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Trophic Transfer of Heavy Metals to Top Predators: Quantifying
the Role of Non-native Species

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INTRODUCTION

Lake Erie's food web recently has been dramatically modified by non-native dreissenid mussels and the round goby, *Neogobius melanastomus*. The introduction and spread of these exotic species have led to a shift in the food web from a pelagic-based food web to a benthic-based one, likely creating a new pathway for contaminant transfer to top predators such as smallmouth bass *Micropterus dolomieu*, and humans.

The zebra mussel *Dreissena polymorpha* invaded the Great Lakes in the mid-1980's (Herbert et al. 1989; Griffiths et al. 1991) and the quagga mussel *Dreissena bugensis* was introduced in 1989 (Mills et al. 1993). With their close contact to contaminated surficial sediments, dreissenids may link pelagic with benthic systems via contaminant transfer. Bivalves' bioaccumulate heavy metals in their mussel tissue through filtration of contaminated water, suspended solids, and phytoplankton (Klerks et al 1997, Al-Asam et al. 1998, Cope et al. 1999, Camusso et al. 2001). That portion of heavy metals not bioaccumulated by dreissenids are excreted, rather than ingested, in the form of pseudofeces. As suspended solids in the water column increase, the amount of contaminated pseudofeces returned to the sediment can be substantial (Klerks et al 1997). Due to dreissenids' high filtration rates (Mackie 1991), wide distribution, and high local densities, their impact on metal cycling in a polluted system can be significant.

Concurrent with the spread of these two exotic bivalves in the Great Lakes came the invasion of the round goby, *Neogobius melanastomus*, in 1990 (Charlebois et al. 2001). The round goby invaded the eastern and central basins and quickly spread to the western basin of the lake in 1996 and has become quite abundant in Lake Erie (Chotkowski and Marsden 1999). As a benthic fish whose diet consists mainly of

dreissenids (Kovtun et al. 1974, Jude et al. 1995, Ghedotti et al. 1995, Ray and Corkum 1997) the round goby has the potential to accumulate contaminants. Few studies have examined their role in the transfer of metals through the food web. We suspect that round gobies accumulate heavy metals via food (dreissenid mussels).

With their increasing abundance the round goby has become a large part of the smallmouth bass diet. The round goby began to show up in diets of smallmouth bass from the central basin in 1996. In 1999 they accounted for 40% of smallmouth bass diets sampled from the central basin of Lake Erie and continue to be an important diet item. (pers. comm. Carey Knight, Ohio Division of Wildlife). For fish, heavy metal accumulation likely occurs through bioconcentration (uptake from water) or bioaccumulation (uptake from food source) (Chen et al. 2000). Smallmouth bass gain most metals via food (an important component of which is the round goby). Therefore contaminants transferred to smallmouth bass from the round goby could be a concern for human consumption.

We have focused our study on two heavy metals, lead (Pb) and mercury (Hg), that are “pollutants of concern” in Lake Erie (Lambert 1998) and that may behave differently as they are transferred through the food web. To evaluate the impact of Hg, we focused not only on total Hg, but also on methyl mercury (MeHg), the more toxic form of Hg. Pb and Hg have been shown to biodiminish (decline in concentration) with increasing trophic level in pelagic-based food webs (Chen and Folt 2000), whereas MeHg biomagnifies (increases in concentration) through the food web to top predators (Chen et al. 2000, Downs 1997, Hudson 1998, Mason et al 2000, Watras et al. 1998,). We have little information about how these metals move through a benthic based food chain as we

currently have in Lake Erie.

In this study, we seek to understand trophic distribution and routes of exposure of Hg, MeHg, and Pb in this newly benthic food web. Other studies have quantified the bioaccumulation of heavy metals via food-web linkages in natural systems (Francis et al. 1998, Chen et. al. 2000). Our study will characterize how Hg, MeHg and Pb in sediments and dreissenids, previously unavailable to pelagic sport fishes, are now being accumulated by round gobies and, consequently, smallmouth bass in the western basin of Lake Erie. Using historical data, we will compare total Hg concentrations in smallmouth bass before the invasion of the round goby into Lake Erie to current concentrations.

METHODS

As the smallest and shallowest of the Great Lakes, Lake Erie also is exposed to substantial agriculture and urbanization. The western basin of Lake Erie is very shallow with an average depth of 7 meters. It warms rapidly in spring and summer, is very productive and is the site of one of the largest freshwater sport fisheries in the country. Both Hg and Pb can be released into the lake by industrial stormwater runoff, domestic wastewater discharges, and atmospheric deposition. Lake Erie's highest sediment contaminant concentrations historically have occurred in the western basin, adjacent to the Detroit River with declining concentrations from the western to eastern basin. Hg and Pb sediment concentrations decreased in all basins of Lake Erie from 1971 to 1998, but still exceed the Canadian and Province of Ontario sediment quality guidelines and remain a concern for bioaccumulation through the food web (Painter et al. 2001). Today we can find the dreissenid-goby-smallmouth bass food web around the lake. We chose

sampling sites in the western basin to incorporate a range of sediment Pb and Hg concentrations.

We sampled Maumee Bay, Gibraltar Island, and Sandusky Bay. Maumee Bay, with historically high Pb (>91 mg/kg) and Hg (> 0.486 mg/kg) sediment concentrations (Painter et al. 2001), was deemed by USEPA (1990) an Area of Concern due to agriculture runoff and combined stormwater/sewage overflows. The following sediment data have been collected by various state agencies over a ten year period and compiled into a Pb and a Hg map by Dan Button of the USGS. A draft copy of these maps was made available to us by Julie Letterhos and John Estnik, Ohio EPA, Columbus Ohio, 43208. Recently measured sediment Pb concentrations in Maumee Bay were 35 - 91 mg/kg and Hg concentrations were 0.174 - 0.486 mg/kg. Gibraltar Island (in the Bass Islands) also had sediment Pb concentrations of 35 - 91 mg/kg and Hg concentrations of 0.174 - 0.486 mg/kg. The Bass Islands are in the path of discharge of the Detroit River and receive the contaminants associated with that water. Finally, Sandusky Bay has the lowest Pb sediment concentrations (< 35 mg/kg), and Hg concentrations (< 0.174 mg/kg).

Sample Collection and Processing

We analyzed total Pb and total Hg concentrations in water, sediment, zebra mussels, round gobies, and smallmouth bass samples collected from the three sites during July through September of 2002. MeHg concentrations were measured in each food web component in samples collected from Maumee Bay and Sandusky Bay. The smallmouth bass from Maumee Bay were collected in October 2002 because they were not found in this location during the summer months. Dissolved oxygen and temperature were measured at each site with a YSI 550 meter. Ph was measured at the sediment water

interface using a Horiba pH meter. Ultra clean techniques (Chen and Folt 2000).were used during all phases of equipment preparation, sample collection, storage, and analysis

At each site, water samples were collected from 1-m depth using a Van dorin sampler. Unfiltered water samples were placed in ultra-clean glass containers and preserved in the field with nitric acid for total Pb and Hg analysis. Methyl mercury water samples were preserved with HCl in the field. DOC samples were filtered through 0.45 μ m teflon filters into ultra-clean glass containers and preserved with sulfuric acid. Total suspended solids (TSS) samples were not filtered and placed into plastic sample bottles. After preservation, all aqueous samples were placed on ice. Surficial sediment samples were collected from each site with an acid-washed, stainless steel Eckman dredge and placed into ultra-clean glass containers and placed on ice before analysis of total Pb, Hg, and MeHg. Both sediment and water samples were stored at 4°C prior to analysis.

At each site, all sizes of dreissenids were collected by hand with the aid of SCUBA, placed in coolers with lake water, and transported back to the lab. The dreissenids were held without food for 24 hours to allow gut clearance, given that food and sediment particles can distort heavy metal analysis (Wiesner et al. 2001). Dreissenids were separated into two sizes classes, 2-7mm shell length ($N = 6$ samples per site) and 8-14mm shell length ($N = 6$ samples per site). Each sample consisted of about 100 dreissenids from a given size class. Both of these size classes are vulnerable to round goby predation, but larger mussels are not (Ray and Corkum 1997). We removed soft tissue from the shells with acid-washed, stainless steel forceps to obtain enough tissue, approximately 8 g (wet weight), for analysis. Composite samples were placed in

polypropylene bags and kept frozen at -20°C until analysis. Twelve dreissenid samples per site were analyzed for total Pb and total Hg. Three dreissenid samples from Maumee bay and 3 from Sandusky bay were analyzed for MeHg.

Round gobies 50-100mm total length (TL) were collected by hook and line from each site. These sizes of round goby prey primarily on dreissenids (Ghedotti et al. 1995). Upon collection round goby were measured (nearest mm) and weighed (nearest g) and composite samples ($N = 5$ gobies per sample) were placed in polypropylene bags and immediately frozen on dry ice. Because round gobies are consumed whole by predators, 12 whole body samples per site were analyzed for total Pb and total Hg. Three round goby samples from Maumee bay and three from Sandusky bay were analyzed for MeHg.

Six smallmouth bass from each of two size classes, 180-300 mm TL and 301-450 mm TL, were collected by electrofishing and hook and line at each site. In the field, smallmouth bass were measured (nearest mm) and weighed (nearest g). Because smallmouth bass are consumed as fillets by humans, we analyzed fillets for total Pb, total Hg, and MeHg. The dorsal muscle tissue of each fish was removed from both sides with an acid washed, stainless steel fillet knife. Fillets were double bagged in polypropylene bags, labeled, and placed on dry ice. Samples were kept frozen at -20°C until analysis. Total Pb and total Hg were measured in all fish; in 3 of the 12 smallmouth bass from Maumee and from Sandusky Bay, we measured total Hg in one fillet and MeHg in the other. Otoliths were removed from all smallmouth bass and preserved for age determination.

Sample Analysis

Sediment and water samples were shipped within 48 hours of collection, and tissue samples within 2 weeks of collection, to ACZ laboratories (ACZ, Steamboat Springs, CO) for total Pb and total Hg analysis. Total Pb was analyzed using an Agilent 7500I inductively coupled plasma-mass spectrometer. Digestion/preparation procedures for water, sediment, and tissue samples were performed according to EPA Methods 200.2, 3050B, and 200.11. ICP/MS analysis of digested water samples was performed using EPA Methods 200.8. Sediment and tissue samples were analyzed by EPA Method 6020. The minimum detection limits for Pb were 0.0001 (mg/L) in water, 0.05 mg/kg in sediment, 0.01 mg/kg in zebra mussels, 0.01-0.03 mg/kg in round gobies, and 0.009-0.02 mg/kg in smallmouth bass.

Total Hg was analyzed using cold vapor atomic absorption (CVAA) spectrometry. The CVAA analysis of total Hg in water was analyzed using EPA Method 245.1. Sediment and tissue samples were analyzed using EPA Method 7471. The minimum detection limits for Hg were 0.0002 mg/L in water, 0.04 mg/kg in sediment, 0.04 mg/kg in zebra mussels, 0.04-0.05 mg/kg in round gobies, and 0.04 mg/kg in smallmouth bass.

All MeHg samples were immediately shipped to Frontier Geosciences Inc. (Frontier, Seattle, WA). MeHg was analyzed using cold vapor atomic fluorescence spectrometry (CVAFS). Water samples were distilled to liberate the MeHg (Horvat et al. 1993) and analyzed using CVAFS (Bloom 1989). Sediment samples were cold extracted instead of distilled and analyzed according to (Bloom 1989). Homogenized tissue

samples were digested with KOH/Methanol for analysis. Tissue samples were analyzed using CVAFS (FGS 0.70.2).

Quality Assurance

Quality assurance for total Pb and total Hg analysis included procedural blanks, duplicates, laboratory control samples, and matrix spike samples. All samples were quantified using matrix-matched standard stock solutions of ultra high purity grade. All QC samples were within control limits. Precision (relative percent difference) of duplicate analysis was within 10% for total Pb and Hg in all samples.

For MeHg quality assurance, reagents were all ultra-pure grade and were previously analyzed for trace metals. For each analytical set one matrix duplicate, two matrix spikes and at least three method blanks were co-processed and analyzed the same as ordinary samples. Additional standards were run every 10 samples. All QC samples were within control limits.

Data Analysis

We used two-factor ANOVAs to test for the effects of site and trophic level on total Pb, total Hg, and MeHg concentrations. Our sediment data were analyzed separately from the dreissenid, round goby, and smallmouth bass data, which were included in one analysis. The data for each metal in each trophic level were normalized using a \log_{10} transformation. We used Tukey's studentized range tests to do pair-wise comparisons of sites and trophic levels. We also used an ANOVA to test the effects of total Hg concentrations in smallmouth bass before and after the incorporation of the round goby into their diet. All statistical tests were run using SAS version 8.

RESULTS

Lead bioaccumulated through the food chain at all three sites (Figure 1), with significant decreases in concentration from dreissenids to round gobies to smallmouth bass (ANOVA, $p < 0.0001$, Table 1). Dreissenid Pb concentrations were about 40 times lower than sediment Pb concentrations. Round goby Pb concentrations were about 7 times lower than dreissenid Pb concentrations. Finally the smallmouth bass Pb concentrations were approximately 100 times lower than those in the sediment. Concentrations of Pb in biota from Sandusky Bay were significantly lower than those from Maumee Bay and Gibraltar Island (ANOVA, $p = 0.004$, Table 1). Average Pb concentrations in the sediment at the three sites were 19.1 - 24.1 mg/kg and did not differ between sites (ANOVA, $p = 0.554$, Table 1).

In contrast to Pb, MeHg concentrations biomagnified through the food web to top predators (Figure 2), with significant increases in concentration from dreissenids to round gobies to smallmouth bass (ANOVA, $p < 0.0001$, Table 2). MeHg concentrations in the dreissenids were about 20 times higher than sediment MeHg concentrations. Round goby MeHg concentrations were about 6 times higher than MeHg concentrations in dreissenids. Smallmouth bass MeHg concentrations were 1,000 times higher than MeHg concentrations in the sediment. Concentrations of MeHg in biota did not differ between sites (ANOVA, $p = 0.79$, Table 2). It appeared as if the MeHg concentrations in smallmouth bass were higher in Sandusky Bay than in Maumee Bay. However when running the ANOVA with dreissenids, round gobies and smallmouth bass in one model there was no difference detected between sites. This may be due to the fact that smallmouth bass MeHg concentrations were increasing from Maumee to Sandusky Bay

and there was a decrease in MeHg concentrations in round gobies from Maumee to Sandusky Bay. This interaction may be preventing the detection of site differences. When running a separate ANOVA on smallmouth bass MeHg concentrations from Maumee and Sandusky Bay, the smallmouth bass from Sandusky Bay had significantly higher MeHg concentrations than those from Maumee Bay. The MeHg sediment concentrations were low ranging from 0.0002 to 0.0004 mg/kg and showed no differences between sites (ANOVA, $p = 0.27$, Table 2).

Total Hg concentrations decreased from sediment to dreissenids and round gobies but increased to smallmouth bass (Figure 3). Because the concentrations of total Hg in dreissenids and round gobies were below detection limits, these two food web components were not included in the analysis. Therefore only total Hg concentrations in smallmouth bass were used in the ANOVA to test site effects. The smallmouth bass from Maumee Bay had significantly lower total Hg concentrations than those from Sandusky Bay or Gibraltar Island, whose total Hg concentrations did not differ (ANOVA, $p = 0.0002$; Table 3). The total Hg concentrations in the sediment were 0.09 - 0.16 mg/kg and did not differ between sites (ANOVA, $p = 0.20$; Table 3).

Mercury concentrations in smallmouth bass between 1993 and 1996 were 0.09-0.12 mg/kg (Figure 4). These data were collected by the Ohio Division of Natural Resources (ODNR) and represent smallmouth bass Hg concentrations before the inclusion of round gobies into their diets. In 1998 the average Hg concentration in smallmouth bass was 0.08 mg/kg, the first year of data available after smallmouth bass began to eat round gobies. Since 1998 there have been no Hg data collected for smallmouth bass by ODNR. The concentrations of total Hg in smallmouth bass in 1998

and 2002 did not differ from earlier concentrations (ANOVA, $p = 0.81$; Table 4) (Figure 4).

DISCUSSION

Total Pb concentrations bioaccumulated through the food web to top predators. This is the first study that has documented this pattern in Lake Erie's recently shifted benthic food web. The bioaccumulation of Pb has been documented in other freshwater pelagic systems (Chen and Folt 2000, Chen et al 2000). This bioaccumulation may be occurring because surface-associated metals such as Pb adsorb onto the cell walls of phytoplankton (Hudson 1998, Sunda and Huntsman 1998) and are not efficiently transferred to the tissue of grazers (Hudson 1998) such as dreissenids. Pb also has been shown to accumulate in higher levels in shells of mussels instead of the tissue (Babukutty and Chacko 1994) and is quickly eliminated from these filter feeders (Boisson et al. 1998). Diminution of metals from lower to higher trophic levels can depend on concentrations of metals in algae and horizontal complexity in the food chain (Stemberger and Chen 1998). Metal concentrations can fluctuate as size distribution and density of phytoplankton change (Chen et al. 2000). As Pb is transferred up the food web it is concentrated mostly in the liver and kidneys or bones and scales of organisms (Mason et al 2000). Therefore it is efficiently excreted and is not concentrated in large amounts in the tissue of organisms.

In contrast to Pb, MeHg bioaccumulated through the food web to top predators. This pattern has also been demonstrated in other freshwater systems (Chen et al. 2000, Downs et al. 1997, Hudson 1998, Mason et al. 1997, Mason et al 2000, Watras et al. 1998), but this study is the first to demonstrate the MeHg bioaccumulation pattern in

Lake Erie's recently shifted benthic food web that includes exotic species. MeHg is an intracellular, organo-metallic contaminant (Hudson 1998); it is efficiently transported into cell cytoplasm and muscle tissue of organisms and is less efficiently excreted (Foster et al. 2000, Watras and Bloom 1992, Mason et al 2000). Mercury is transformed into MeHg at rates that vary with concentrations of dissolved organic carbon (DOC) and pH of water (Watras et al. 1995b). High DOC and low pH, characteristics of anoxic sediments and water, increase methylation of Hg. Diffusion and advection then transport the MeHg throughout the system (Xun et al. 1987). As a neurotoxin, MeHg can bioaccumulate 100,000 times in concentration from water to fish (Boudou et al 1979). MeHg accumulation increases in fish with increasing size and age (Driscoll et al. 1994, Stafford and Haines 1997, Neumann and Ward 1999). Magnification of metals through the food web to top predators also depends on their diet (Castro et al. 2002). In a study comparing pelagic and benthic food webs, higher Hg levels in channel catfish *Ictalurus punctatus* than common carp *Cyprinus carpio*, likely results from channel catfish including fish in their diet as compared to carp that feed directly on benthos (Francis et al. 1998). In contrast, Lindqvist (1984) recognizing that both water and sediment can be pathways of Hg to fish, suggests that bioaccumulation from sediments via the benthic food chain is of greater importance. This implies that the fluxes of Hg through the lower food web determines Hg levels at high trophic positions.

Most previous studies of Lake Erie sport fish and dreissenids have measured only total Hg as it is far less expensive to measure than MeHg (OEPA 1992b). In fish Hg is primarily in the methylated form, accounting for 90-95% of the total Hg (Bloom 1992, Wiener and Spry 1996, Francis et al. 1998). It has been shown that there is a decrease in

concentration of inorganic Hg through the food web, so that by the third trophic level all the Hg is methylated (Watras and Bloom 1992). However, little is known about the ratio of MeHg to total Hg in lower food-web levels. The ratios of MeHg to total Hg found in this study were 0.2% for sediment and about 22% for water. Watras et al. (1998) found 0.1 to 5.4% of total Hg in sediment was methylated and 15% of total Hg in water was MeHg. Cope et al. (1999) found 50% of the total Hg in zebra mussels was in the methylated form. Since MeHg seems to be most critical, comparing total Hg concentrations in lower food web levels may be misleading because MeHg usually constitutes a smaller portion of the Hg pool than other forms (Bloom 1992). Because MeHg 1) biomagnifies through the food web, 2) is more particle-reactive, and 3) has higher potential for transport and uptake by biota than other forms of Hg it is important to know the concentration of MeHg in lower food web components (Watras and Bloom 1992).

At Sandusky Bay and Gibraltar Island the smallmouth bass were found at the same time of year and at approximately the same location as the dreissenids and round gobies. There are ongoing tagging studies being done by Mark Turner at the ODNR that suggest that smallmouth bass tagged from the Bass Islands and areas around Sandusky bay are mostly retrieved in the same areas (ODNR 2002 Annual Report). Therefore we can assume that the concentrations of Pb and Hg in smallmouth bass are responding to the lower trophic level contaminant concentrations in these areas. However the smallmouth bass in Maumee Bay were only found in October 2002 and, based on anecdotal evidence from fishermen and bait shop owners, smallmouth bass come into the near shore areas of the bay only in the fall. Because these fish may not be

residing in Maumee Bay for the entire year, their observed contaminant concentrations may not be responses to contaminant levels in lower trophic levels collected from this area.

According to the Ohio Department of Health's Fish Tissue Monitoring Report (1998), Hg is one of the most common chemicals detected in Ohio sport fish because it accumulates in the muscle tissue of fish and, unfortunately, trimming fat and skin from fish does not reduce human exposure. Although the smallmouth bass Hg concentrations in this study (0.15 mg/kg) were below state guidelines set for human consumption purposes (0.5 mg/kg), we recommend continued monitoring of Hg in smallmouth bass in the western basin of Lake Erie. The oldest smallmouth bass used in our analysis was 4 years old. As these fish continue to prey upon round gobies over their lives, their Hg concentrations may also continue to increase. Although we should be most concerned about the methylated form of Hg, because the ratio of MeHg to total Hg is so consistent in top predators (95-99%) (Watras and Bloom 1992, Wiener 1996, and this study), it is sufficient to monitor total Hg rather than the more expensive MeHg.

CONCLUSION

Since the invasion of these exotic species to the Great Lakes there have been many documented changes to the Lake Erie system (Berkman et al. 1994, Dermott and Munawar 1993, Graham et al. 1992, Jude et al. 1995, Klerks et al. 1997). An important change is the shift from a pelagic to a benthic based food chain. When looking at the historical and current Lake Erie food webs it appears as if the dreissenids have merely "replaced" the role of zooplankton in the food web. However with their high filtration rates and ability to resuspend bottom sediments (Klerks et al 1997, Mackie 1991)

dreissenids may be more effective at cycling contaminants through this system than zooplankton. Dreissenid metal concentrations are also driven by concentrations of metals in surface waters and phytoplankton (Hudson 1998, Boisson et al. 1998). This may lead to the transfer of higher concentrations of contaminants to predators such as round gobies, smallmouth bass, and humans. Despite the current Pb concentrations in the sediment in the western basin of Lake Erie, because of the biodiminishing pattern shown by our data, there should be less concern for the accumulation of high levels of Pb in top predators and ultimately humans.

Table 1. ANOVA table for Total Pb in sediment at the three sites, and Total Pb in biota (dreissenids, round goby, and smallmouth bass) at the three sites.

| <u>Sediment</u> | | | |
|-----------------|-----------|----------------|----------------|
| Source | df | F value | P value |
| Site | 2 | 0.61 | 0.554 |
| <u>Biota</u> | | | |
| Source | df | F value | P value |
| Trophic Level | 2 | 195.46 | <0.0001 |
| Site | 2 | 5.83 | 0.004 |

Table 2. ANOVA table for MeHg in sediment at the three sites, and MeHg in biota (dreissenids, round goby, and smallmouth bass) at the three sites.

| <u>Sediment</u> | | | |
|-----------------|-----------|----------------|----------------|
| Source | df | F value | P value |
| Site | 1 | 1.61 | 0.273 |
| <u>Biota</u> | | | |
| Source | df | F value | P value |
| Trophic Level | 2 | 42.37 | <0.0001 |
| Site | 2 | 0.07 | 0.799 |

Table 3. ANOVA table for Total Hg in sediment at the three sites, and Total Hg in smallmouth bass at the three sites.

| <u>Sediment</u> | | | |
|-----------------|-----------|----------------|----------------|
| Source | df | F value | P value |
| Site | 2 | 1.79 | 0.200 |

| <u>Smallmouth bass</u> | | | |
|------------------------|-----------|----------------|----------------|
| Source | df | F value | P value |
| Site | 2 | 10.84 | 0.0002 |

Table 4. ANOVA table for Total Hg in smallmouth bass before (1993, 1994, 1995, 1996) and after (1998, 2002) the inclusion of round gobies into diets.

| <u>Smallmouth bass</u> | | | |
|------------------------|-----------|----------------|----------------|
| Source | df | F value | P value |
| before/after | 1 | 0.06 | 0.810 |

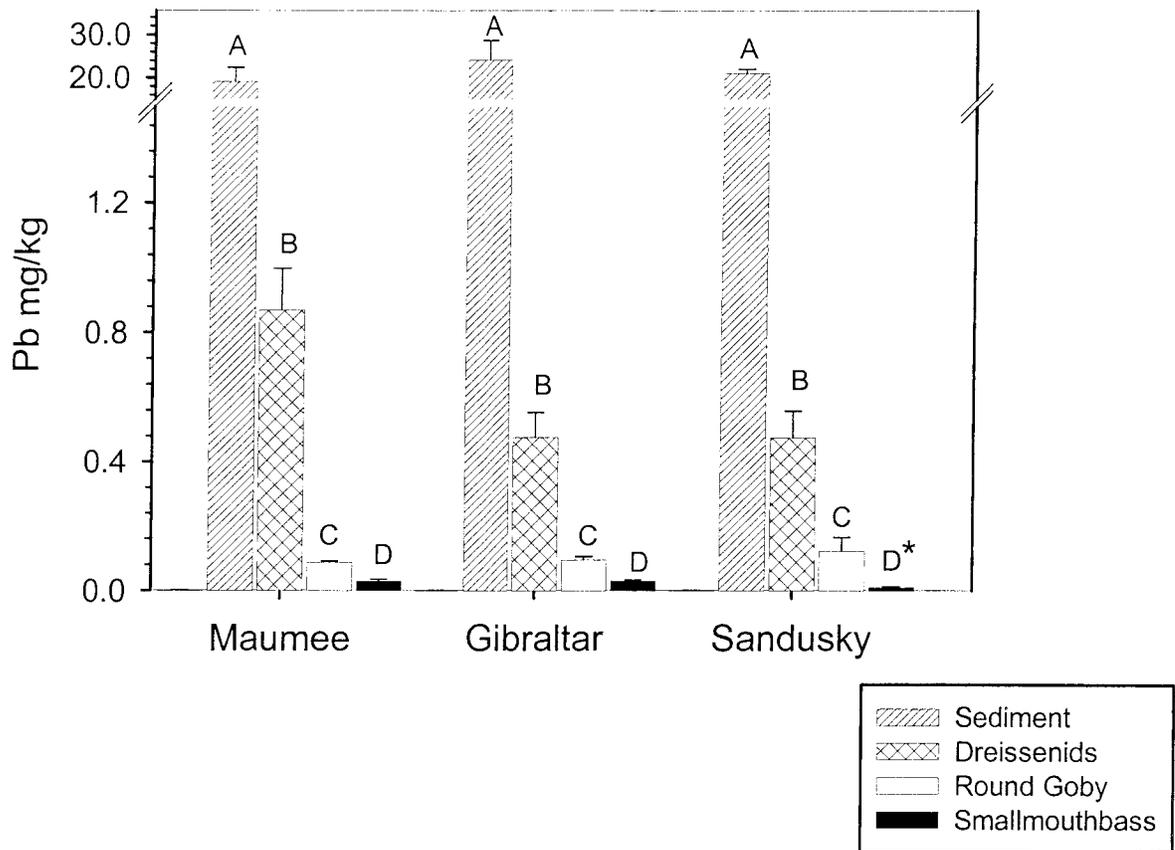


Figure 1. Total Pb concentrations in mg/kg in four food web components at three sites in Lake Erie. The letters represent statistical differences ($p < 0.05$) in Pb concentration between food web components within sites. The asterisk represents the fact that Pb concentration in Sandusky was significantly lower than in Maumee and Gibraltar.

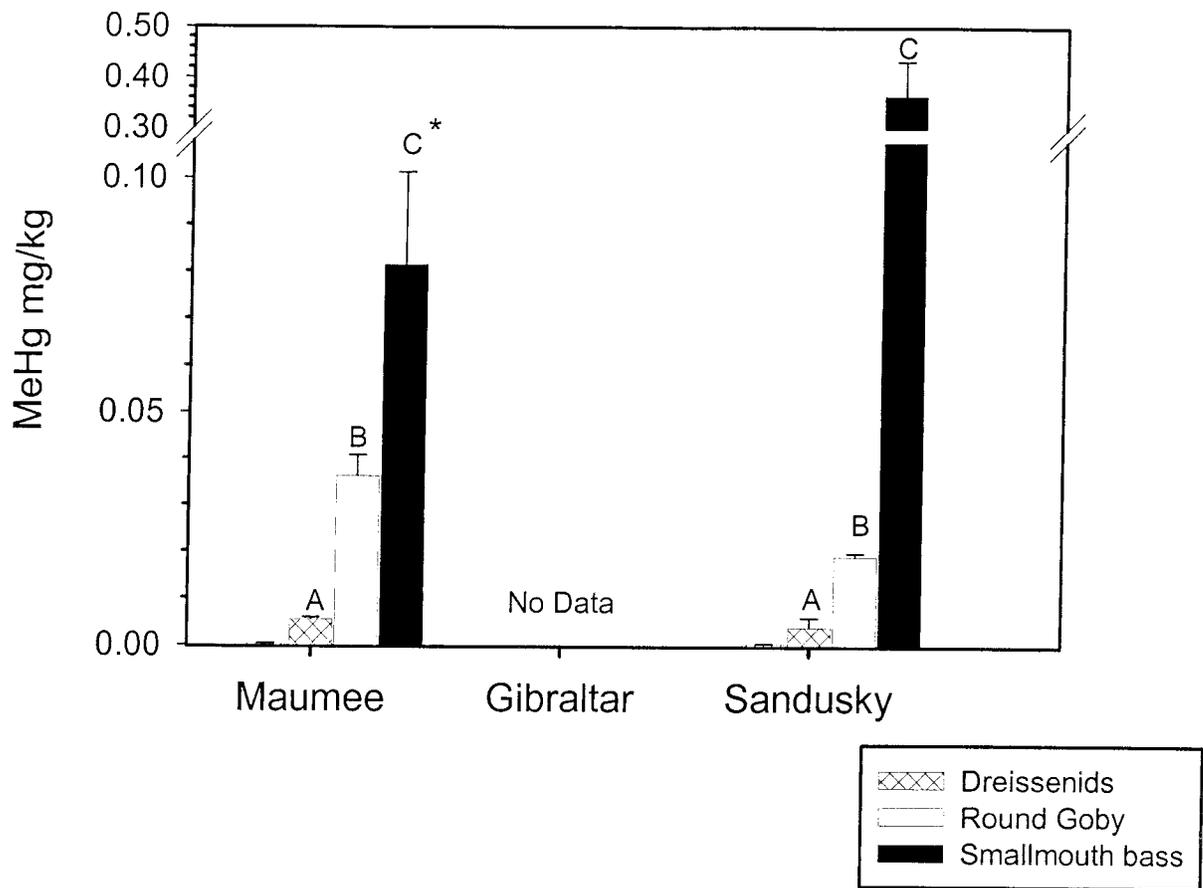


Figure 2. MeHg concentrations in mg/kg in three food web components at two sites in Lake Erie. The letters represent statistical differences ($p < 0.05$) between food web components within sites. The asterisk represents statistical differences between sites.

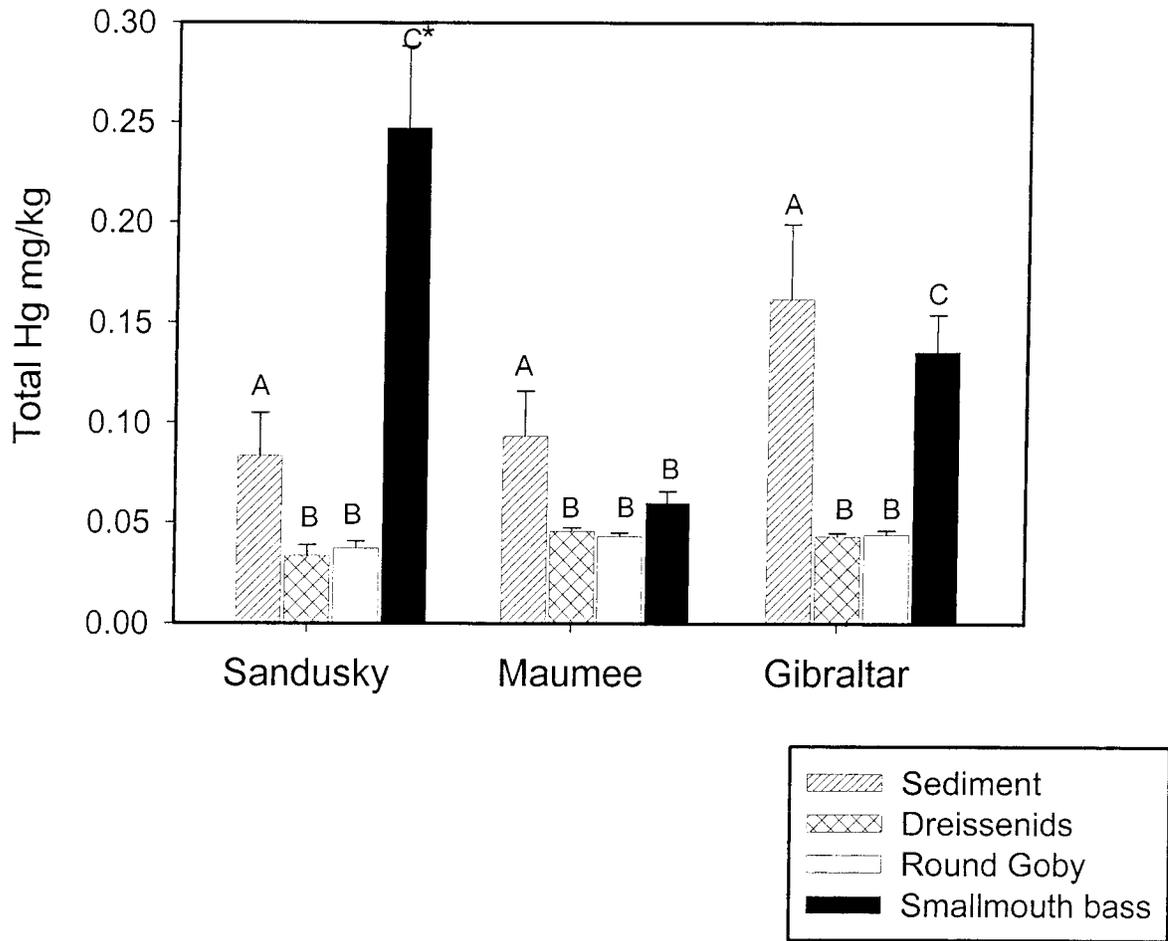


Figure 3. Total Hg concentrations in mg/kg in four food web components at three sites in Lake Erie. The letters represent statistical differences ($p < 0.05$) between food web components within sites. The asterisk represents statistical differences between sites.

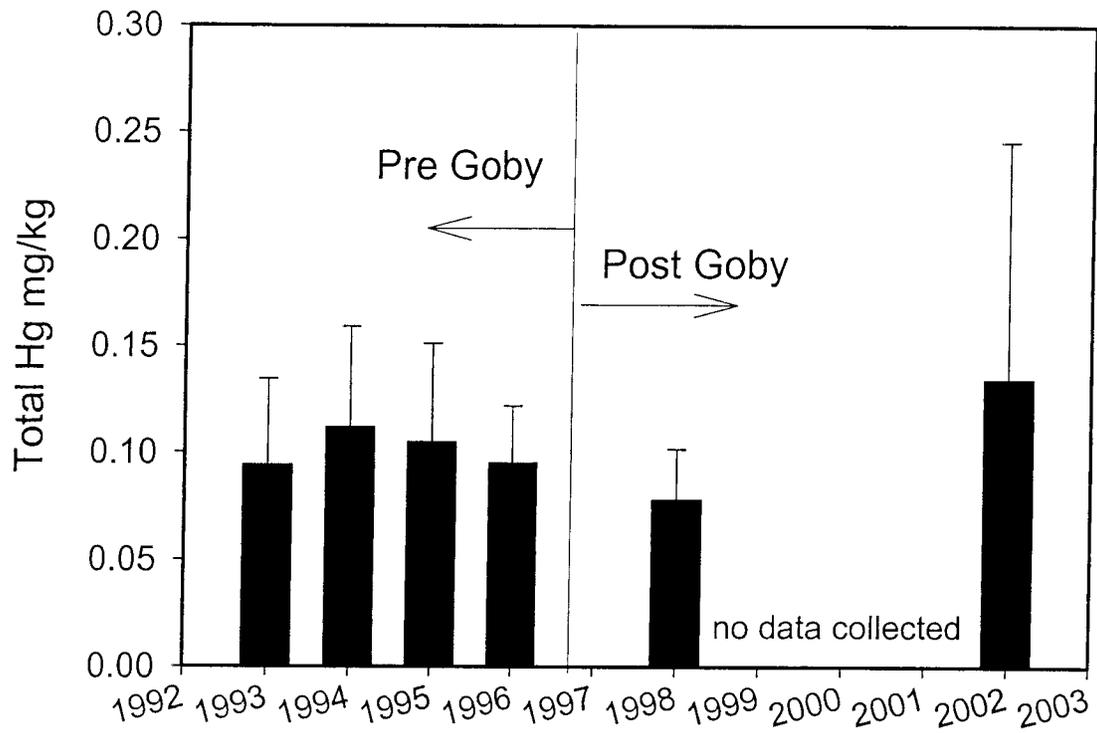


Figure 4. Total Hg concentrations in mg/kg in smallmouth bass from the central and western basins of Lake Erie between 1993 and 2002. No data were collected in 1997, 1999, 2000, or 2001. The data to the left of the line represent Hg concentrations in smallmouth bass before they incorporated round gobies into their diets. The data to the right of the line represent Hg concentrations after smallmouth bass began to eat round gobies.

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