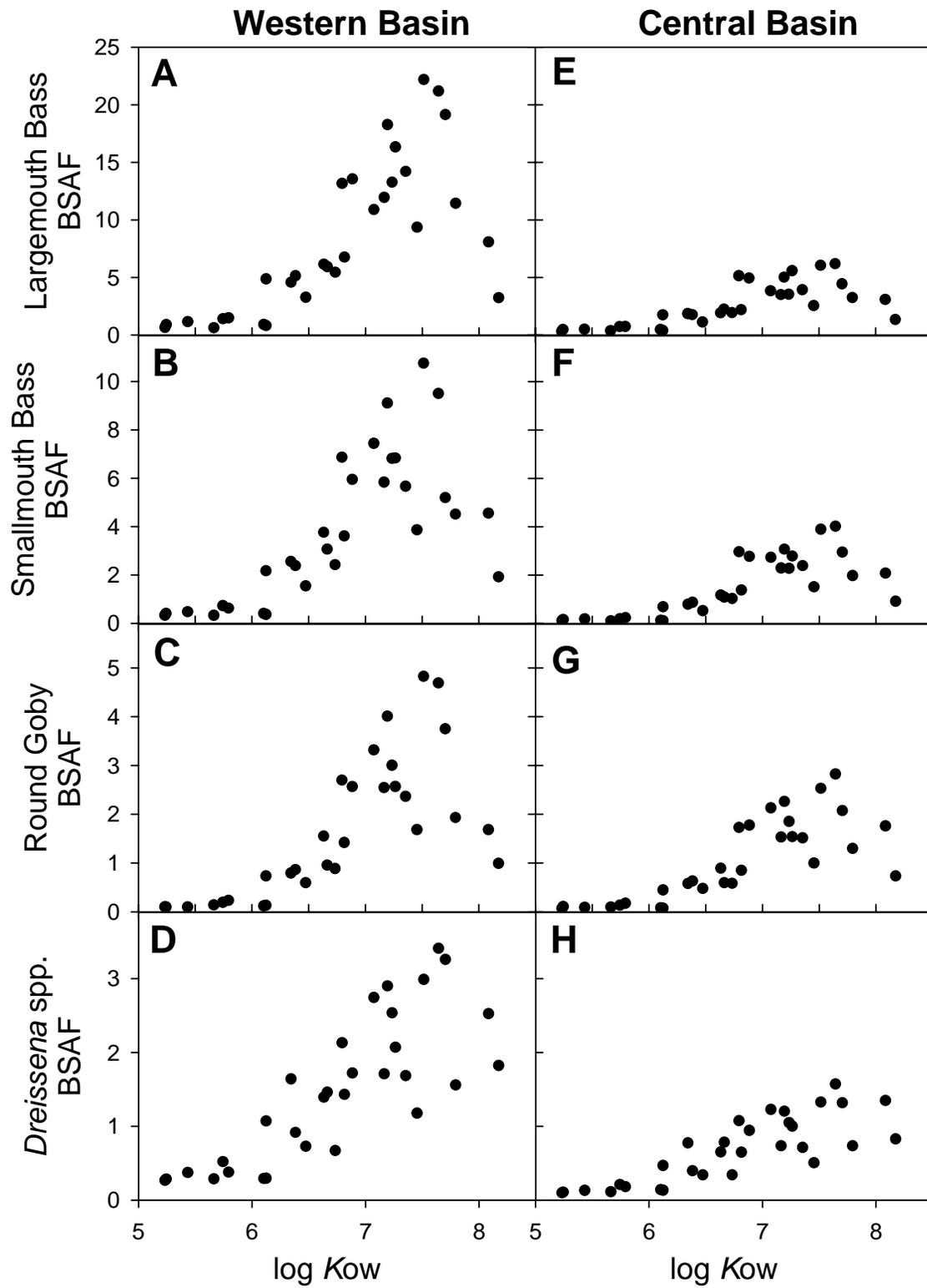


Figure 4.

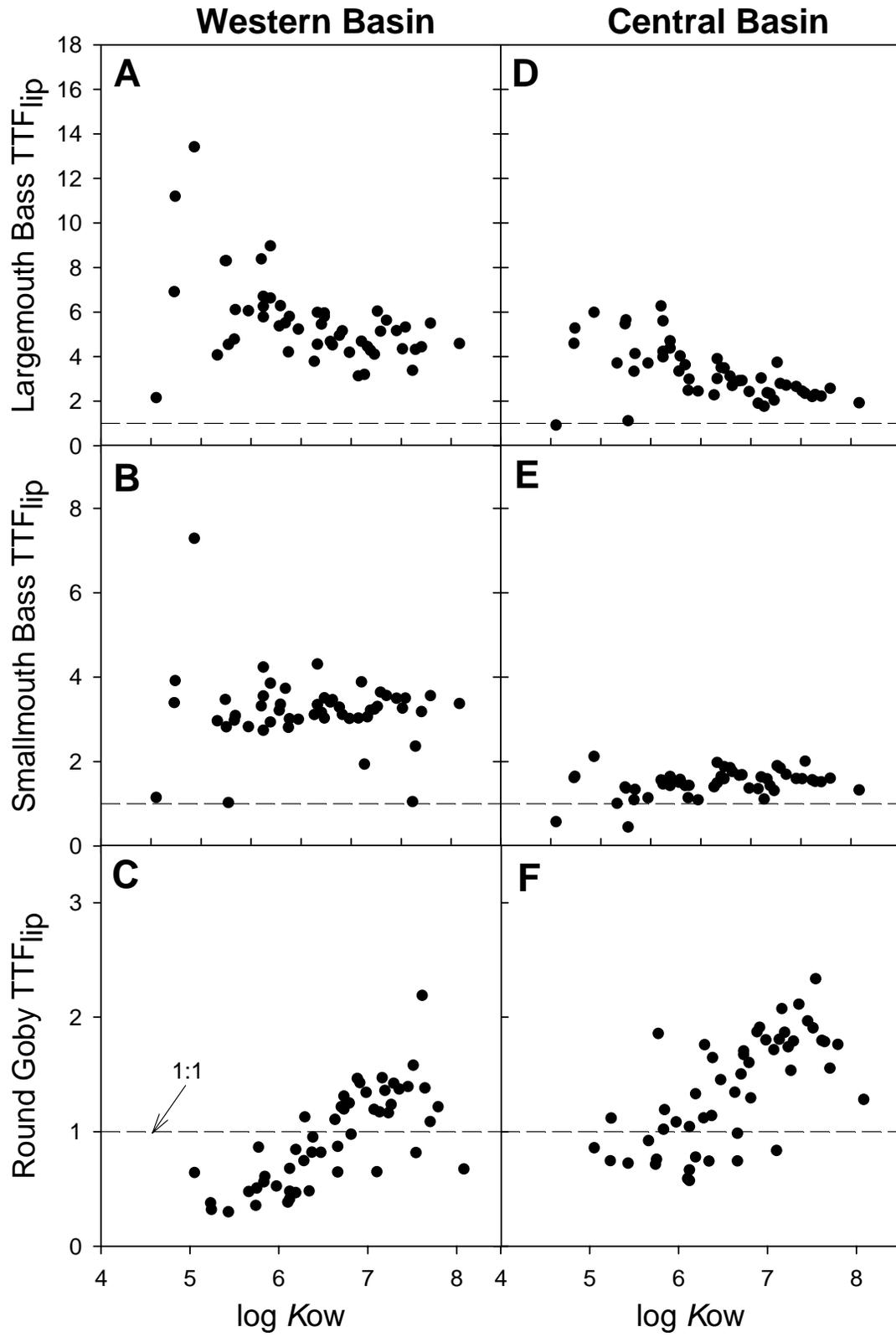


Figure 5.

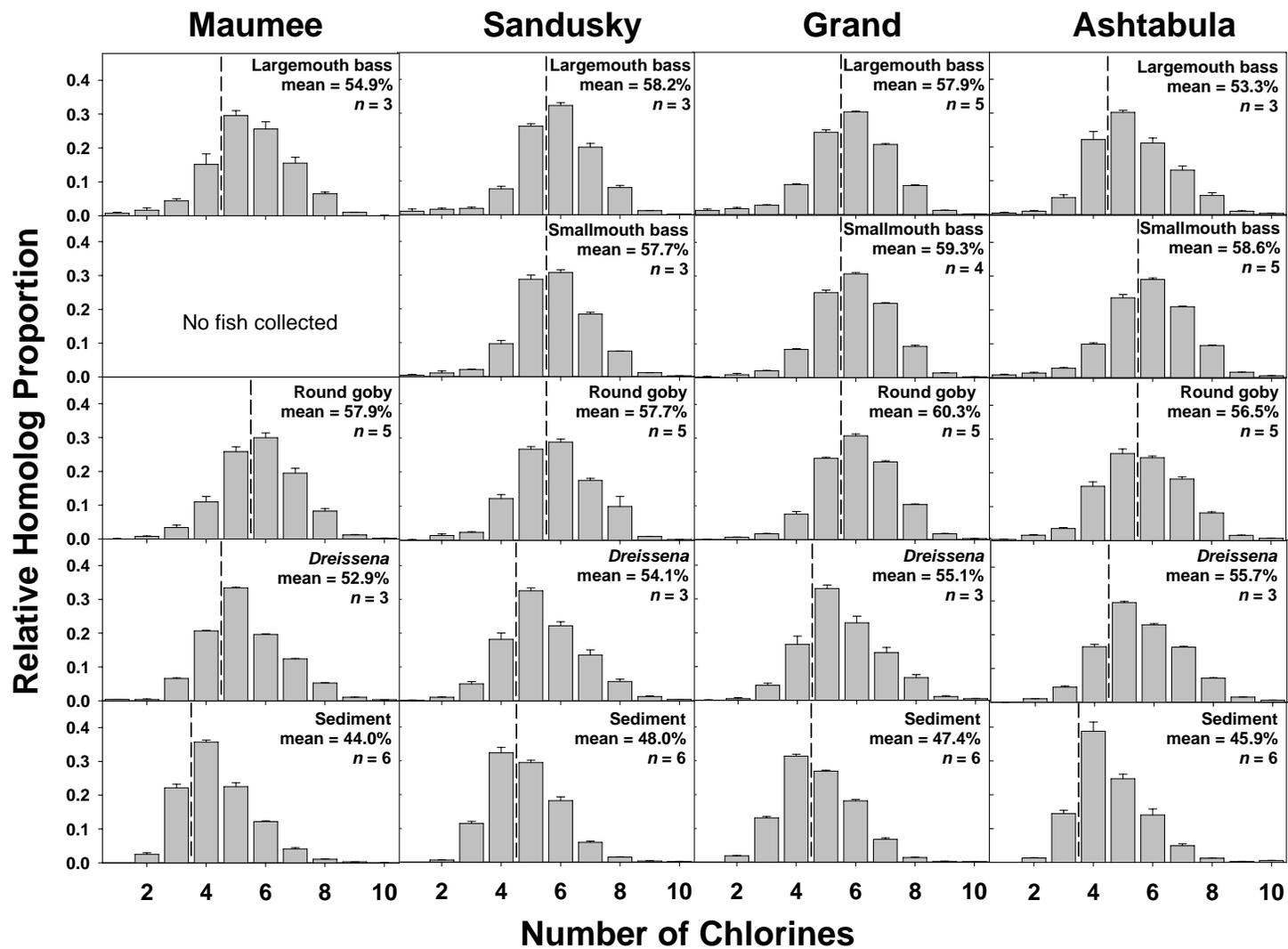


Figure 6.

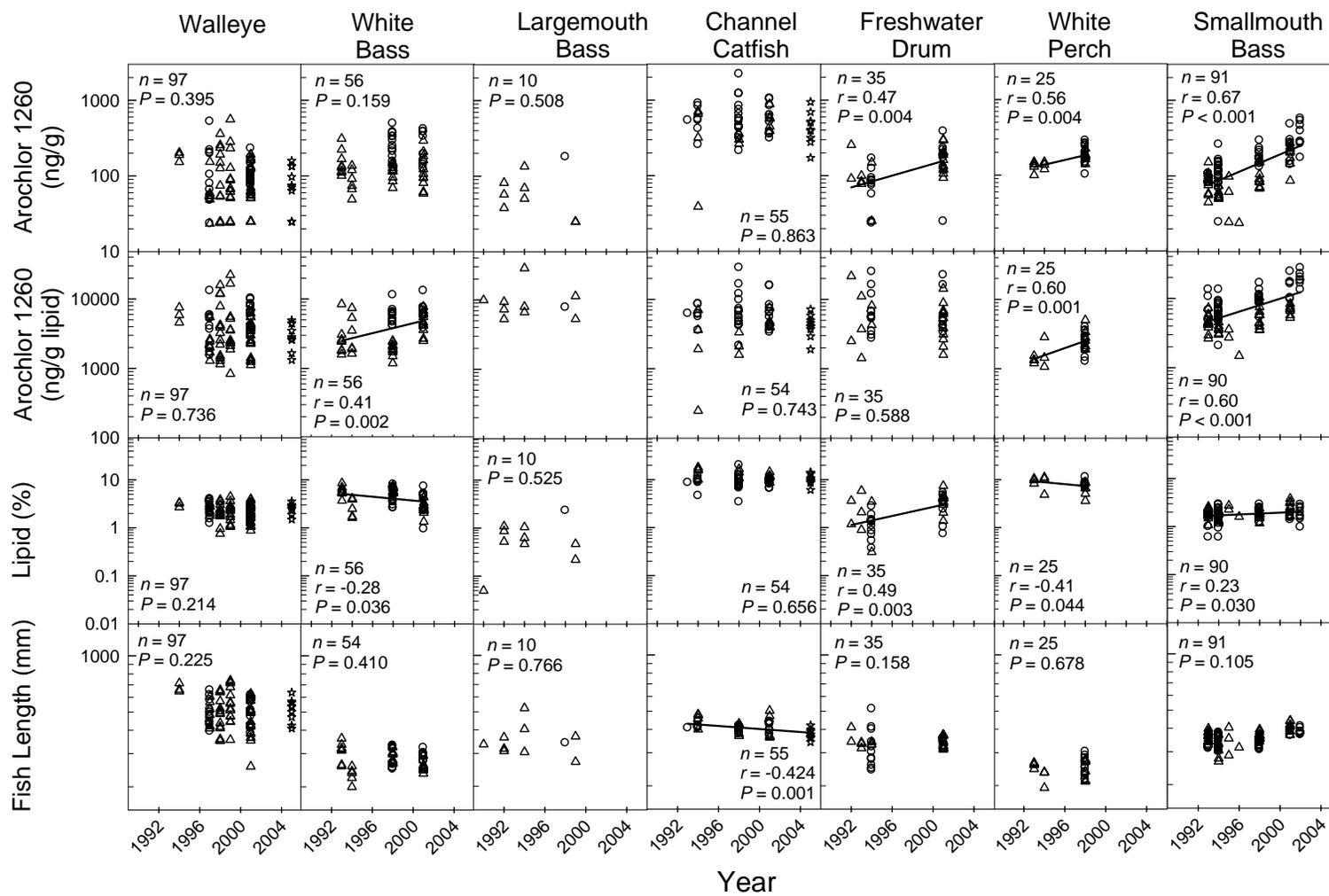


Figure 7.

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Chapter 2

The Role of Dreissenid Mussels, Sediment Characteristics, and Organic Pollutants in Structuring Nearshore Benthic Macroinvertebrate Communities in Lake Erie

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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 20th 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 benthos (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); for example, 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). In the early 1990s, improved conditions 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. 1994). This is especially relevant at harbor sites in Lake Erie, which still are 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 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 1). 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 ¹³C-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 × 100. We assessed sediment grain size in duplicate, according to methods in Folk (1980), estimating 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 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 τ 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 1 – 3), 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. 1994; 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 3; 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 Δi 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 1A). Whereas chironomid density did not differ spatially (Figure 1B), dreissenid mussel density (Figure 1C) and relative oligochaete density did (Figure 2A). 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 1C). The area outside Maumee was unique, given that it was shallowest among all outside harbor locations (Table 1). 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 2A). 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 2B-C). Other density estimates are provided in Table 2.

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 3) 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 τ ; $\alpha < 0.003$, Figure 4). Along axis 2, densities of dreissenid mussels, *Hexagenia*, amphipods, and snails related positively (Kendall's τ ; $\alpha < 0.003$, Figure 4). 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 4), 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 was associated with high densities of dreissenids, *Hexagenia*, amphipods, and snails and these associations were consistent between sampling years (Figure 4). 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 4). 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 4).

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 4-7). 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 6). 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 7).

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 4). For chironomid density, the global model (which contained all terms) ranked highest among the model set (Table 5). Density of dreissenid mussels was explained best by the global and null models (Table 8).

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, respectively (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 (1955) posited that sites with >100 *Hexagenia*/m² and <1000 oligochaetes/ m² (primarily Tubificidae) indicate low levels of pollution, <100 *Hexagenia*/m² and between 1,000 and 5,000 oligochaetes/ m² indicate moderate pollution, and <100 *Hexagenia*/m² and >5000 oligochaetes/ m² indicate heavy pollution. Based on this index (Wright 1955), 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. 1994; 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. 1994; 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. In 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).

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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	
		4 [‡]	41° 42.532 N	-83° 27.750 W	2.1	
	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	
4 [†]			41° 29.242 N	-82° 45.380 W	2.1	
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. 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: [†]Samples collected during both years, [‡]Samples collected during 2002 only, and [§]Samples collected during 2001 only.

	Maumee		Sandusky		Grand		Ashtabula	
	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside
Gastropods (no./m ³)	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 ³)	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 ³)	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 ³)	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 2. 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)	358.3 (22.0)
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 3— 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	Δi	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 4. 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 (Δi), 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	Δi	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 5. 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 (Δi), 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	Δi	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 6. 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 (Δi), 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	Δi	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 7. 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 (Δi), 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	Δi	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 8. 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 (Δi), 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 Legend

Figure 1. Mean densities (± 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 2. Mean densities (± 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 3. 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 4. 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 τ ; $\alpha = 0.003$). Note: the designation bivalve excluded dreissenid mussels.

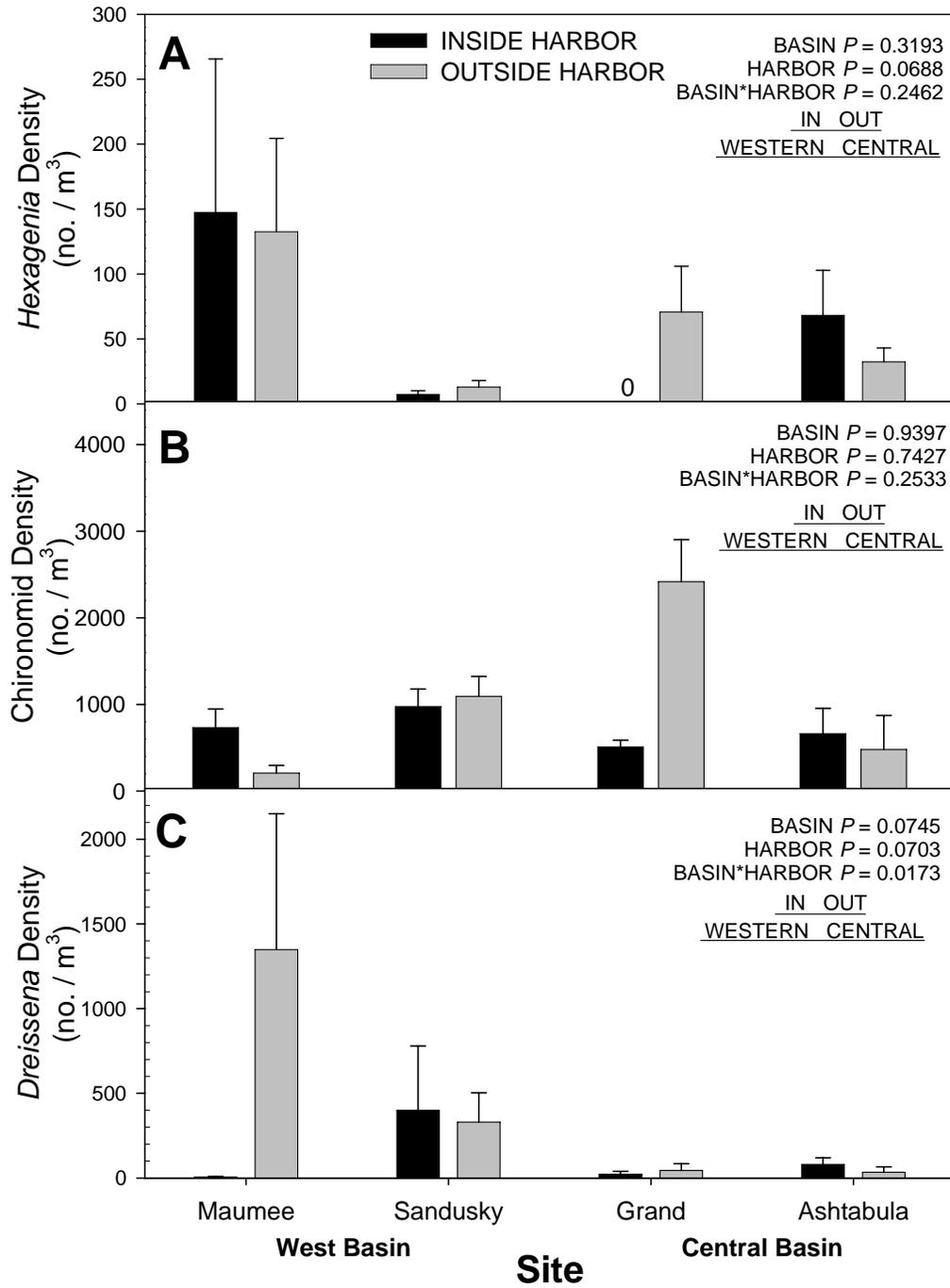


Figure 1.

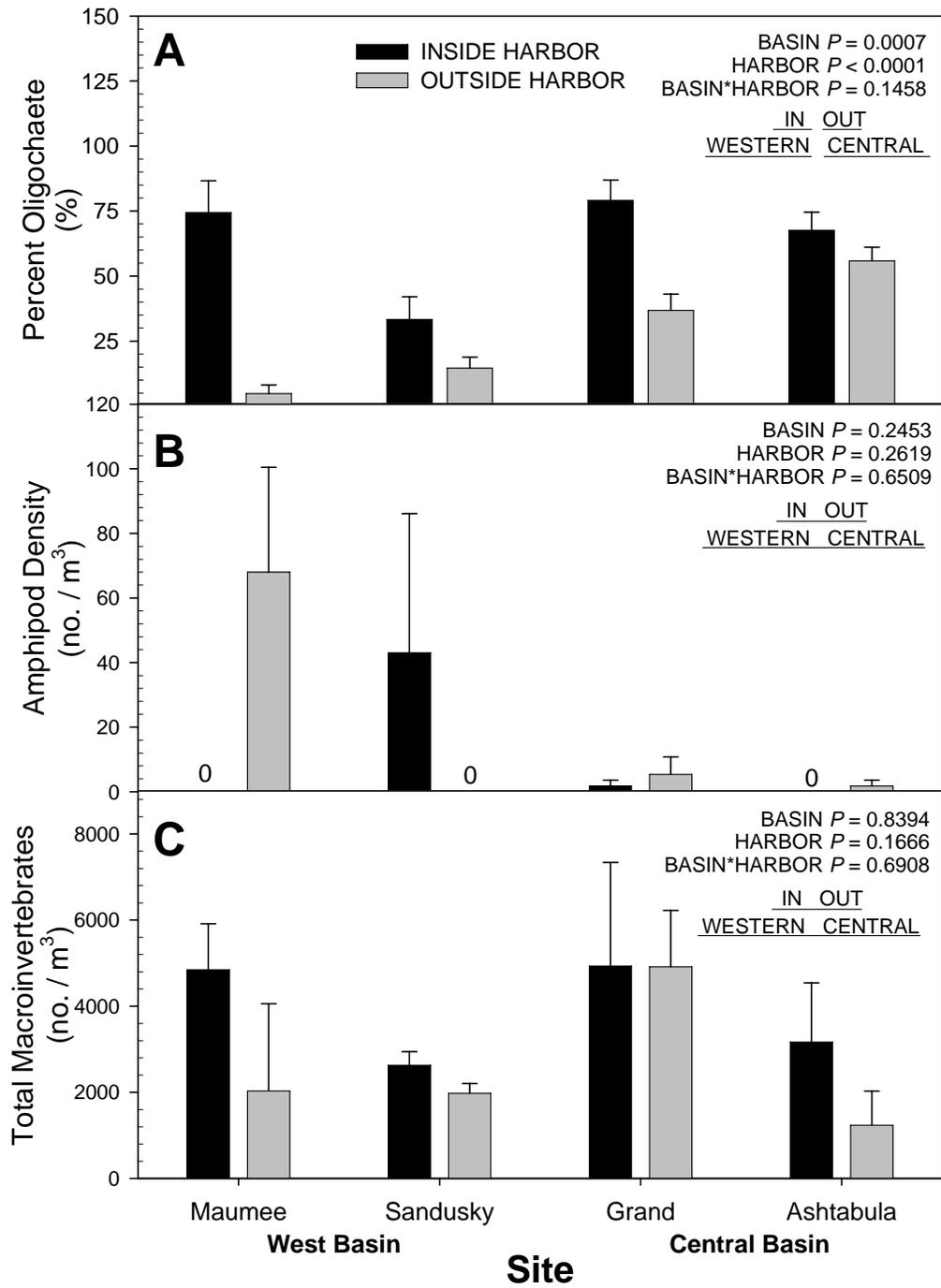


Figure 2.

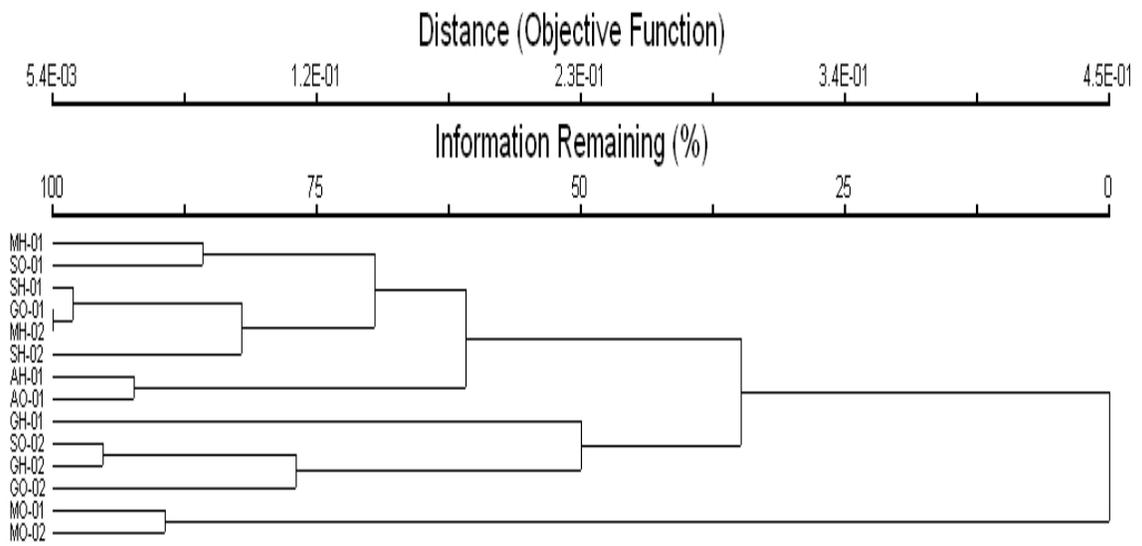


Figure 3.

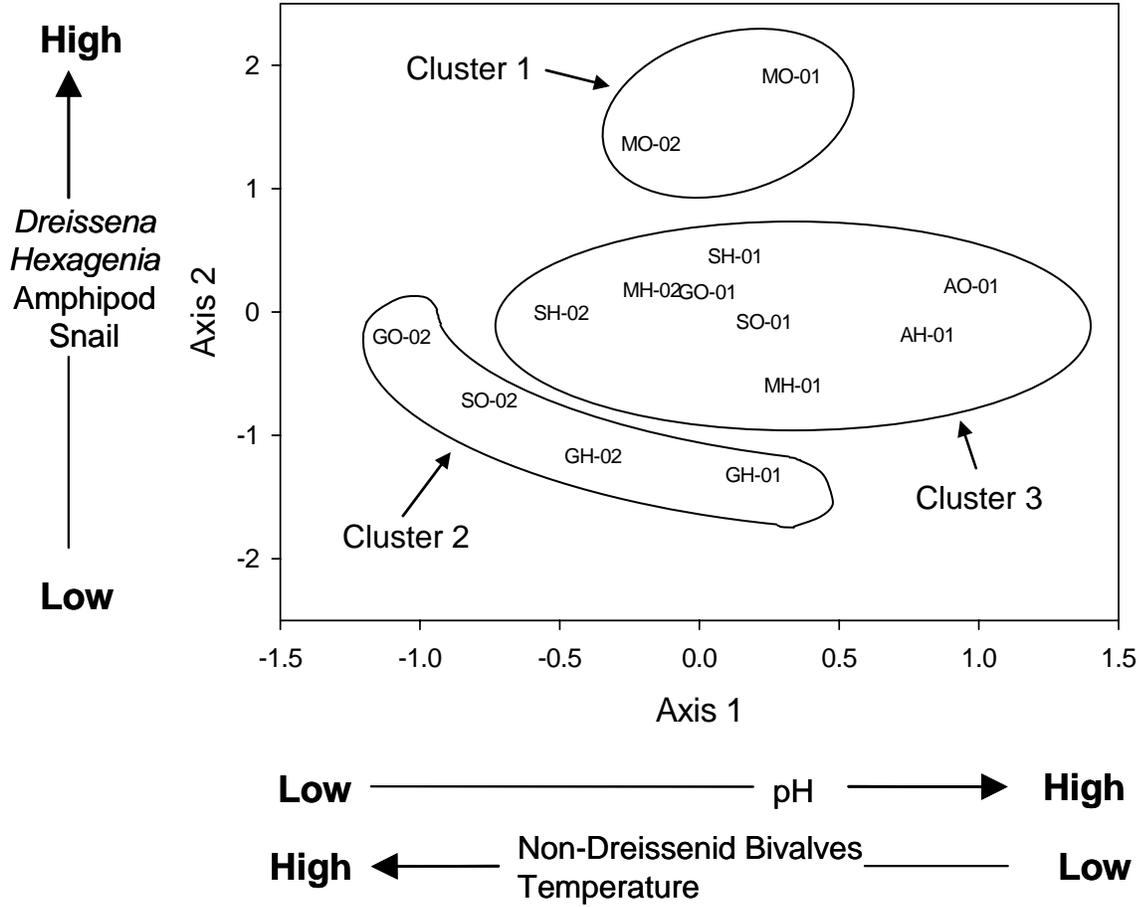


Figure 4.

Chapter 3

Bioaccumulation of sediment-associated 2,2',4,4',5,5' hexachlorobiphenyl by *Chironomus riparius*, *Lumbriculus variegatus*, and *Hyalella azteca*

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Abstract

Bioassays using spiked sediments were performed to determine how feeding behavior and sediment location influenced the uptake of 2,2',4,4',5,5' hexachlorobiphenyl (HCBP). Sediments from inshore and offshore sites at the Maumee River, Sandusky River, and Grand River were spiked with ^{14}C labeled HCBP. Three organisms with different feeding strategies, including *Lumbriculus variegatus*, *Chironomus riparius*, and *Hyaella azteca* were then placed in the spiked sediments and sampled for radioactivity over 48 hours. Uptake rates (ks) and bioaccumulation factors (BAFs) were determined for each organism in sediments from each site over the sample period. Sediments were also analyzed for total organic carbon (TOC). *C. riparius* had significantly higher uptake rates than *L. variegatus* and *H. azteca* when sediments from all locations were taken into consideration. Significant differences were not found between *L. variegatus* and *H. azteca*. At all locations, *L. variegatus* had the highest BAFs. *C. riparius* consistently had intermediate BAFs, while *H. azteca* had the lowest BAFs for all sediments. *C. riparius* had the highest uptake rates because of constant, nonselective feeding and infaunal behavior. *L. variegatus* may have had lower uptake rates because of selective feeding on fine sediment with high organic carbon content and an avoidance response to the other organisms. *H. azteca* may have had lower uptake rates because of epibenthic behavior and an avoidance response that led them to spend a disproportionate amount of time in the water column. *L. variegatus* had the highest BAFs because of their inability to eliminate HCBP relative to the other organisms. While significant differences were found between uptake rates at inshore and offshore locations in the Maumee and Grand Rivers, no pattern could be established with sediment TOC. No statistical differences were found between inshore and offshore sites in the

Sandusky River. Results for the inshore and offshore site analysis were inconclusive. Further sediment analysis should be performed.

Introduction

Background and Chemistry of PCBs

Atmospheric transport and deposition has been considered to be the major source through which organic contaminants, including polychlorinated biphenyls (PCBs) are introduced to aquatic systems (Muir et al., 1990). These hydrophobic contaminants tend to sorb to suspended particulates in aquatic systems based on the lipophilicity of the chemical and the organic carbon content of the particulates (Eisenreich, 1987; Swackhamer and Skoglund; 1993). The particulates settle to the bottom with the associated contaminants and accumulate in the sediments (Eisenreich, 1987). This process effectively removes hydrophobic contaminants from the water column (Baker, et al., 1991). However, highly contaminated sediments may become a source and reintroduce these contaminants to the water column and food web (Larsson, 1985; Larsson, 1986; Larsson, 1990). Benthic macroinvertebrates that utilize organic particulates associated with sediments ingest and assimilate the contaminants and act as an entry point for the chemicals to the food web (Lee et al, 1990; Landrum and Robins, 1990). This process makes the contaminants available to higher trophic levels, including fish, birds, and possibly humans, through trophic transfer (Baudo and Muntau, 1990). For this reason PCBs are considered a possible health concern to the general public. PCBs were first synthesized in the 19th century, and were put to commercial use in 1929 (Safe, 1992). They are highly nonpolar and have a strong electronegativity that results from organically bound chlorine ions. The chlorine atoms stabilize the biphenyl molecule by reducing the reactivity of the carbon backbone, creating a heat resistant molecule with a high dielectric constant that is stable and resistant to degradation in the

environment (Rieneke, 1984). Based on these properties, PCBs were marketed for a variety of different uses, including electrical insulators in transformers and capacitors, lubricants, hydraulic fluids, and flame retardants (Hutzinger et al, 1974; Safe, 1992). They were widely used for these functions until their ban in 1979 (Erickson, 1986). PCBs consist of biphenyl rings that are attached at the 1, 1' position and have 10 possible sites where chlorine ions can bond. Variation in chlorination at these locations allow for 209 total congeners (Hanson, 1994, Figure 1). Approximately 103 are actually produced during industrial synthesis (Widmark, 1971). Commercial PCBs were generally sold in mixtures under the trade name Aroclor in the United States. The content of the mixture was designated by a four digit number. The first two digits represented the number of carbons present in the biphenyl molecule and the second two digits represented the percentage weight accounted for by chlorine (Hutzinger et al. 1972). For example, Aroclor 1254 contains a mixture of PCBs with 12 carbons in the biphenyl skeleton and 54% of the weight is contributed by chlorine.

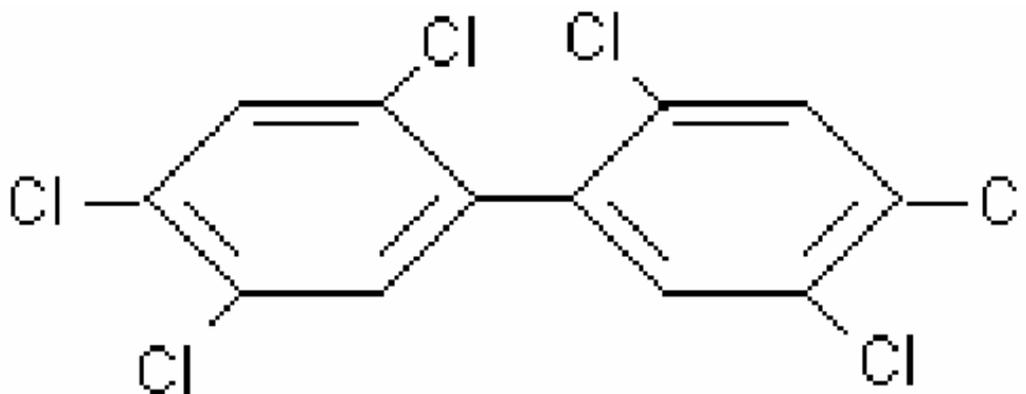


Figure 1. Chemical structure of 2,2',4,4',5,5' hexachlorobiphenyl.

The number and position of chlorine ions are important factors in the chemical and physical behavior of PCBs. Increasing the number of chlorine ions increases the molecular weight and tends to increase the melting point and vapor pressure of the molecule (Hanson, 1994). The solubility of the molecule in water decreases with increased chlorination (Hanson,

1994). In general, PCBs with fewer chlorine atoms are less stable and have a higher volatility and solubility in water while those with greater chlorination tend to be more stable and have lower volatility and solubility in water (Haque and Schmedding, 1976). The positioning of the chlorine ions on the biphenyl rings affects the behavior and structural orientation of the molecule as well. The rings can rotate at the 1 and 1' positions, and have a relative degree of coplanarity based on chlorine position. Chlorines located at the ortho positions (2,2',6,6') cause steric interference and reduce the coplanarity of the molecule (McKinney et al., 1983). This tends to increase the compound's volatility and water solubility (McKinney et al., 1983).

Environmental Fate and Toxicity of PCBs

Unfortunately, the same properties that make PCBs useful also make them important environmental contaminants. The stable qualities of these compounds make them extremely resistant to degradation and, thus, they persist in the environment for years after introduction (Hooper et al., 1990). PCBs with higher chlorination tend to be more persistent in the environment (Hutzinger et al., 1974; Kalmaz et al., 1979). Soon after the development of the gas chromatograph, the extent of the persistence of PCBs in the environment was discovered. Environmental samples revealed that PCBs were present in many different species of vertebrates from a wide range of areas, including the Arctic (Risebrough, 1968). In addition to being persistent, the high nonpolarity of PCBs makes them very lipophilic, giving them a high affinity for organic carbon (Eisenreich, 1987). As such, PCBs thermodynamically prefer to associate with organic carbon in aquatic systems and tend to accumulate in the tissues of aquatic organisms or the organic carbon fraction of soil and sediment (Eisenreich, 1987; Swackhamer and Skoglund, 1993).

PCBs are included in a group of compounds that account for 60% of environmental contaminants and impact the function of organisms through narcosis (Veith et al., 1983). These narcotic chemicals exert toxicity by accumulating in phospholipid membranes (Lipnick, 1995), which results in the disruption of the function of those membranes (van Wezel and Opperhuizen, 1995). Due to the broad range of compounds that behave in this manner, it is thought that disruption occurs through direct interaction with membranes rather than at a specific receptor site (van Wezel and Opperhuizen, 1995). The mechanism through which this occurs is not well understood and may be through one of several pathways. These pathways include the interruption of water and membrane macromolecule associations (Chiou et al., 1990), altered transition between membrane phases (Jorgensen et al., 1991), inhibition of membrane proteins function (Franks and Lieb, 1981, Franks and Lieb, 1984), and interruption of the phospholipid-protein associations (Cascorbi and Ahlers, 1989; Fraser et al., 1990; Ahlers et al., 1991). The effects on membrane function may result in the reduced ability of nerve cells to maintain action potentials and propagate nerve signal transmissions properly (Mullens, 1954; Franks and Lieb, 1994).

Introduction of narcotic contaminants to aquatic food webs can have adverse impacts on both wildlife and humans. These chemicals have been found to interfere with a variety of different organismal functions at multiple trophic levels. In invertebrates, exposure to PCBs has been found to influence the efficiency of molting in several different crustaceans (Fingerman and Fingerman, 1977; Nimmo et al., 1971). Oligochaetes exposed to sediments associated with narcotic compounds displayed reduced activity and weight (Keilty et al., 1988). Fish exposed to narcotic compounds tended to suffer from reduced sense of balance, lethargic movement, and were less responsive to stimuli (Van Hoogen and Opperhuizen, 1988; Sijm et al., 1993).

Rainbow trout (*Salmo gairdneri*) exposed to several narcotic compounds expressed decreases in metabolic, respiratory, and cardiovascular rates to an extent that tissue hypoxia occurred followed by death (McKim et al., 1987). Birds and other terrestrial top level predators may be exposed to aquatic contaminants through the consumption of aquatic organisms. This has resulted in a number of problems, including developmental abnormalities, embryoletality, and reduced reproductive productivity, which have led to population declines in eagles, gulls, cormorants, terns and herons (Giesy et al., 1994).

The toxicity of nonpolar narcotic compounds to aquatic organisms is determined by the extent of exposure and the sensitivity of the organism to the compound. Narcosis occurs when a sufficient concentration of the contaminant has been assimilated to cause a disruption in membrane function (van Wezel and Opperhuizen, 1995). The critical body residue method (CBR) can be used to evaluate the exposure of organism to a contaminant and predict toxicity of that contaminant (McCarty and Mackay, 1993). This method takes in to account the bioavailability, accumulation kinetics and biotransformation of the compound, resulting in relatively constant concentrations among different organisms and different contaminants (McCarty and Mackay, 1993; van Wezel and Opperhuizen, 1995). Lethal CBRs have been determined for both aquatic invertebrates (Pawlisz and Peters, 1993; Landrum et al., 1994) and vertebrates (McCarty et al., 1992; Sijm et al., 1993) and are consistently found to be between 2 and 8 $\mu\text{mol/g}$ wet weight.

In addition to narcotic effects, some PCBs may have structures that influence mixed-function oxidase (MFO) activity (Mcfarland and Clarke, 1989). PCBs that have no chlorine substituted at the ortho-position tend to be coplanar and PCBs that have one chlorine substituted at the ortho-position tend to be semi-coplanar. The coplanar structure of these compounds may

allow them to act as inducers of aryl hydrocarbon hydroxylase (AHH) (Safe, 1987). The result is the activation of 3-methylchloranthrene type and mixed type oxidases, similar to the function of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), as well as phenobarbitol type oxidases (Macfarland and Clark, 1989).

The greatest threats that PCBs present to humans are generally through chronic exposure rather than acute exposure. While there is not a lot of evidence that fully details the toxicity of PCBs to humans, there have been a couple of mass exposures that have provided some insight into the results of PCB poisoning. In Japan in 1968, 136 people were exposed to PCBs through the consumption of contaminated cooking oil. Mean blood levels of PCBs reached 6 ppb in contaminated individuals. Within five years, nine people had died from malignant tumors, a proportion well above average. In addition, several individuals died from cerebral hemorrhage or cirrhosis of the liver, though a much more debatable correlation is drawn here. Exposed individuals also suffered from a number of other maladies, including chloracne, hyperkeratinosis, and melanin disturbances (Kuratsume, 1976). A second case occurred resulting from the mass exposure of approximately 2000 people from December 1978 to October 1979 in Taiwan. Exposed individuals had a mean PCB concentration of 89.1 ppb in the blood. Children born to exposed females showed abnormal development in ectodermal tissue, slower development overall, and reduced growth compared to the children of mothers that were not exposed (Rogen et al., 1988). The observations made from these exposures suggest that PCBs may have both carcinogenic and teratogenic effects, and can cause a number of other ailments as well.

Consumption of PCB contaminated fish can also lead to problems within human populations, especially unborn children (Fein et al., 1984; Jacobson et al., 1985). Pregnant women that consumed contaminated fish from Lake Michigan in 1980 and 1981 were observed

to examine the response of exposed fetuses. These children tended to express developmental deficits, including decreased birth size, gestation times, and head circumference (Fein et al., 1984; Jacobson et al., 1985). They also behaved abnormally and had poor recognition memory (Fein et al., 1984; Jacobson et al., 1985). At four years of age, prenatally exposed children were smaller and tended to have reduced responsiveness and poor short-term memory compared with other children of their age group (Jacobson et al., 1990a; Jacobson et al., 1990b). At 11 years of age, exposed children tended to have lower IQs and were more likely to be distracted than children that were exposed to lower concentrations of PCBs (Jacobson et al., 1996).

The study of the fate of PCBs in aquatic ecosystems is important in determining potential sources of human exposure. Because PCBs tend to accumulate in aquatic organisms at higher concentrations than environmental levels, the aquatic food web becomes a possible point of introduction. It has been well documented that PCB concentrations are elevated at higher trophic levels in aquatic food webs (Oliver and Niimi, 1988; Rasmussen et al., 1990; Zaranko et al., 1997). Sport fish, including those represented in these higher trophic levels, generally tend to have PCB concentrations several times higher than those of the benthic invertebrates and fish that occupying lower trophic levels (Oliver and Niimi, 1988; Rasmussen et al., 1990; Zaranko et al., 1997). These sport fish are the primary target of game fishing, making them a concern for human exposure through dietary consumption.

The most important property that influences the fate of PCBs in the environment is hydrophobicity. This characteristic is often reported as the log of the octanol/water partition coefficient ($\log K_{ow}$), where the coefficient is obtained from a ratio of the concentration of the PCB in n-octanol and water. Higher $\log K_{ow}$ s correlate to compounds with greater lipophilic properties, thus making them more soluble in lipids (Smith et al., 1988). This measurement of

lipophilicity has been used to determine a compound's behavior in sediment-water partitioning (Paris et al., 1978) and tendency for bioconcentration in aquatic organisms (Tulp and Hutzinger, 1978).

The PCB of interest for this study is 2,2',4,4',5,5' hexachlorobiphenyl (HCBP), a common contaminant in aquatic ecosystems (McFarland and Clarke, 1989). No studies have reported any metabolism by benthic invertebrates. Log K_{ow} values for HCBP have been reported as between 6.7 (Connell et al., 1988; Evans and Landrum, 1989) and 6.9 (Gobas et al., 1988).

The initial introduction of contaminants to aquatic food webs often occurs at the sediment-water interface. The hydrophobic nature of PCBs results in high concentrations of these compounds in the sediments and much lesser concentrations in the water column. Dipinto et al. (1993) found that the concentrations of PCBs were three orders of magnitude higher in the sediments than in the water column because the hydrophobicity of the contaminants caused them to preferentially partition to the sediments. When PCBs are highly concentrated in sediments, they can become the primary source of available PCBs to aquatic systems (Larsson et al., 1990). The lipophilic interaction that occurs between sediments and PCBs is generally based on the log K_{ow} of the compound and the organic carbon content of the sediment. Higher contaminant log K_{ow} s result in a greater interaction with the sediment, as these compounds tend to be more hydrophobic and are less likely to be found in the water column (Paris et al., 1978). The organic carbon associated with sediment provides a site of lipophilic interaction where the contaminant can bind to the sediment. Sediments with high organic carbon content tend to have a greater affinity for PCBs and thus accumulate elevated levels of PCBs (Landrum et al., 1985; Landrum et al., 1987).

PCBs associated with sediments may enter the food web through several routes. One of the first methods investigated involves the passive uptake of dissolved contaminants by aquatic organisms through a process called bioconcentration. This process is greatly influenced by the log K_{ow} of the contaminant in question (Smith et al, 1988). The contaminants are distributed between different compartments in the environment based on thermodynamic properties. These compartments include sediment, water, and organisms. The chemical in questions reaches equilibrium between compartments based on fugacity, or the thermodynamically driven potential of a contaminant to leave a compartment (Mackay, 1979; Mackay and Paterson, 1982). Because of their high lipophilicity, the majority of PCBs partition to sediment or dissolved organic carbon (DOC) rather than remain dissolved. PCBs bound to sediments or DOM are not directly available to organisms through bioconcentration, but some contaminants will be thermodynamically driven to dissolve in the water column as the system tends towards equilibrium (Coats and Elzerman, 1986). As a result, there will always be a source of PCBs available for uptake via bioconcentration.

Uptake through bioconcentration usually occurs across respiratory surfaces (Nichols et al., 1990; Nichols et al., 1991), though smaller organisms may absorb the contaminants across the cuticle (Lien and McKim, 1993). This is the quickest method of introduction for organic contaminants entering aquatic organisms (Reynoldson, 1987).

Early studies suggested that bioconcentration was the primary source of accumulated PCBs in aquatic organisms (Mackay, 1982; Schneider 1982; Smith et al, 1988). However, many observations have been made that show organisms with PCB body burdens well above the levels predicted by water-tissue partitioning models (Oliver and Niimi, 1988; Rasmussen et al., 1990; Evans et al, 1991; Zaranko et al., 1997). This suggests that there are other factors involved in

PCB uptake than just bioconcentration, such as assimilation from food sources. A number of studies have supported the idea that contaminant uptake is heavily influenced by diet, including the following: Opperhuizen and Schrap (1988) revealed that at least 50% of the body burden in male guppies (*Poecilia reticulata*) is acquired through dietary consumption; Thomann and Connolly (1984) suggested that up to 99% of PCBs in Lake Michigan lake trout (*Salvelinus namaycush*) were accumulated through food consumption rather than bioconcentration from water; Rasmussen et al. (1990) discovered that adding a trophic level to a food web would increase the PCB body burden of lake trout by 3.5 times in Ontario lakes; Zaranko et al (1997) found that fish and leeches occupying higher trophic levels in Pottersburg Creek, ON, consistently had higher PCB body burdens than invertebrates that occupied lower trophic levels, even at equal lipid content. In these cases, contaminant uptake must be accounted for from all sources. The process through which this occurs is referred to as bioaccumulation.

In many aquatic systems where the sediments are the primary source of PCBs, several processes are believed to contribute to contaminant concentration in the food web. These processes include consumption of contaminated sediments and trophic transfer (Opperhuizen and Schrap, 1988; Landrum and Robbins, 1990). Contaminants that are stored in the sediment must first be freed before they can enter the food web. The primary mechanism through which this occurs is the ingestion of contaminated sediment by benthic organisms (Lee et al, 1991; Landrum and Robins, 1990). These sediment consuming organisms assimilate the stored PCBs and act as a point of entry through which PCBs are mobilized and introduced to the food web (Baudo and Muntau, 1991). From here, ingestion of contaminated prey organisms transfers PCBs up the food web.

PCB assimilation from food is a more complicated process than direct uptake from water and is not wholly understood. Assimilation consists of a series of steps in which the compound must disassociate with the sediment and cross the intestinal lining into the organism where it will most likely be sequestered in tissues with high lipid content. The initial dissociation of hydrophobic chemicals from sediments may be a result of metabolic activities that take place within the organism's digestive system (Fisher, 1995). These metabolic activities include both the increase of sediment surface area through which the contaminant can be released and the decrease in the distance over which the compound must diffuse to reach the gut lining of the organism (Fisher, 1995). Studies have shown that decreasing sediment pH releases residues of hydrophobic compounds from sediments by breaking down organic carbon (Pignatello, 1990). These conditions are similar to those that sediment particles would experience in the digestive system of an organism (Fisher, 1995).

After separating from the sediment, the compound is free to be assimilated by the animal. While, again, this process is not well understood, Gobas et al. (1993) found that dietary uptake efficiency of goldfish (*Carassius auratus*) for several organochlorines was significantly higher from food with lower fat content than from food with higher fat content. These results suggested that contaminant uptake depends on diffusion across the intestinal lining by the following procedure: Lipophilic contaminants in the gut become sequestered in micelles formed by the fatty acids from digested triglycerides. These micelles diffuse to the intestinal lining of the organism, where the fatty acids then diffuse across the lining of the gut and increase the lipophilicity of the gastrointestinal cells. This creates a driving force for the diffusion of the contaminant into the intestinal cells. Upon entering the cells, contaminants can be associated

nto reassembled triglyceride complexes and travel with them to their destination or the contaminants can individually diffuse into the blood stream (Gobas et al., 1993).

The entry of PCBs into the food web may result in organisms with accumulated levels of PCBs that far exceed environmental concentrations. These levels increase with trophic level so that top predators accumulate the greatest levels of contaminants (Oliver and Niimi, 1988; Rasmussen et al., 1990; Zaranko et al., 1997). The process through which this occurs is called biomagnification, a relatively controversial topic in the field of toxicology. While a number of studies have observed this concept for several compounds, the idea does not seem to be universal for all organic contaminants, even those that are hydrophobic and persistent. Several studies have shown unpredictable patterns of organic contaminant concentrations based on trophic levels (Burns and Teal, 1979; Biddinger and Gloss, 1984; Macek et al., 1984). LeBlanc (1995) suggested that organisms occupying higher trophic levels may be able to achieve high levels of contaminants through bioconcentration rather than biomagnification. While it does appear that biomagnification may not be observed for a number of organic contaminants, there is substantial evidence that supports the idea that very lipophilic compounds ($\log K_{ow} > 6$) that are very stable and cannot be metabolized do indeed biomagnify (Suedel et al., 1994). HCBP is considered to be part of this group, and thus increases in concentration with increasing trophic level.

As previously stated, sediment consuming benthic organisms are an important point of entry for PCBs destined for the food web. These animals often show variation in levels of contaminant bioaccumulation despite their presence in identical media. This is likely to be the result of varying exposures to contaminants based on feeding strategies (McElroy et al., 1989). Harkey et al. (1994a) found different levels of uptake and accumulation in *Chironomus riparius*, *Lumbriculus variegatus*, and *Diporeia* spp exposed to organic contaminants in the same

sediment. *Diporeia* preferentially consumed particles with a high organic carbon content, which resulted in increased exposure and accumulation of several of the organic contaminants tested. *C. riparius*, on the other hand, was the least selective feeder and showed the lowest rates of accumulation for the compounds tested. In another experiment, Wood et al. (1997) found that selective feeding in benthic macroinvertebrates resulted in a PCB congener pattern different from the pattern found in the sediments. This suggested that feeding selectivity did influence how the organisms accumulated sediment associated PCBs. Shuler et al (2002) performed a multi-species exposure in which *Hyalella azteca*, *C. tentans*, and *L. variegatus* were exposed to Benzo(a)pyrene. *L. variegatus* tended to accumulate higher levels of PAHs because of their deposit feeding strategy when compared to *H. azteca*. *H. azteca*, on the other hand, had the lowest levels of accumulation because they spent the least amount of time in the sediment. Generally, organisms that employ deposit feeding strategies, like *Diporeia* and *L. variegatus*, will accumulate higher levels of sediment bound contaminants, despite the actual contaminant level of the sediment. This is because they selectively feed on sediment particles that have a higher capacity for binding to organic contaminants (McMurthy et al., 1983; Adams, 1987; Landrum, 1989; Harkey et al., 1994b). Organisms that utilize less selective feeding strategies, on the other hand, will accumulate lower levels of contaminants and contain body burdens that reflect the concentration of contaminants in the sediment (Knezovich and Harrison 1988).

The organisms selected for this study, *Chironomus riparius*, *Hyalella azteca*, and *Lumbriculus variegatus*, all apply different feeding strategies in the benthic environment. *C. riparius* are infaunal dipteran larvae that employ a collector-gathering feeding strategy. Like almost all other Chironomids, *C. riparius* spends only part of its life cycle

in the water. The egg, four larval instars, and pupa are all aquatic stages while the adult is terrestrial (Oliver, 1971). Larvae dwell slightly below the surface of the sediment and build a case made out of substrate particles that are held together by silky threads secreted by the salivary glands (Oliver, 1971). The larvae are detritivores that feed on detritus associated with sediment particulates. As the larvae remain anchored in the retreat, they collect materials that are just outside the retreat. They tend to be nondiscriminant feeders and consume almost anything that they can collect. This approach tends to be more quantity than quality, and they digest relatively little of the organic material that they consume (Cummins, 1973). *C. riparius* is widely distributed throughout aquatic habitats (Pinder, 1986), and is an important food source for many benthic feeding predators (Pennak, 1978).

H. azteca are epibenthic detritivores that are common inhabitants of lakes and streams throughout North America (Pennak, 1989). While they are usually found at the sediment-water interface, they often burrow into the sediment. They complete their entire life cycle in the benthic environment (USEPA, 2000). Primary food sources for *H. azteca* are bacteria and algae and they commonly consume the sediments with which these food sources are associated (Hargrave, 1970). The burrowing behavior of *H. azteca* is greatly reduced when other organisms are introduced to the system (Reynoldson et al, 1994). This is the result of *H. azteca* trying to avoid contact with other organisms present in the sediment. This alteration in behavior has been shown to decrease the amphipods exposure to sediment bound contaminants, thus reducing its potential for contaminant accumulation (Shuler et al., 2002).

L. variegatus are freshwater, deposit feeding oligochaetes that tunnel through the upper layer of sediments in a variety of aquatic habitats throughout the United States and Europe (Cook, 1969). When they are not tunneling, they bury their anterior end into the sediment and

extend their posterior into the water column for respiratory exchange. Their feeding behavior consists of a conveyor belt like strategy that ingests bacteria and algae associated with sediments and defecates the remaining sediment on the benthic surface. They generally tend to selectively feed on fine-grained, organic rich particles (McMurthy, 1983) that have the potential to contain high concentrations of contaminants (Klump et al., 1987). Given their feeding strategy and the fact that they are continuous feeders, they are important in placing buried sediments and contaminants on the sediment surface through defecation (Karickhoff and Morris, 1985).

Organic content and sediment type may also have important influences on the uptake of contaminants from the sediment by benthic organisms. Organic contaminants have a greater affinity for finer sediments that tend to have greater organic carbon content. These sediments provide a greater source for contaminants to benthic organisms than do larger sediments with smaller organic fractions (Lee, 1991). Wood et al. (1997) suggested that contaminant characteristics, including organic carbon content, can influence how benthic invertebrates accumulate sediment bound contaminants. Harkey et al. (1994b) revealed that *Diporeia* spp. had elevated accumulation and uptake rates for organic compounds that were associated with fine sediments rich in organic carbon. In another study, *Mysis relicta* were observed selectively feeding on organic rich sediments with high levels of associated HCBP, resulting in elevated assimilation of HCBP from fine sediments over larger sized sediments (Klump et al., 1991).

A point of interest is the ability of benthic organisms to assimilate sediment bound PCBs from sediments in inshore and offshore zones of Lake Erie. Inshore sites generally tend to have greater organic carbon content than do offshore sites (Krieger and Ross, 1993) and thus have a greater potential for association with hydrophobic contaminants. For this study sediments were collected from three inshore sites and three offshore sites in Lake Erie. These locations included

an inshore site in the Maumee River and an offshore Maumee River site in the western basin; an inshore Sandusky Harbor site and an offshore Sandusky River site in the western basin; and an inshore Grand River site and an offshore Grand River site located in the central basin.

Comparison of the ability of benthic macroinvertebrates to assimilate PCBs may provide some insight into the dynamics of contaminant accumulation for the different sediments.

This study utilized bioaccumulation factors (BAF) and uptake clearance coefficients (k_s) to analyze and compare the assimilation of sediment associated contaminants by benthic invertebrates. The BAF measures the ability of an organism to accumulate a contaminant from all sources, and thus includes the partitioning behavior of the contaminant, the characteristics of sediments, food sources, the behavior and physiology of the organism, and the elimination rate of the compound from the organism (Landrum and Robbins, 1990; Landrum, 1992). It is calculated from the kinetic parameters that measure contaminant uptake and elimination (Landrum and Robbins, 1990). The units of BAF are expressed as g sediment/g organism.

The k_s measures the effectiveness of the organism in removing and assimilating a contaminant from sediment. It is considered to be a coefficient rather than a constant because the value may vary depending on physical and biological factors involved (Lee, 1991). The value can be obtained through the slope of the linear uptake phase of accumulation (Landrum, 1992). It is then normalized by the weight of the organism and the concentration of the contaminant in the sediment so it can be used for comparison with other organisms in different sediment types (Lee, 1991). The units for this value are g sediment/g tissue x time. The gram units are not canceled out to prevent confusion with similar forms of evaluation (Lee, 1991).

Objectives

This study addresses two objectives that deal with the bioaccumulation of PCBs in benthic invertebrates. First, the study compared how different feeding behaviors influence the bioaccumulation of HCBP in *H. azteca*, *C. riparius*, and *L. variegatus*. This objective was carried out through a bioassay that simultaneously exposed the three benthic invertebrates to sediments spiked with ^{14}C labeled HCBP. Due to its preference for fine sediments that are rich in organic content, *L. variegatus* should display the highest rates of accumulation for the contaminant. Further, it was hypothesized that *H. azteca* should show the lowest rate of contaminant uptake as it should spend more time in the water column to avoid the other two invertebrates in question. This will reduce its contact with sediment, resulting in a reduced exposure to the HCBP. Accumulation levels in *C. riparius* should be between the other two invertebrates because of the collector-gatherer foraging strategy. This feeding type is less selective than deposit feeding, so it will feed less on organic rich sediments with higher contaminant content and accumulate lower levels of PCBs than *L. variegatus*. On the other hand, the infaunal behavior of the midge will keep it in closer contact with the sediments, allowing it to accumulate a higher concentration of HCBP than *H. azteca*.

The second objective of this study compared the accumulation of HCBP inshore and offshore sediments for the three test organisms. This analysis was performed through a bioassay that exposed the organisms to sediments from inshore and offshore locations spiked with ^{14}C labeled HCBP. Inshore sediments should have higher organic carbon content and a greater capacity to associate with the contaminant. This should result in greater accumulations of HCBP for organisms exposed to these treatments.

Methods

Test organisms

Three invertebrate species, *Hyalella azteca*, *Chironomus riparius*, and *Lumbriculus variegatus* were used as each animal employs a different feeding strategy. Adult *H. azteca* and *L. variegatus* were obtained from laboratory reared populations that had been maintained according to the protocol described by the U.S. Environmental Protection Agency (2000). Third instar *C. riparius* were obtained from laboratory reared populations that had been maintained according to the guidelines laid out by Estenik and Collins (1979). All animals were removed from their tanks, counted out, and placed in bubbled 100ml beakers containing the hard standard reference water described below. They were then placed in an environmental chamber (FormaScientific) set to 20°C with a 16:8h light:dark photoperiod (fluorescent lights, $\lambda=500\text{nm}$) for 24 hours prior to the beginning of the experiment. This was performed to acclimate them to experimental conditions. They were not fed during this period to ensure that they would quickly begin feeding at the onset of the experiment.

Chemical

¹⁴C-labeled 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP, 12.6 mCi/mmol) was obtained from Sigma Chemical Company (St. Louis, MO, USA). Radiopurity was tested by thin-layer chromatography (silica gel F-254 plastic-backed TLC plates; 80 hexane:20 benzene v/v solvent) and liquid scintillation counting, and was determined to be > 97%.

Media

Hard standard reference water (HSRW, pH 8.5, hardness = 160mg/L CaCO₃, alkalinity = 130 mg/L CaCO₃) was used throughout the study. HSRW was mixed according to the guidelines laid out by the U.S. EPA (1975).

Sediments were collected from six inshore and offshore sites at three different rivers that empty into Lake Erie. These included an inshore Maumee River site (MRB; 41° 42.018 N, 83° 27.664 W) and an off shore Maumee River site (MRO; 41°41.944 N, 83°23.632 W); an inshore Sandusky River site (SRB; 41°27.710 N, 82°44.365 W) and an offshore Sandusky River site (SHO; 41°28.648 N, 82°39.114 W); and an inshore Grand River site (GRB; 41°45.962 N, 81°16.660 W) and an offshore Grand River site (GRO 41°47.879 N, 81°16.835 W). Multiple sediment samples were taken at each site by using a PONAR grab (Figure 2). These samples were placed into 1000 ml plastic bottles and stored in a cooler with ice for transport. Upon arriving back at the laboratory, the sediment was stored at 4°C in 1000 ml plastic bottles until the beginning of the experiment.



Figure 2. PONAR grab used to collect sediments from inshore and offshore sites at the Maumee River, Sandusky River, and Grand River. From HELCOM, 2002.

Sediment was analyzed for total organic carbon (TOC) at The Penn State University Agricultural Analytical Services Laboratory using a Fisons NA 1500 Elemental Analyzer. Percent TOC for sediment collected from the research sites are presented in Table 1.

Sediment spiking

Sediments were prepared for spiking by passing them through a 1-mm screen sieve to remove debris and organisms. Samples collected from within a site were homogenized, then washed with deionized water and centrifuged. Otherwise, the sediments were not autoclaved or exposed to any similar preparatory measures in an attempt to maintain as much of the natural characteristics as possible. A sediment-water slurry was made by placing the sediments with HSRW in a 1:4 (m:v) sediment:water ratio. The sediment-water slurry was then mixed by placing it on a mechanical stirrer. As the slurry mixed, radiolabeled HCBP was added in an acetone carrier and mixed for 12 hours at room temperature. This allowed for the acetone to evaporate off and the HCBP to associate with the sediments. After the mixing was completed, the slurry was centrifuged in 100 ml glass centrifuge tubes at 2200 rpm for 30 minutes. The water was decanted off and the sediments were mixed, weighed out in 5 g portions, and placed in 10 ml beakers for the bioassay. In addition, 7 ml of HSRW were added and the sediment was mixed to create an even surface at the bottom of the beaker. The beakers were then placed in an environmental chamber (FormaScientific) set to 20°C with a 16:8h light:dark photoperiod (fluorescent lights, $\lambda=500\text{nm}$). Sediments and HSRW were maintained under these conditions for 24 hours before the experiment began to allow the sediments to settle at the bottom of the beaker and to allow the temperature of the sediments and water to equilibrate to 20°C.

Bioassay

At the start of the experiment, 2 *H. azteca*, 2 *L. variegatus*, and 2 *C. riparius* were placed into each beaker. Beakers were then placed into the environmental chamber and allowed to sit until sampling time. There were 7 sample times at 6h, 12h, 18h, 24h, 32h, 40h, and 48h, and three replicates for each site at each sample time.

At each sample time, beakers designated to be sampled were retrieved from the environmental chamber. A one ml sample of the HSRW was taken to determine the concentration of HCBP in the water. Approximately one gram of sediment was then removed, weighed and placed in a scintillation vial to determine the concentration of HCBP in the sediment. All organisms were then removed from the sediment, rinsed off with deionized water, and placed in a beaker containing fresh HSRW. The animals were allowed to purge their guts for about 1 to 2 hrs. While previous studies have show that purging is not necessary for experiments similar to this one (Lydy and Landrum, 1993, Harkey et al., 1994a), it was necessary to remove all organisms at a given sample time in the most expeditious manner to prevent overexposure to the contaminated sediment. Removing organisms from the sediment and preparing them for analysis right away would have resulted in overexposure of organisms sampled subsequently for the same sample time.

After approximately 1h of purging time spent in the HSRW, organisms were removed, separated by species, blotted dry with a Kimwipe, placed in pre-weighed scintillation vials and weighed. To facilitate contaminant extraction from animal tissue, 50 ul H₂O₂ and 100 ul nitric acid were added to the vial, then swirled, and heated at 50°C for one minute. The vials were then allowed to cool and received 10 ml of scintillation cocktail (Scintiverse, Fisher Chemical, Fair Lawn, NJ, USA). All vials were then shaken and placed in the dark at 4°C for at least 24 hours before analysis. Scintillation vials containing sediment or water also received 10 ml of scintillation cocktail and were placed in the dark at 4°C for at least 24 hours before analysis. All samples were analyzed for radioactivity through liquid scintillation counting in a Beckman LS6000IC. Each sample was counted for five minutes, after which the data were collected and corrected for quench using the external standards ratio method.

Data Analysis

The initial rates procedure described by Landrum et al. (1992) was used to determine the k_s for each organism at each site. The slope of the uptake curve was determined and fit into the following equation:

$$dCa/dt = k_s C_s - k_d C_a \quad (\text{equation 1})$$

where C_a is the total concentration in the animal (ug/g, wet wt.), C_s is the concentration of the contaminant in the sediment (ug/g, wet wt.), k_s is the uptake coefficient (g sediment wet wt. /g organism wet wt/h), k_d is the elimination rate (1/h), and t is time (h). This yielded the values for k_s . The values for k_d were obtained from previous studies and are as follows: 0.007/h for *C. riparius* (Boulet-Stoeckel, 1995), 0.0013/h for *L. variegatus* (Fisher et al., 1999), and 0.012/h for *H. azteca* (Shuler et al., 2003).

BAFs were calculated using k_s and the k_d in the following equation as described by Landrum et al. (1992):

$$BAF = k_s / k_d \quad (\text{equation 2})$$

Statistics

A General linear model (GLM) was used to find significant differences in mean uptake rates among organisms and among sites. Tukey's honestly significant difference test was used to make pair-wise comparisons between organisms and between sites. Statistical tests were performed using SPSS for Windows (Release 9.0.0, Copyright © 1989-1999 by SPSS Inc.). Differences between means were considered to be significant if $p < 0.05$.

Results

Contamination of Sediment and Water

Sediments were analyzed for ^{14}C labeled HCBP concentration using liquid scintillation counting. Concentrations of HCBP were not significantly different between inshore and offshore sites at any of the three study locations (Table 1). MRO had a HCBP sediment concentration of 0.28 ug/g (± 0.041) compared to a concentration of 0.288 ug/g (± 0.288) at site MRB. Both sites GRO and GRB had HCBP sediment concentrations of 0.237 ug/g (± 0.03 and ± 0.013 , respectively). Sandusky River sites did show some variation between SHO and SRB, with SHO sediments having the highest HCBP concentration (0.294, ± 0.031) and SRB having the lowest sediment concentration (0.225, ± 0.026). However, these differences were not significant.

Organic carbon concentrations ranged between 1.43% and 2.53% at all locations (Table 2). At the Maumee River location, the MRO site had an organic carbon content of 1.43% while the MRB site had an organic carbon content of 2.14%. At the Sandusky River location, sediments from site SHO had an organic carbon fraction of 1.73%, compared to 2.53% for site SRB. At the Grand River location, the organic carbon fraction was 2.16% at GRO, while site GRB had an organic carbon fraction of 1.57%.

Table 1. Concentration of HCBP in bioassay sediments for each location.

Sediment		
Location	Concentration (ug/g)	St. Dev (+/-)
MRO	0.280	0.041
MRB	0.288	0.037
SHO	0.294	0.031
SRB	0.225	0.026
GRO	0.237	0.030
GRB	0.237	0.013

Table 2. Percent total organic carbon for sediments collected from the six study sites.

Location	%OC
MRO	1.43
MRB	2.14
SRO	1.73
SRB	2.53
GRO	2.16
GRB	1.57

Water samples were taken from bioassays for each site and analyzed for dissolved HCBP. The results are reported in Table 3. The HCBP water concentration was $2.07\text{E-}4$ ug/ml ($\pm 7.72\text{E-}6$ ug/ml) at site MRO and $1.88\text{E-}4$ ug/ml ($\pm 4.96\text{E-}5$ ug/ml) at site MRB. At the Sandusky River locations, SHO had a HCBP water concentration of $1.40\text{E-}4$ ug/ml ($\pm 1.68\text{E-}5$ ug/ml) and SRB had a HCBP water concentration of $1.07\text{E-}4$ ug/ml ($\pm 1.76\text{E-}5$ ug/ml). Bioassays utilizing sediments from site GRO had HCBP water concentrations of $1.46\text{E-}4$ ug/ml ($\pm 3.40\text{E-}6$ ug/ml) while GRB bioassays had HCBP water concentrations of $2.27\text{E-}4$ ug/ml ($\pm 2.55\text{E-}5$ ug/ml).

Contaminant Uptake Rates for Organisms

Uptake coefficients (ks) and bioaccumulation factors (BAF) were determined for each organism at each site. A general linear model statistical analysis revealed that there were statistically significant differences for both organisms and sites in the Maumee and Grand Rivers ($p < 0.05$). However, no statistically significant differences were found at the Sandusky River. General linear modeling comparing organisms across sites revealed that *C. riparius* had significantly higher uptake rates than *L. variegatus* or *H. azteca* when all sites were taken into consideration ($p < 0.05$). No significant differences were found between *L. variegatus* and *H. azteca* ($p > 0.05$).

Table 3. Concentration of HCBP in bioassay water for each location.

Location	Water	
	Concentration (ug/ml)	St. Dev (+/-)
MRO	2.07E-04	7.72E-06
MRB	1.88E-04	4.96E-05
SHO	1.40E-04	1.68E-05
SRB	1.07E-04	1.76E-05
GRO	1.46E-04	3.40E-06
GRB	2.27E-04	2.55E-05

Table 4. Toxicokinetic parameters for HCBP in *L. variegatus*.

Site	k_s ($g\ g^{-1}\ h^{-1}$)	St.Dev.	k_d (h^{-1})	BAF ($g\ g^{-1}$)
MRO	0.127	0.011	0.0013	97.960
MRB	0.065	0.006	0.0013	49.974
SHO	0.108	0.010	0.0013	83.458
SRB	0.080	0.006	0.0013	61.757
GRO	0.062	0.009	0.0013	47.309
GRB	0.054	0.007	0.0013	41.566

Table 5. Toxicokinetic parameters for HCBP in *C. riparius*.

Site	k_s ($g\ g^{-1}\ h^{-1}$)	St.Dev.	k_d (h^{-1})	BAF ($g\ g^{-1}$)
MRO	0.109	0.004	0.007	15.580
MRB	0.086	0.006	0.007	12.342
SRO	0.107	0.013	0.007	15.325
SRB	0.143	0.015	0.007	20.377
GRO	0.096	0.024	0.007	13.761
GRB	0.071	0.010	0.007	10.211

Table 6. Toxicokinetic parameters for HCBP in *H. azteca*.

Site	k_s ($g\ g^{-1}\ h^{-1}$)	St.Dev.	k_d (h^{-1})	BAF ($g\ g^{-1}$)
MRO	0.055	0.015	0.012	4.543
MRB	0.065	0.024	0.012	5.376
SHO	0.138	0.041	0.012	11.488
SRB	0.065	0.032	0.012	5.431
GRO	0.092	0.022	0.012	7.631
GRB	0.055	0.009	0.012	4.615

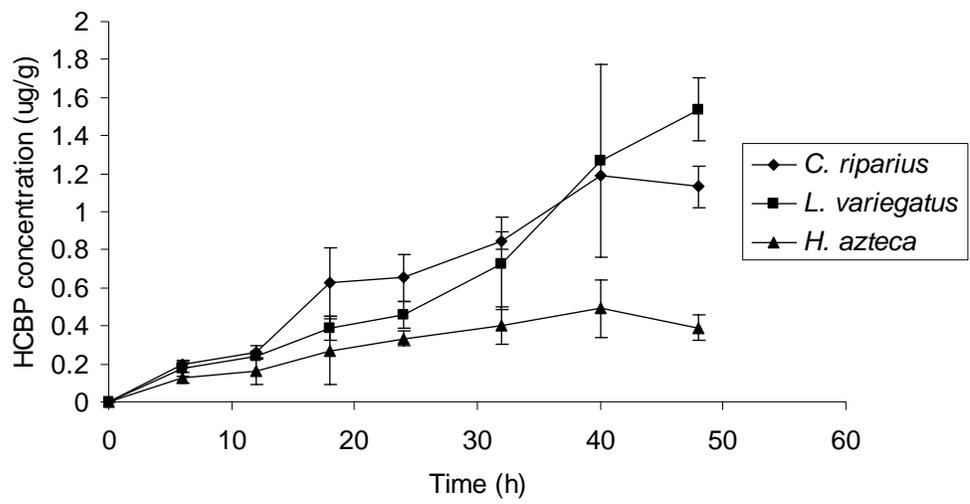


Figure 3. Uptake of HCBP for *C. riparius*, *L. variegatus*, and *H. azteca* in sediment collected from site MRO.

At the MRO site, *L. variegatus* had the highest k_s value ($0.127 \text{ g g}^{-1}\text{h}^{-1}$, Table 4). *C. riparius* a similarly high value of $0.109 \text{ g g}^{-1}\text{h}^{-1}$ (Table 5), while *H. azteca* had a much lower k_s at $0.055 \text{ g g}^{-1}\text{h}^{-1}$ (Table 6). Uptake curves for all three organisms are displayed in Figure 3.

At the MRB site, *C. riparius* had the highest k_s at $0.086 \text{ g g}^{-1}\text{h}^{-1}$ (Table 5). *L. variegatus* and *H. azteca* both had lower k_s values of $0.065 \text{ g g}^{-1}\text{h}^{-1}$ (Table 4 and Table 6, respectively). The uptake curves for the three organisms are presented in Figure 4.

The General linear model found that there were statistical differences for both organisms and sites at the Maumee River locations ($p < 0.05$; Table 7). It appeared as though k_s values were higher for both *L. variegatus* and *C. riparius* at MRO than they were at MRB (Tables 4 and 5). *H. azteca*, on the other hand, had a higher k_s values at the MRB site than the MRO site (Table 6). Tukey's honestly significant difference test revealed significantly higher uptake rates for *C. riparius* and *L. variegatus* when compared to *H. azteca* at these sites ($p < 0.05$). No significant differences were found between *C. riparius* and *L. variegatus*.

At site SHO, *H. azteca* had a particularly high k_s of $0.138 \text{ g g}^{-1}\text{h}^{-1}$ (Table 6). This was the highest k_s for *H. azteca* at all locations, but was not significantly higher than the other organisms. *L. variegatus* and *C. riparius* also had high k_s values of $0.107 \text{ g g}^{-1}\text{h}^{-1}$ and $0.108 \text{ g g}^{-1}\text{h}^{-1}$, respectively (Tables 4 and 5). Uptake curves for the organisms exposed to sediments from this site are displayed in Figure 5.

At the SRB site, *C. riparius* had a k_s value of $0.143 \text{ g g}^{-1}\text{h}^{-1}$ (Table 3). This was the highest uptake rate for all organisms across all sites in this study, but was not significantly higher than the other organisms for these sediments. *L. variegatus* had a lower k_s of $0.080 \text{ g g}^{-1}\text{h}^{-1}$ (Table 2). *H. azteca* had the lowest uptake rate at this site, with a k_s of $0.065 \text{ g g}^{-1}\text{h}^{-1}$ (Table 4),

Table 7. Statistical values for general linear model analysis of variance comparing kd means between sites and between organisms.

Location	test variable	DF	F	P
MR	site	1	7.4	0.019
	organism	2	7	0.010
SR	site	1	1.97	0.182
	organism	2	1.41	0.277
GR	site	1	8.63	0.012
	organism	2	3.86	0.048

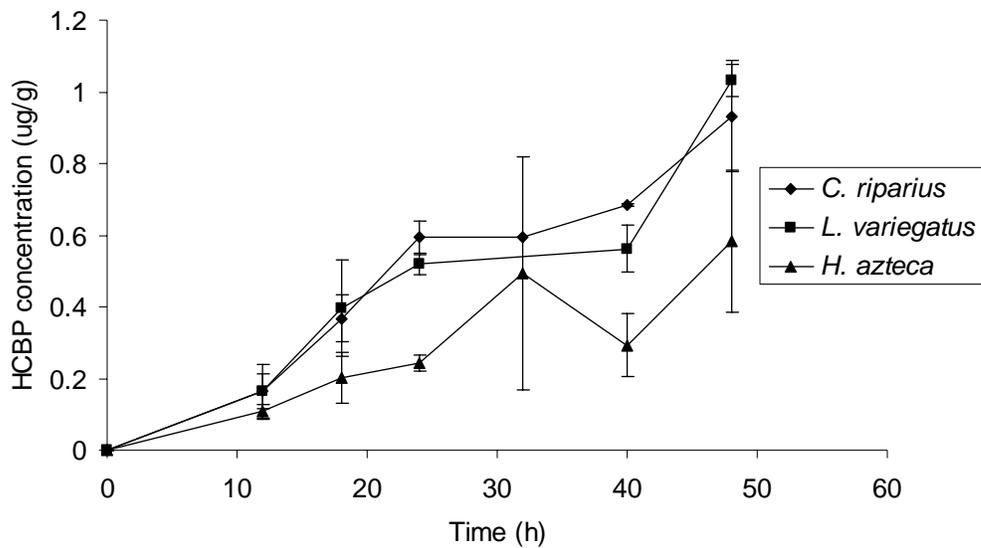


Figure 4. Uptake of HCBP for *C. riparius*, *L. variegatus*, and *H. azteca* in sediment collected from site MRB.

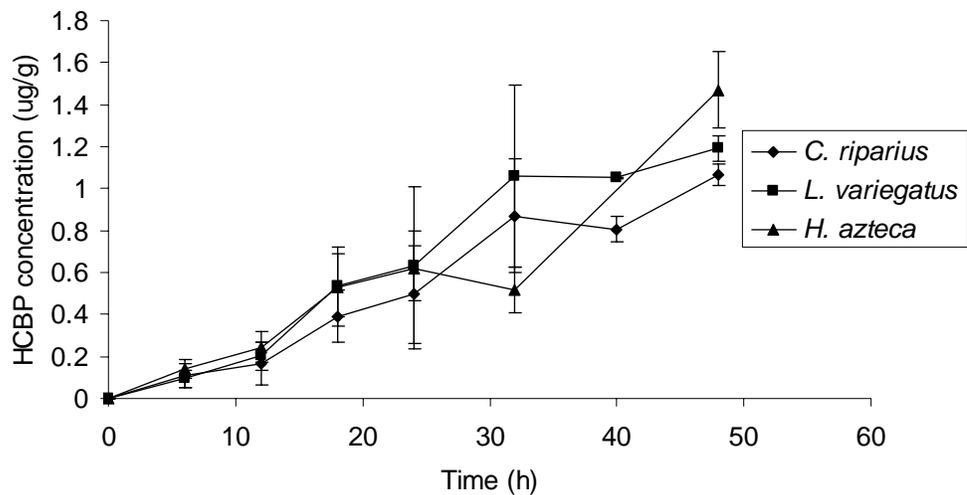


Figure 5. Uptake of HCBP for *C. riparius*, *L. variegatus*, and *H. azteca* in sediment collected from site SHO.

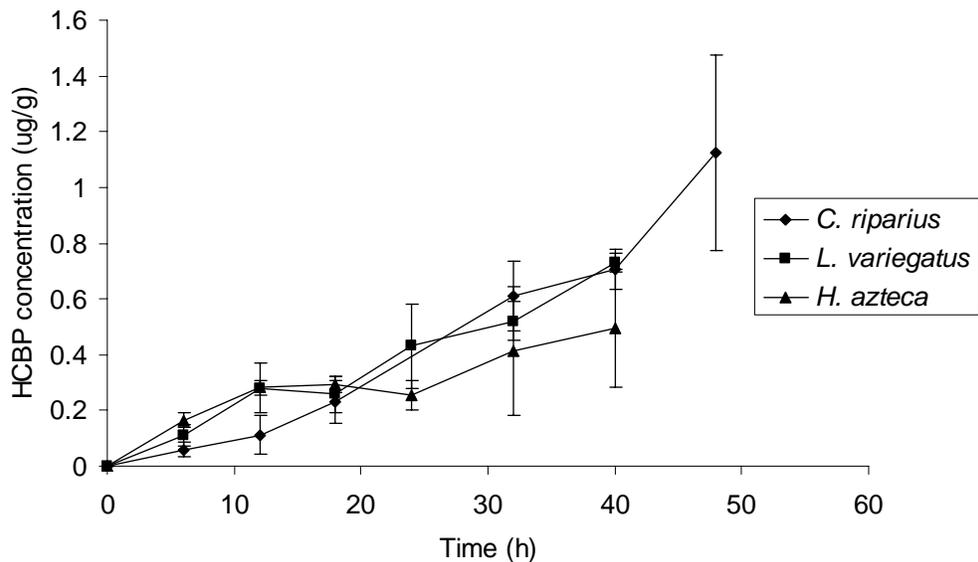


Figure 6. Uptake of HCBP for *C. riparius*, *L. variegatus*, and *H. azteca* in sediment collected from site SRB.

though this was not significantly lower than the uptake rate for *L. variegatus*. The uptake curve is expressed in Figure 6.

Despite a high degree of variation, the General Linear Model ANOVA found no significant differences between sites or organisms for the Sandusky River locations (Table 7). This is likely due to the high standard deviations for the organism k_s values at these sites. Likewise, Tukey's honestly significant difference test found no significant differences between any organisms.

C. riparius and *H. azteca* had insignificantly different uptake rates for site GRO, with values of $0.096 \text{ g g}^{-1}\text{h}^{-1}$ and $0.092 \text{ g g}^{-1}\text{h}^{-1}$ respectively (Tables 5 and 6). *L. variegatus* had a significantly lower uptake for this site, with a k_s of $0.062 \text{ g g}^{-1}\text{h}^{-1}$ (Table 4). The uptake curves are displayed in Figure 7.

At the GRB site, *C. riparius* had a significantly higher uptake rate than the other organisms, which was $0.071 \text{ g g}^{-1}\text{h}^{-1}$ (Table 5). *L. variegatus* and *H. azteca* had insignificantly different k_s values of $0.54 \text{ g g}^{-1}\text{h}^{-1}$ and $0.55 \text{ g g}^{-1}\text{h}^{-1}$ (Table 4 and Table 6, respectively). *C. riparius* had its lowest uptake rates at this site when compared to all other sites. This held true for *L. variegatus* as well. *H. azteca* also had a particularly low value, though the uptake rate ($0.055 \text{ g g}^{-1}\text{h}^{-1}$) was the same as from MRO. The uptake curves for all three organisms can be found in Figure 8.

The General linear model revealed significant differences between sites and organisms for Grand River bioassays (Table 7). All three organisms had higher uptake clearance values at GRO when compared to GRB, with *C. riparius* having the highest

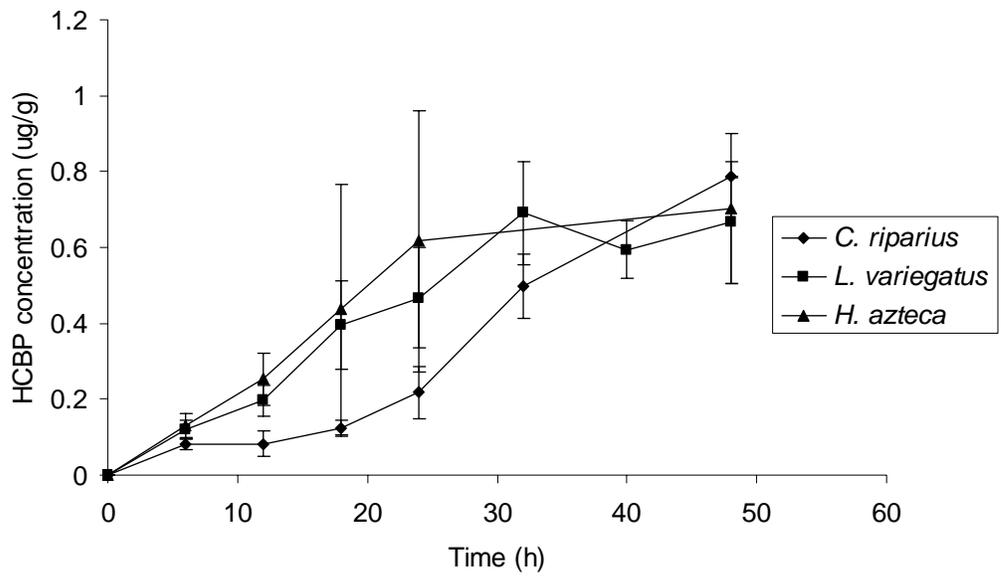


Figure 7. Uptake of HCBP for *C. riparius*, *L. variegatus*, and *H. azteca* in sediment collected from site GRO.

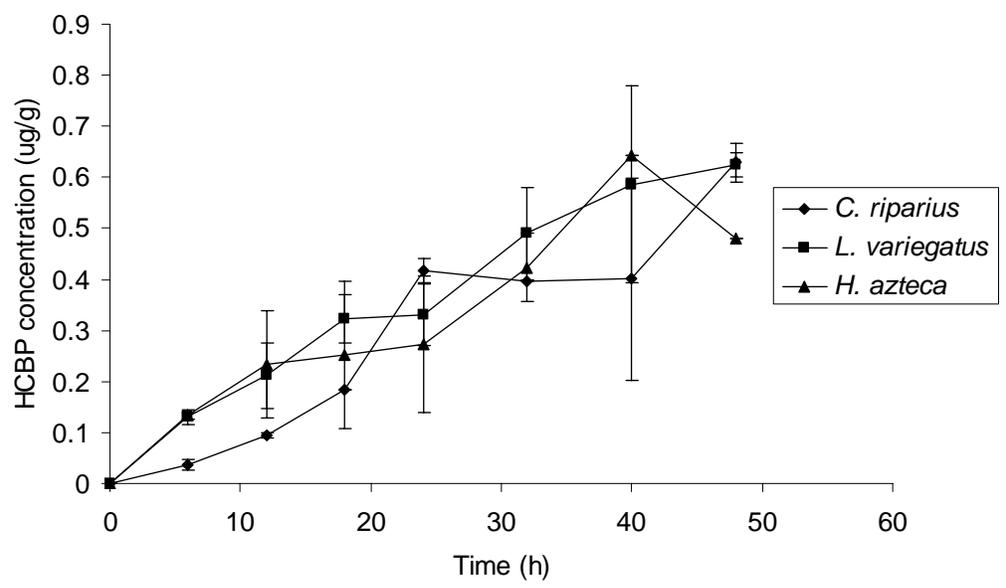


Figure 8. Uptake of HCBP for *C. riparius*, *L. variegatus*, and *H. azteca* in sediment collected from site GRB.

significant differences between *C. riparius* and *L. variegatus* for both locations. *C. riparius* had significantly higher uptake rates than *L. variegatus*. No significant differences were found between *H. azteca* and either of the other two organisms when both sites were included in the analysis.

Bioaccumulation Factors

While BAFs varied between sites for each organism, a consistent pattern was observed between organisms. Because they had the lowest elimination rate, *L. variegatus* had the highest BAFs for all of the organisms in all of the sites (Table 4). The highest BAF for these organisms was found at site MRO (97.960 g g⁻¹), while the lowest BAF was found at site GRB (41.566 g g⁻¹). In all cases, *L. variegatus* had higher BAFs at offshore sites than at inshore sites.

C. riparius had intermediate BAFs at all study sites (Table 5). The highest BAF for these organisms was observed at SRB (20.377 g g⁻¹), while the lowest BAF was observed at GRB (10.211 g g⁻¹). *C. riparius* had higher BAFs at the offshore sites for both the Maumee and Grand Rivers, while the organisms in the inshore sediments had higher BAFs at the Sandusky River.

H. azteca had the lowest BAFs for all the organisms investigated in this study (Table 6). *H. azteca* exposed to sediments from SHO had particularly high BAFs (11.488 g g⁻¹), while those exposed to sediments from MRO had the lowest BAFs (4.543 g g⁻¹) for all sites. Higher BAFs were observed at the inshore sites for both the Sandusky and Grand Rivers, while the offshore site revealed the higher BAFs in the Maumee River.

Discussion

Organism uptake rates

The three organisms investigated during these experiments display varying foraging strategies that may influence uptake rates of the contaminants from sediment. The larvae of

Chironomus riparius spend their entire larval existence in the sediment surviving on algal-detrital materials that are associated with sediments (Oliver, 1971). The foraging strategy employed by *C. riparius* is a collector-gathering strategy in which the larvae consume any materials, including sediment, in the immediate surroundings (Cummins, 1973). This foraging behavior is not very selective, and many of the materials consumed are not digested and assimilated (Cummins, 1973).

Lumbriculus variegatus are burrowing oligochaetes that live out their entire life history in the sediments of freshwater lakes (Cook, 1969). The primary food sources for *L. variegatus* are organic materials associated with benthic sediments. The feeding strategy utilized to obtain these materials is a deposit feeding behavior in which the organism selectively feeds on fine-grain particulates that tend to be rich in organic carbon (McMurtry et al., 1983). These sediments tend to be associated with higher concentrations of organic contaminants because of the organic carbon fraction. As a result, *L. variegatus* may be exposed to higher levels of organic contaminants because of this feeding strategy (Klump, et al., 1987).

Hyalella azteca are epibenthic detritives that employ a grazing-deposit feeding strategy in consuming algae and detritus (Ingersoll, 1995). *H. azteca* live their entire life history at the sediment-water interface, both burrowing in the sediment and swimming in the water column just above the sediment (USEPA, 2000) and consume food material associated with both periphyton and sediments (Hargrave, 1970). The epibenthic behavior of these organisms reduces contact with contaminated sediments, which reduces exposure to sediment-associated contaminants (Ingersoll, 1995).

Because of the selective preference for fine particulates that are high in organic carbon, *L. variegatus* was predicted to have the highest uptake rates for HCBP. The preferred food sources

of these organisms have a high affinity for HCBP. This should have resulted in an increased exposure of *L. variegatus* to the contaminant. However, the bioavailability of the HCBP on the organic carbon fraction may have influenced this result. *C. riparius* was predicted to have an intermediate uptake rate because of the less selective collector-gatherer feeding strategy. Consumed sediment particles should not have a consistently high organic carbon fraction, resulting in a reduced uptake rate when compared to that of *L. variegatus*. However, the infaunal behavior of the organism maintained constant contact with the sediment, which should have resulted in consistent exposure to contaminated sediments and a moderate uptake rate. *H. azteca* was predicted to have the lowest uptake rate. The epibenthic behavior should have reduced the contact of the organism with the sediments, resulting in a decreased exposure to the contaminants.

The investigation of feeding behavior during these experiments revealed that foraging strategy did influence contaminant uptake rates in the three test organisms. Statistically significant differences were found for Maumee River sediments, where *C. riparius* and *L. variegatus* had significantly higher uptake rates than *H. azteca*, and Grand River sediments, where *C. riparius* had significantly higher uptake rates than *L. variegatus* (Tables 4, 5, and 6). No significant differences were found at the Sandusky River site.

At the Maumee River location, *H. azteca* may have had the lowest uptake rate because it spent the least amount of time in the sediment. HCBP concentrations in the water column averaged 0.00017 ug/g (\pm 0.05 ug/g), which were much lower than sediment concentrations (0.26 ug/g, + 0.04 ug/g). This supports the idea that the optimal source of the contaminant was from the spiked sediments for this experiment. Sediment contaminants are more difficult to assimilate than dissolved contaminants (Lee, 1991). However, K_{ow} is an important factor in

determining the primary source of a contaminant from an aquatic system (Landrum, 1989; Lee, 1991). Compounds that have high K_{ow} s, usually greater than 6, quickly sorb to sediments and have relatively low concentrations in both the interstitial water and the water column. As a result, sediment ingestion becomes an important source of these contaminants to benthic organisms (Landrum, 1989; Landrum and Robbins, 1990; Lee, 1991). *H. azteca* has a tendency to dwell both in the water column and in the sediment; however, they may have been spending a disproportionate amount of time in the water column because of the high density of organisms found in the sediments. This reduced the organisms contact with the contaminated sediment and was expressed through reduced uptake rates.

Similar results have been reported in previous studies. Shuler et al. (2002) also observed a reduction in the uptake rates of sediment associated organic contaminants for *H. azteca* when placed in a bioassay with other organisms. *H. azteca* assimilated sediment-associated benzo(a)pyrene (B(a)P) at uptake rates of $0.018 \text{ g g}^{-1} \text{ h}^{-1} (\pm 0.002)$ and $0.016 \text{ g g}^{-1} \text{ h}^{-1} (\pm 0.002)$ when placed in bioassays with *C. tentans* ($0.357 \text{ g g}^{-1} \text{ h}^{-1}, \pm 0.004$) or *L. variegatus* ($0.0243 \text{ g g}^{-1} \text{ h}^{-1}, \pm 0.002$), respectively. In this case, it was reasoned that *H. azteca* spent more time in the water column than in the contaminated sediments to avoid contact with the other organisms. This reduced the organism's contact with the contaminant and reduced its uptake rate. Reynaldson et al. (1994) discovered that *H. azteca* maintained in beakers with oligochaetes had a growth rate reduced by 60%. This resulted from the ingestion of preferred food resources in the sediments by the oligochaetes. The *H. azteca* instead settled for secondary food sources found in the water column and avoided contact with the oligochaetes.

The design of my experiment may have reduced a potentially higher uptake rate for *H. azteca*. Shuler et al. (2003) investigated the influence of sediment aging on HCBP

bioavailability. Short-term experiments, which took place over 7 days, were similar in design to my experiment, with the exception of maintaining isolated organisms in the bioassays.

Sediments were spiked with HCBP in concentrations that ranged between 12.57 ug/kg (± 0.28) and 13.29 ug/kg (± 0.84). The short-term study revealed that *H. azteca* had higher uptake rates ($0.101 \text{ g g}^{-1}\text{h}^{-1}$, $\pm 3.13\text{E-}005$) than *C. tentans* ($0.054 \text{ g g}^{-1}\text{h}^{-1}$, $\pm 7.96\text{E-}006$) in similar isolated bioassays. *L. variegatus*, which were also included in the study, had a slightly higher uptake rate ($0.122 \text{ g g}^{-1}\text{h}^{-1}$, $\pm 2.63\text{E-}005$) than *H. azteca*. The design for this study may not be a flaw as it is more likely to project what occurs in the sediments of a lake. *H. azteca* will be in constant contact with other benthic organisms under natural conditions, thus spending less time in contact with contaminant source sediments and accumulating contaminants at a slower rate than organisms that remain in constant contact with the sediments.

C. riparius and *L. variegatus* did not have significantly different uptake rates from each other for the Maumee River experiments. Despite different feeding strategies, neither organism expressed a consistent rate of uptake that was higher or lower than that of the other organism. *L. variegatus* had a higher uptake rate at site MRO, while *C. riparius* had a higher uptake rate at MRB (Tables 3 and 4).

These results conflict with those found in previous studies. Shuler et al. (2002) discovered that *C. tentans* tended to have higher uptake rates for sediment bound B(a)P than *L. variegatus*. Similar to *H. azteca*, this variation was believed to be caused by interaction with other organisms. *L. variegatus* has a response reflex to movement that assists in predator avoidance. Contact with other organisms in the sediment have may resulted in increased reflex activity and interrupted burrowing and feeding behaviors (Shuler et al., 2002). Reduced feeding will result in reduced uptake rates for sediment bound contaminants. This decrease in uptake

rate may have also resulted from fecal consumption. *L. variegatus* may have preferentially fed on other organisms' feces, which may have contained lower concentrations of B(a)P than the sediment (Shuler et al., 2002). Harkey et al. (1994a) had differing observations in isolated bioassays comparing uptake rates of *L. variegatus*, *C. riparius*, and *Diporeia* spp. for several organic contaminants. In these experiments, *C. riparius* generally had lower uptake rates than those of *Diporeia* spp. or *L. variegatus*. It was suggested that this was the result of the selective feeding behaviors of *Diporeia* spp. and *L. variegatus*. These organisms generally tend to consume sediments with higher organic carbon fractions. These high organic carbon sediments also have a higher capacity for binding to organic contaminants. Thus, *L. variegatus* should be exposed to higher concentrations of contaminants because of diet selectivity. Harkey et al., (1994b) observed HCBP and B(a)P uptake rates in *Diporeia* spp., for sediments with varying characters. They observed that selective feeding in *Diporeia* spp. did result in higher uptake rates of HCBP due to the preference for particulates that had a high sorption capacity for HCBP. However, increasing TOC for these preferred particulate sizes tended to decrease uptake rates because of the high sorption affinity of HCBP for the organic fraction (Harkey et al., 1994b). Landrum and Faust (1991) also observed that increasing TOC of sediments resulted in a decreased uptake rate for several PCBs and PAHs in *Diporeia* spp.

The assimilation efficiency (AE) of an organism may be important in determining how an organism will accumulate contaminants from a food source. This method attempts to determine how efficient an organism is in accumulating a contaminant from possible sources (Harkey, 1994b). Determination of the AE for an organism can be very difficult to calculate and depend on the portioning of the contaminant into sources and the feeding behavior of the organism (Harkey, 1994b). *C. riparius* tend to have very low AE for organic material associated with

sediments. Rasmussen (1984) found that *C. riparius* assimilated only 5.9% of the organic carbon associated with consumed sediments. Boulet-Stoeckel (1995) observed that the AE of *C. riparius* for HCBP was low and was not affected by the organic carbon fraction of the sediments. While the low AE for *C. riparius* would suggest a smaller uptake rate for HCBP, this study observed a relatively high uptake rate compared to the other organisms. This may be due to the fact that the qualities of available food sources influence the feeding rate of Chironomids (Johannsson, 1980). Boulet-Stoeckel (1995) argued that the sediment preparation process, which included drying and autoclaving the sediment, killed many of the microorganisms associated with the sediments. This may have reduced the quality of the sediment as a food source, resulting in reduced feeding rates and decreased AE (Boulet-Stoeckel, 1995). Because this study attempted to maintain nutritional qualities of natural sediment, these steps were not performed. The nutritional quality of the sediments may have been higher, possibly leading to higher feeding rates for *C. riparius*. However, since feeding rates and AE were not measured in this study, this can not be concluded and must be targeted in future studies.

As previously stated, *L. variegatus* is a selective deposit feeder that preferentially consumes fine particulates that tend to be high in organic carbon (McMurtry et al., 1983). However, the selectivity is based more on particle size rather than organic carbon content (Kukkonen and Landrum, 1995). The AE of *L. variegatus* for sediment associated HCBP ranges between 15% and 30% (Klump et al., 1987). This is higher than the AEs found for *C. riparius* in the literature, and may conflict with the findings of this study. Based on the experiments, *L. variegatus* should be more effective at assimilating sediment sorbed organic materials (Klump et al., 1987). However, as with *C. riparius*, this is determined by a number of factors, including food quality and feeding rate (Kukkonen and Landrum, 1995). Because these values were not

obtained through these experiments, the influence of AE on contaminant uptake cannot be determined.

The AE of intermittent feeders is very difficult to measure and is not well understood (Harkey et al., 1994b; Kukkonen and Landrum, 1995). As *H. azteca* tends to spend more time in the water column than the other organisms, it has an intermittent contact with the contaminated sediments that may be used as a food source. This may make a calculation for the AE of *H. azteca* more difficult and less effective than calculations made for *C. riparius* and *L. variegatus*, though it still merits pursuit in continuing investigations along this line of research.

Statistically significant differences were observed between *C. riparius* and *L. variegatus* at the Grand River location. *C. riparius* had significantly higher uptake rates than *L. variegatus* at both sites for this location (Tables 3 and 4). This result was similar to that of Shuler et al. (2002) and conflicted with some of the studies discussed above, including Harkey et al. (1994a) and Shuler et al. (2003). *H. azteca* were not found to be significantly different from *C. riparius* or *L. variegatus* at this location, and had similar uptake rates to *C. riparius* at GRO and similar uptake rates to *L. variegatus* at site GRB (Table 5).

No significant differences were observed at the Sandusky River location. At SHO, *H. azteca* had the highest uptake rate of all three organisms and the highest uptake rates for *H. azteca* at all sites. These results were not significantly different from *C. riparius* or *L. variegatus* due to a high degree of variation. One replicate in particular was much higher than the other two replicates. Omission of this replicate decreased the uptake rate so that it was closer to those of the other organisms ($0.116 \text{ g g}^{-1}\text{h}^{-1}$, ± 0.022). However, this is still unusually high for *H. azteca* when compared to all other sites. TOC at SHO (1.73%) was lower than that of SRB (2.53%), however it was not unusually high or low when compared to other sites. A more detailed

sediment analysis could discover a site effect that explains the unusually high uptake rates for this site. The SRB site had results that were similar to those from the other sites. Here *C. riparius* had the highest uptake rate (Table 4) while *L. variegatus* had an intermediate uptake rate (Table 3) and *H. azteca* had the lowest uptake rate (Table 5).

General linear modeling found that *C. riparius* had significantly higher uptake rates than *L. variegatus* and *H. azteca* when all sites were taken into consideration. No significant differences were found between *L. variegatus* and *H. azteca* for the same analysis. These results partially support the hypothesis. *C. riparius* was predicted to have intermediate uptake rates when compared to the other organisms. The hypothesis stating that *C. riparius* will have a higher uptake rate than *H. azteca* appears to be supported by the results. However, *C. riparius* also appears to have higher uptake rates than *L. variegatus*, despite the prediction that *L. variegatus* would have the highest uptake rates.

These results appear to agree with those made by Shuler et al. (2002). Similarly, that study found the *C. tentans* had the highest rates of B(a)P uptake when a multi-species bioassay was performed. As stated above, interactions between *L. variegatus* and the other organisms may have stimulated a predator avoidance behavior that reduced foraging time and resulted in reduced contaminant uptake rates (Shuler et al., 2002). Similarly, contact with macroinvertebrates may have caused *H. azteca* to spend a disproportionate amount of time in the water column and reduced the contact of the organisms with the sediment and preferred sediment food sources (Shuler et al., 2002). Because *C. riparius* tend to remain sequestered in their sediment casings, they may have had reduced contact with the other organisms and spent more time foraging resulting in elevated uptake rates. However, because organism interactions were

not observed during the study, this cannot be confirmed. Further research is required to determine if this is the case.

Another explanation for the lower uptake rates of *L. variegatus* during the study may involve the organic carbon fraction of the sediment. Harkey et al. (1994b) stated that increasing organic carbon fraction of the selected particulate size may decrease the uptake rate of organic contaminants. While no distinct pattern is observed between study sites, TOC, and uptake rates for *L. variegatus*, it is possible that the HCBP had a higher affinity for particles on which *L. variegatus* selectively consumed. This may have reduced the available HCBP, resulting in a reduced uptake rate for the oligochaetes. Further investigations must be performed with a more detailed sediment analysis to determine how sediment TOC may have influenced the results of the experiment.

Site effects on organism uptake rates

Organic content of sediments and site location were also investigated to observe their effects on uptake rates. Non-polar organic contaminants have a high affinity for sediments with high organic carbon fractions. These sediments tend to accumulate greater organic contaminant concentrations than sediments with smaller organic carbon fractions (Landrum and Robbins, 1990; Lee, 1991). Because of the higher levels of associated contaminants, inhabiting organisms are exposed to greater contaminant concentrations (Lee, 1991).

Inshore harbor sites and offshore basin sites may have different organic carbon fractions despite being close in location. Inshore sites tend to have higher organic carbon fractions than offshore sites because of a closer proximity to land (Krieger and Ross, 1993). The higher organic carbon content may influence how benthic communities at inshore sites accumulate organic contaminants when compared to offshore sites.

It was hypothesized that HCBP uptake rates would be higher at inshore, harbor sites, including MRB, SRB, and GRB, because of higher organic carbon fractions. These sediments should have higher concentrations of HCBP sorbed, providing a greater exposure of contaminants to the inhabiting organisms.

The investigation of site effects on organism uptake rates revealed significant differences in ks by site; however no obvious pattern can be observed with the data available. Higher uptake rates should have been observed at sites with higher organic carbon sediment fractions due to the higher sorbing capacity of HCBP to these sediments resulting in greater exposure through sediment consumption. This, however, does not appear to be the case.

At the Maumee River sites, both *C. riparius* and *L. variegatus* had higher uptake rates at MRO, the offshore site. This site had a lower organic carbon fraction than sediments from the inshore site, MRB. While the lower organic carbon fraction was expected, the higher uptake rates at this site were not. *H. azteca* was the only organism that had a higher uptake rate at MRB; however this was only a slight difference and was not significantly different.

This contradiction was also observed at the Sandusky River sites. In this case, both *L. variegatus* and *H. azteca* had higher uptake rates at SHO, the offshore site with a lower organic carbon fraction. General linear model analysis comparing uptake rates by both site and organism found no significant differences at this location. However, a one-way ANOVA comparing only individual organisms at SHO to individual organisms at SRB did reveal significant differences between *L. variegatus* at SHO and *L. variegatus* at SRB, as well as *H. azteca* at SHO and *H. azteca* at SRB. *C. riparius* had higher uptake rates at SRB, but these results were not significant.

The Grand River sites were the only sites where the predicted pattern was observed. However, rather than observing the expected higher organic carbon content from inshore

sediments, here higher organic carbon was found at the offshore site, GRO. In this case, *L. variegatus*, *C. riparius*, and *H. azteca* all had higher uptake rates at GRO. While general linear modeling found significant differences between the inshore and offshore sites with all organisms together, there were no significant differences found for any of the three organisms on a single organism analysis.

These results conflict with arguments presented in the literature. Lee (1991) argues that sediments with higher organic fractions tend to be a more effective source of organic contaminants than sediments with lower organic fractions. Capel and Eisenreich (1990) found that the uptake of several chlorinated hydrocarbons was correlated to the organic carbon on the sediment for deposit feeders. Increasing organic content on the sediment provided a greater availability for organic contaminants to deposit feeders. Harkey et al. (1994b) found that *Diporeia* spp. accumulated sediment associated HCBP from sediment particles with higher organic carbon fractions. However, there was also a size component to this selectivity, with *Diporeia* spp. preferentially choosing sediments within a specific size range. This suggested that this system is more complicated than a simple organic carbon content relationship (Harkey et al., 1994).

The results for the inshore/offshore comparison were inconclusive and did not support or refute the hypothesis. While the inshore sites did have higher organic carbon fractions at two of the three rivers, the test organisms generally had higher uptake rates at offshore sites. The inconsistencies found in these results suggest that the organic carbon fraction of the sediments is not the only factor in determining locations of high contaminant uptake. Other factors, including the above mentioned particle size, may play a role as well.

The one general pattern found in these data is the higher uptake rates at offshore sites for all three locations. While this observation is not consistent for all organisms, it is a pattern that warrants further investigation. It is possible that there are factors in offshore sediments that allow for more efficient contaminant uptake. Further sediment analysis must be performed to determine what those factors may be.

Bioaccumulation factors

Bioaccumulation factors (BAF) measure the accumulation of contaminants from all sources, including direct uptake from water and uptake through ingestion (Landrum, 1992). In addition, the elimination rate of the contaminant from the organism is accounted for (Landrum, 1992). Because of the large number of factors involved, the BAF can vary between sediments and within a species (Lee, 1991; Landrum, 1992).

The variability of the BAFs in this study were highly dependent on the elimination rate constants of the organisms involved. Elimination rate constants (k_d) were not measured for this study, rather they were obtained from the literature. The elimination rate constant for *C. riparius* (0.007 h^{-1}) was obtained from Boulet-Stoeckel (1995). The elimination rate constant for *L. variegatus* (0.0013 h^{-1}) was obtained from Fisher et al. (1999). Finally, the elimination rate for *H. azteca* (0.012 h^{-1}) was obtained from Shuler et al. (2003).

Because of the importance of elimination rate constants, it was predicted that organisms that could not effectively eliminate HCBP would have elevated BAFs. This effect may be reduced by a high uptake rate. *L. variegatus*, having a k_d value that was not found to be significantly different from 0 h^{-1} (Fisher et al. 1999), could not metabolize or remove HCBP through any effective pathway. This was believed to result in the highest BAF for these

experiments. *C. riparius* and *H. azteca*, both of which had a limited capacity for eliminating HCBP, would have lower BAFs as a result of the k_d values.

The results supported this hypothesis, as *L. variegatus* had the highest BAFs at all sites. The BAFs for *L. variegatus* ranged between 41.6 g g⁻¹ at site GRB to 98.0 g g⁻¹ at site MRO. *C. riparius* had intermediate BAFs, with a range of 10.2 g g⁻¹ at site GRB to 20.377 g g⁻¹ at site SRB. *H. azteca* had the lowest BAFs, with a range of 4.5 g g⁻¹ at site MRO to 11.5 g g⁻¹ at site SHO. This pattern reflected the general trend found in the literature, where *L. variegatus* generally has the highest BAFs for HCBP. Shuler et al. (2002) found comparable results in a similar study using B(a)P, with *L. variegatus* having the highest BAFs, *C. tentans* having intermediate BAFs, and *H. azteca* having the lowest BAFs. This pattern was observed in studies that both isolated all three organisms and included all three organisms together (Shuler, 2002). Shuler et al. (2003) observed a similar pattern for HCBP, though BAFs for *C. tentans* were slightly lower than those of *H. azteca*. In this case, uptake rates for *C. tentans* were lower than those observed in *C. riparius* for this study. The uptake rates and BAFs in *C. riparius* for this study are similar to those found in Boulet-Stoeckel (1995), in which BAFs for *C. riparius* ranged between 1.79 g g⁻¹ and 20.58 g g⁻¹.

It appears as though the elimination rate did influence the BAFs for organisms in this study. *L. variegatus* had considerably higher BAFs than the other two test organisms, despite having only intermediate uptake rates. This contradicts the findings of Schuler et al (2003), in which elimination rates are found to be too small to be influential. Based on BAFs, *L. variegatus* appears to be more effective in accumulating contaminants from sediment when compared to the other organisms in these experiments. *C. riparius* has the intermediate effectiveness in this

process, while *H. azteca* tends to accumulate the least amount of contaminants from the sediments.

Conclusions

This study attempted to determine how the different feeding behaviors influenced the uptake of HCBP by *C. riparius*, *L. variegatus*, and *H. azteca*. The results suggest that *C. riparius* has the highest uptake rate in comparison to the other organisms. There are a number of possibilities for this conclusion. *C. riparius* tends to be both less selective in food preference than the other organisms involved in the study, and is constantly consuming sediments. The less selective feeding behavior may bring *C. riparius* into contact with a number of different sediment particulate types ranging in food quality and associated HCBP. Some of these sediment particulate types may be more likely to dissociate with attached HCBP, increasing the uptake in *C. riparius*. The continuous feeding of *C. riparius* may have also contributed to higher uptake rates. The constant consumption of sediments may have resulted in a higher exposure to sediment bound HCBP throughout the course of the experiment.

The relatively smaller uptake rates of *L. variegatus* when compared to *C. riparius* were unexpected. This may be due to one of two factors. The uptake rates of *L. variegatus* may have been suppressed as a result of interaction with other organisms. A predator avoidance behavior may have been stimulated in response to the other organisms in the bioassay. This could have resulted in the oligochaete spending more time moving and trying to avoid interaction with the other organisms, and less time feeding. The reduced feeding rate would result in less exposure to sediment-bound HCBP through ingestion. Alternatively, the selective feeding behavior may reduce the uptake rate of *L. variegatus*. The fine particulates that *L. variegatus* preferentially

feed on tend to be high in organic carbon. This high organic carbon content may form a stronger interaction with HCBP, making it less available for uptake by *L. variegatus*.

While *L. variegatus* did have lower uptake rates than *C. riparius*, the bioaccumulation factor was actually higher. This was due to a low elimination rate for HCBP. The contradiction of uptake rates and BAFs suggests that the uptake of sediment-bound HCBP is a complicated process that requires a more detailed study of the organisms and contaminant sources involved. Assimilation efficiencies were not found for this study. However, the effectiveness of the organism in assimilating the contaminants from sediments may be more effective for this analysis and should be pursued in further investigations.

H. azteca tended to have lower uptake rates and had the lowest bioaccumulation factors of the organisms involved in this study. This may be due to the epibenthic behavior of the organism. *H. azteca* tends to spend more time in the water column and less time in the sediments than either of the other organisms. This may reduce the contact of *H. azteca* with the contaminated sediments, resulting in reduced uptake rates. Further investigations should take organism interaction and behavior into account to determine if reduced time in contact with contaminated sediments reduces the uptake of sediment bound contaminants.

Site comparisons for this study were inconclusive. It was believed that inshore sites with a higher organic carbon fraction in the sediment may result in increased availability of organic contaminants to sediment ingesting organisms. This is not supported by the results, as no pattern associating organic carbon content and organism uptake rates could be observed. A more detailed analysis of the sediments at these sites is required to determine if uptake rates do differ between inshore and offshore locations.

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