

**Uptake of Mercury and Relationship to Food Habits of Selected Fish Species
in the Shenandoah River Basin, Virginia**

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ABSTRACT

Mercury poses significant challenges to human health and fisheries management. Historical industrial practices in Waynesboro, Virginia left portions of the Shenandoah River basin contaminated with mercury and stringent health advisories for fish consumption. I investigated processes affecting the bioaccumulation of mercury in *Catostomus commersoni*, *Ictalurus punctatus*, *Lepomis auritus*, and *Micropterus dolomieu* by studying food habits, total mercury and methylmercury in common prey items, and bioaccumulation dynamics of methylmercury in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River. Additionally, I evaluated sexual and seasonal variations of total mercury in *M. dolomieu* in the South Fork of the Shenandoah River.

Algae, aquatic insects, crayfish, detritus, and fish accounted for 75-97% of the diet. Total mercury in aquatic invertebrates and forage fish in contaminated rivers ranged from 66.7-398.3 and 198.0-594.9 ng/g wet weight, while total mercury in aquatic invertebrates and forage fish in the reference river were 4.4 and 29.3 ng/g. Model simulations indicated that dietary pathways accounted for 87% of methylmercury uptake by fish in contaminated rivers, but only 57% in the reference river. Total mercury in *M. dolomieu* was 19-20% higher in females than males and 14-21% higher during spring than summer and fall. Results of this study indicate that bioenergetics-based bioaccumulation models are valuable tools for evaluating field data, identifying processes critical to contaminant accumulation, and comparing outcomes of alternative management options associated with pollution control, ecosystem management, and/or restoration activities for management guidance prior to costly expenditures.

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INTRODUCTION

Mercury in Freshwater Systems

Mercury is a Type II heavy metal that occurs naturally in the environment (Church and Scudlark 1998) but is primarily introduced into aquatic systems through anthropogenic pathways, including effluent containing dyes, fungicides used in agriculture, mining and smelting, chlorine-alkali production facilities, industrial waste and emission, and ultimately through atmospheric deposition caused by the combustion of fossil fuels and municipal and medical wastes (Clarkson 1994; Porcella 1994; Watras et al. 1994). Once in the aquatic environment, metallic mercury is readily transformed to organic methylmercury through biological processes that include sulfate reducing bacteria and some fungi (Church and Scudlark 1998; Porcella 1994), greatly increasing its bioavailability to aquatic biota. Mercury accumulation in fish results from the complex interactions of a series of environmental components, including supply, methylation rates, trophic interactions, and fish bioenergetics (Rodgers 1996).

Human exposure to mercury is primarily through the consumption of fish (Clarkson 1994; Trudel and Rasmussen 1997) where it is mainly present in the form of methylmercury (Grieb et al. 1990; Bloom 1992). Mercury and methylmercury are neurological toxicants to humans. In addition, methylmercury is also classified as a Group C possible human carcinogen (USEPA 2000). Primary concerns regarding the consumption of mercury-contaminated fish stem from methylmercury's effects on in utero neurological development, for which evidence of a dose-dependent response is found in human populations (Marsh et al. 1987; Stern 1993; Grandjean et al. 1997). Human exposure to mercury is associated with slow development, blindness, cerebral palsy, and other birth defects (Clarkson 1990; Clarkson 1994). Methylmercury is water-soluble, diffuses readily across membranes, and considered 50-100x more toxic than metallic mercury, making it particularly damaging to humans because the blood-brain barrier in both infants and adults fails to impede the passage of methylmercury to brain tissues (Hughes and Poole 1989; Rodgers 1994).

Due to the widespread presence of mercury in the environment and its strong bioaccumulative potential in aquatic food webs, mercury is the leading cause of health advisories for fish consumption in the United States (Ginsberg and Toal 2000; USEPA 2003). Although each state health department mandates its own action level, the U. S. Food and Drug Administration (U. S. FDA) has an action level of 1.0 µg/g wet weight methylmercury in the edible portion of fish. From 1993 to 2002, the number of health advisories for fish consumption issued due to mercury contamination increased from 899 to 2,140 (138%) and the number of states with advisories increased from 27 to 45 (67%). Currently, there are 19 states with

statewide health advisories for fish consumption due to mercury contamination in freshwater lakes and/or rivers (i.e., CT, FL, IL, IN, KY, ME, MD, MA, MI, MN, MO, NH, NJ, ND, OH, PA, RI, VT, and WI). Fish consumption is regulated for more than 4,884,288 lake ha and 761,519 rkm due to mercury contamination (USEPA 2003).

History of Mercury Contamination in the Shenandoah River Basin

In 1976, during excavation work, employees of E. I. du Pont de Nemours and Company (DuPont) in Waynesboro, Virginia discovered minuscule globules of metallic mercury in disturbed soils near the site of an old chemical building. Although specific details remain unclear, apparently it was in this vicinity that mercuric sulfate was used as a catalyst in an acetic anhydride manufacturing process from 1929 to 1950. During that time, undetermined quantities of mercury were released into the South River through discharges, surface runoff, and perhaps subsurface seepage (Carter 1977; Bolgiano 1980; Messing and Winfield 1998). In the early 1980s, a settlement between DuPont and the Virginia State Water Control Board (later known as the Virginia Department of Environmental Quality) established a trust fund to support mercury monitoring of water, sediments, and fish throughout the Shenandoah River basin, including the South River, South Fork of the Shenandoah River, and Shenandoah River, for a projected 100-year period (VDEQ 2002).

Fish, including *Ambloplites rupestris*, *Catostomus commersoni*, *Cyprinus carpio*, *Hypentelium nigricans*, *Ictalurus punctatus*, *Lepomis auritus*, *Micropterus dolomieu* and *salmoides*, and *Oncorhynchus mykiss*, have been sampled for analysis of total mercury concentration (and a subset for methylmercury) in their tissues every three years at multiple sites throughout the basin. Results of the monitoring program indicate that concentrations of methylmercury in the edible portion of fish regularly exceed the U. S. FDA action level for human consumption (Messing and Winfield 1998; VDEQ 2000, 2001, 2003). Results of the monitoring program also indicate no decrease and even a slight increase (at several sites on the South River) in mean concentrations of total mercury in fish muscle tissue as opposed to decreased trends predicted in a 1982 modeling effort (J. Green, South River Science Team, 6/5/2001). At that time, reductions of 5 and 2% were predicted to occur for fish in the South River and South Fork of the Shenandoah River, respectively (LMS 1989; Messing and Winfield 1998). These trends prompted members of the South River Science Team, which is a collaborative group of stakeholders composed of state and federal agencies, citizen groups, academia, and industry, working collectively to rehabilitate the basin, to investigate processes affecting the bioaccumulation of mercury in fish in the Shenandoah River basin. The purpose of

this study was to elucidate the processes affecting the bioaccumulation of mercury in selected fish species of several trophic levels (*C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu*) in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin. Objectives of this study were to:

1. Determine food habits of the selected fish species to identify dietary pathways and patterns affecting mercury uptake.
2. Establish baseline concentrations of total mercury and methylmercury in common prey items of the selected fish species.
3. Simulate bioaccumulation dynamics of methylmercury in fish communities based on the selected fish species.
4. Assess sexual and seasonal variations of total mercury in *M. dolomieu*.

Selected Fish Species

The selected fish species used throughout this study included *C. commersoni* (bottom feeder), *I. punctatus* (bottom feeder), *L. auritus* (forager/invertivore), and *M. dolomieu* (predator). *Ictalurus punctatus* was added based on angler survey data from the South Fork of the Shenandoah River, which indicated that they are the most commonly consumed fish species (pers. comm. S. Reeser, VDGIF). The use of selected fish species allows for comparison of data among sites over a wide geographic area and is based upon several criteria: selected fish species must be commonly consumed and of commercial, recreational, or of subsistence value; they must have the potential to accumulate high concentrations of chemical contaminants; they must have a wide geographic distribution; and they must be easily identifiable. In addition, the U. S. Environmental Protection Agency recommends that species from a predator, forager, and bottom feeding group be represented, so that contaminants can be monitored at different trophic levels within the aquatic food web (USEPA 2000).

Description of Study Area

This study was conducted in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia (Figure 1). The South River is a fourth-order stream that originates on the western slope of the Blue Ridge Mountains in north central Virginia, drains an area of approximately 373 km², and has a mean annual discharge of 7.4 m³/s. The drainage basin is composed primarily of limestone and shale geology. Some of the land adjacent to the river is forested but most is used extensively for agriculture and livestock. The South River is characterized by a series of riffles

and pools and moderate flow. Substrate in riffles is composed primarily of various sized cobbles and sand. The South River flows in a northerly direction where it converges with the North River at Port Republic to form the South Fork of the Shenandoah River. Currently, there is a health advisory for fish consumption on the South River, which extends from the DuPont footbridge in Waynesboro to the confluence with the North River at Port Republic. The health advisory recommends no fish consumption, except for stocked trout, which have been tested and deemed safe for human consumption (VDEQ 2002). Mean concentrations of total mercury in the muscle tissue of *C. commersoni*, *L. auritus*, and *M. dolomieu* in the mercury contamination zone on the South River range from 0.35-1.70, 0.57-1.30, and 0.50-3.24 µg/g wet weight, respectively. Mean concentrations of total mercury in the muscle tissue of *C. commersoni*, *L. auritus*, and *M. dolomieu* upriver of the mercury contamination zone on the South River are 0.19, 0.19, and 0.21 µg/g wet weight, respectively (VDEQ 2003).

The South Fork of the Shenandoah River is a sixth order stream that meanders for approximately 160 rkm in north central Virginia, drains an area of approximately 4,144 km², and has a mean annual discharge of 39.6 m³/s. Limestone is prominent as outcroppings along the river and forms much of the stream substrate. Areas with reduced flow and backwaters are often silt laden. Shorelines are mostly well vegetated with little direct alteration from humans other than cattle watering areas adjacent to grazing land. The floodplain consists largely of crop, pasture, and forestland and some single-family homes. The three main tributaries of the South Fork of the Shenandoah River are the North River, Middle River, and South River, which converge at Port Republic. The South Fork and North Fork of the Shenandoah River converge at Front Royal to form the main stem of the Shenandoah River, approximately 290 rkm from the Chesapeake Bay. Currently, there is a health advisory for fish consumption for the entire length of the South Fork of the Shenandoah River, which extends from Port Republic to the confluence with the North Fork of the Shenandoah River at Front Royal. The health advisory limits consumption to two meals (1/2 lb each) of fish per month and recommends no fish consumption for women who are pregnant or may become pregnant, nursing mothers, and young children (VDEQ 2002). Mean concentrations of total mercury in the muscle tissue of *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the mercury contamination zone on the South Fork of the Shenandoah River range from 0.60-0.83, 0.55-1.53, 0.46-0.70, and 0.66-1.77 µg/g wet weight, respectively (VDEQ 2003).

The North River was used as the reference river throughout this study. The North River is a fifth order stream that originates in the Allegheny foothills of north central Virginia, drains an area of approximately 1140 km², and has a mean annual discharge of 10.7 m³/s. The North River

converges with the Middle River and then the South River near Port Republic to form the South Fork of the Shenandoah River. Currently, there is no health advisory for fish consumption on the North River. Mean concentrations of total mercury in the muscle tissue of *C. commersoni*, *L. auritus*, and *M. dolomieu* in the North River are 0.27, 0.11, and 0.47 µg/g wet weight, respectively (VDEQ 2003).

The fish assemblage in the Shenandoah River basin consists of 40 native species and subspecies and 18 introduced species (Jenkins and Burkhead 1994). Common taxa in the South River, South Fork of the Shenandoah River, and North River include *A. rupestris*, *Ameiurus spp.*, *Anguilla rostrata*, *Campostoma anomalum*, *C. commersoni*, *Cottus spp.*, *Cyprinella spp.*, *C. carpio*, *Etheostoma flabellare* and *olmstedii*, *H. nigricans*, *I. punctatus*, *Lepomis spp.*, *Luxilus cornutus*, *M. dolomieu* and *salmoides*, *Moxostoma spp.*, *Nocomis spp.*, *Notropis spp.*, *Noturus insignis*, *O. mykiss*, *Pimephales notatus*, *Rhinichthys spp.*, and *Salmo trutta*.

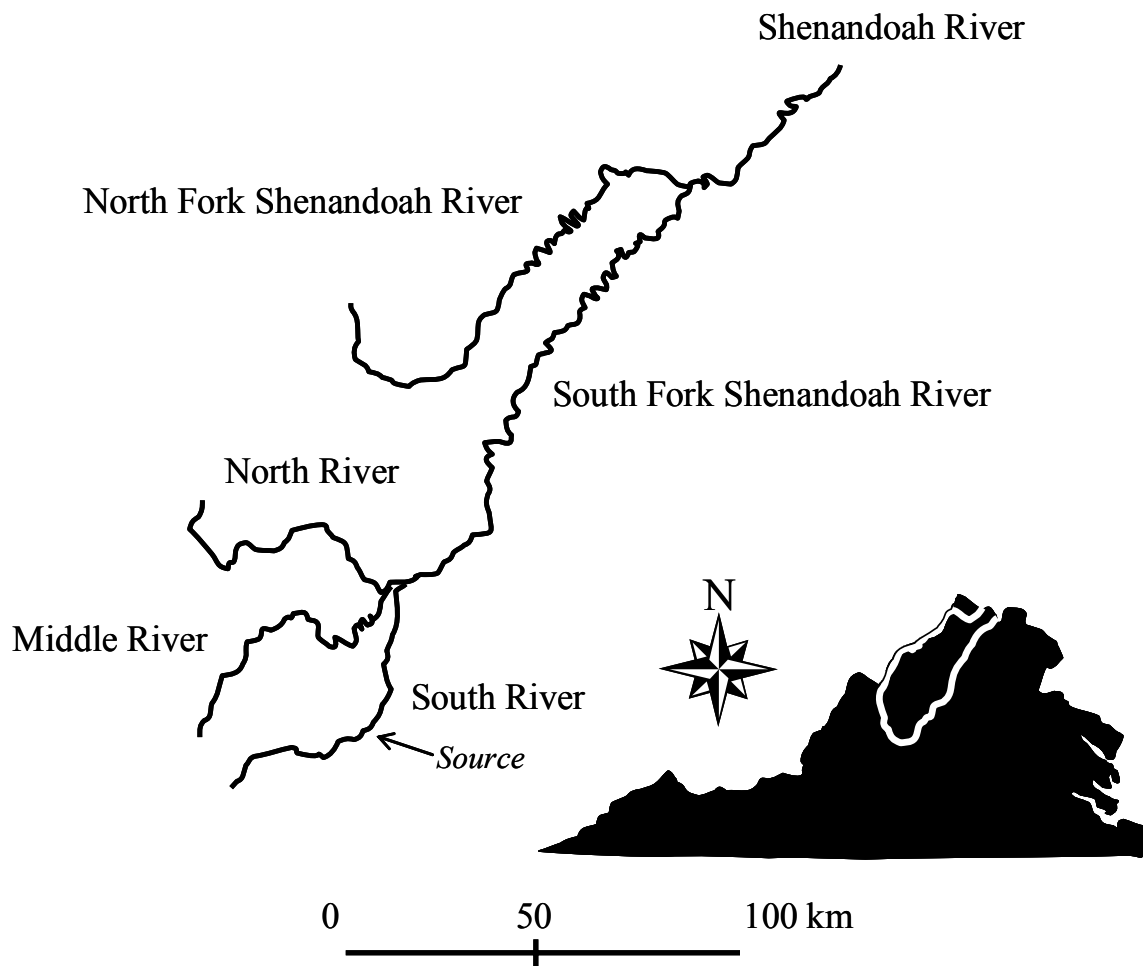


Figure 1. Shenandoah River basin, Virginia.

CHAPTER 1: Food Habits of Selected Fish Species in the Shenandoah River Basin, Virginia

ABSTRACT

Food habits of *Catostomus commersoni*, *Ictalurus punctatus*, *Lepomis auritus*, and *Micropterus dolomieu* were assessed during spring, summer, fall, and winter 2002 to identify dietary pathways and patterns affecting mercury uptake in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia. Algae, aquatic insects, crayfish, detritus, and fish accounted for 75-97% of the diet. Sizeable proportions of Annelida, Bivalvia, Cladocera, Gastropoda, and terrestrial insects were also consumed. As *L. auritus* and *M. dolomieu* increased in size, *L. auritus* diversified their diet, which often included larger items (e.g., crayfish and Gastropoda), and *M. dolomieu* shifted from a diet primarily composed of aquatic insects to one mainly composed of crayfish and fish. Seasonal dietary patterns included decreased consumption of aquatic insects from spring to fall by *C. commersoni* and *M. dolomieu*, increased consumption of terrestrial insects during summer and fall by *L. auritus* and *M. dolomieu*, and decreased feeding during winter by *I. punctatus*, *L. auritus*, and *M. dolomieu*. Intraspecific diet overlap between rivers was high for *C. commersoni* and *L. auritus* because of their common dependence on detritus and aquatic insects, respectively. *Micropterus dolomieu* in the South Fork of the Shenandoah River were more dependent on aquatic insects at larger sizes and for longer periods than *M. dolomieu* in the South River and North River, while *M. dolomieu* in the South River and North River consumed greater proportions of crayfish. Differences in the composition of fish consumed by *M. dolomieu* were also noted among rivers. Interspecific diet overlap was low, except between *L. auritus* and juvenile *M. dolomieu* because of their common dependence on aquatic insects (i.e., Diptera, Ephemeroptera, and Trichoptera). Results of this study have identified the dietary pathways and patterns affecting mercury uptake by the selected fish species in the Shenandoah River basin and clearly indicate that disregarding system- and species-specific dietary information may seriously hamper the results of mercury bioaccumulation studies and ultimately remediation efforts.

INTRODUCTION

For fishery ecologists, the study of food habits is a standard practice, and much of the current knowledge and understanding of the production and ecological role of fish populations is derived from such studies (Wallace 1984). Information on food habits can be useful for the assessment of predator-prey interactions, competition and resource partitioning, bioenergetics,

and contaminant bioaccumulation. Knowledge of prey selection enables mapping the flow of persistent chemical contaminants through aquatic food webs.

Mercury accumulation in fish results from the complex interactions of a series of environmental components, including supply, methylation rates, trophic interactions, and fish bioenergetics (Rodgers 1996). Fish mainly accumulate mercury through dietary pathways (Jernelöv and Lann 1971; Phillips and Buhler 1978; Rodgers and Beamish 1981; Harris and Snodgrass 1993; Hall et al. 1997). Although the general food habits of *Catostomus commersoni* (Stewart 1926; Elder and Carlson 1977; Lalancette 1977; Twomey et al. 1984; Ahlgren 1990a, 1990b, 1996), *Ictalurus punctatus* (Menzel 1943; Perry 1969; Mathur 1970; Starostka and Nelson 1974; Lewis 1976; McMahon and Terrell 1982; Zuerlein 1982; Hubert 1999), *Lepomis auritus* (Sandow et al. 1974; Coomer et al. 1977; Cooner and Bayne 1982; Wallace 1984; Barwick and Hudson 1985; Aho et al. 1986; Johnson and Dropkin 1993, 1995; Pert 1997), and *Micropterus dolomieu* (Surber 1939, 1941; Buynak et al. 1982; Edwards et al. 1983; Austen and Orth 1985; Roell 1989; Stephenson and Momot 1991; Easton and Orth 1992; Johnson and Dropkin 1993; Pert 1997) are well-known, specific food habits of these species in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia, are unknown.

Documentation of food habits is critical to fully understand the processes affecting the bioaccumulation of mercury in fish because even though diets are typically composed of preferred items that are readily available, the composition and proportions of diet components can vary ontogenetically between size classes, temporally with season, spatially between rivers or reaches, and for reasons relatively unknown, major diet components can vary between basins for a given species (Stewart 1926; Surber 1941; Perry 1969; Sandow et al. 1974; Starostka and Nelson 1974; Coomer et al. 1977; Lalancette 1977; Buynak et al. 1982; Cooner and Bayne 1982; Zuerlein 1982; Wallace 1984; Stephenson and Momot 1991; Easton and Orth 1992; Pert 1997). The objective of this study was to identify the dietary pathways and patterns affecting mercury uptake by *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River. Tasks of this objective were to:

1. Identify the principal diet items of the selected fish species.
2. Assess dietary patterns between size classes, seasons, rivers, and species.
3. Relate the observed dietary pathways and patterns to mercury uptake.

MATERIALS AND METHODS

Description of Study Sites

This study was conducted in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia (Figure 1.1). The South River is a fourth-order stream that originates on the western slope of the Blue Ridge Mountains, drains an area of 373 km², and has an average annual discharge of 7.1 m³/s. The North River is a fifth-order stream that originates in the Allegheny foothills, drains an area of 1140 km², and has an average annual discharge of 10.2 m³/s. The South River and North River converge at Port Republic to form the South Fork of the Shenandoah River. The South Fork of the Shenandoah River is a sixth-order stream that flows for 160 rkm and drains an area of 4,144 km² before joining the North Fork of the Shenandoah River at Front Royal to form the main stem of the Shenandoah River, approximately 290 rkm from the Chesapeake Bay. Due to the large size of the study area, many sites were required to adequately describe the food habits of the selected fish species (Table 1.1). Fish sampling occurred at seven sites on the South River, ranging from Waynesboro to Grottoes (SR1-SR7), eleven sites on the South Fork of the Shenandoah River, ranging from Port Republic to Front Royal (SF1a-SF7), and three sites on the North River, ranging from Grottoes to Bridgewater (NR1-NR3).

Data Collection

Catostomus commersoni, *I. punctatus*, *L. auritus*, and *M. dolomieu* were collected during spring (April 8-18, 2002), summer (July 8-25, 2002), fall (September 28-October 9, 2002), and winter (December 9, 2002-January 8, 2003) by use of boat and barge mounted pulsed direct-current electrofisher units. *Ictalurus punctatus* were also collected by use of baited hoopnets. Sampling efforts for *I. punctatus* were restricted to the South Fork of the Shenandoah River because of their limited geographic range (Jenkins and Burkhead 1994). The seasonal collection goal for each species was 30 fish per river.

The length range of fish collected was maximized to assure that fish of all sizes/ages were adequately represented. Fish were anesthetized in a 40 mg/L clove oil solution to facilitate processing (Keene and Noakes 1998). Clove oil was utilized because it provides rapid immobilization, has no toxic effects, assures a humane death, and is inexpensive compared to existing anesthetic compounds (Gardner 1997; Keene and Noakes 1998; Taylor and Roberts 1999; Waterstrat 1999). Anesthetized fish were measured for total length (mm) and weighed (g).

In spring, stomach contents of *I. punctatus*, *L. auritus*, and *M. dolomieu* were obtained using the gastric lavage technique. The gastric lavage technique was not performed on *C. commersoni* because this species lacks a true stomach, making the technique ineffective. Therefore, the entire intestinal tract of *C. commersoni* was removed by dissection. The gastric lavage apparatus consisted of a hand pumped compression sprayer (Ortho® 2-Gallon Heavy Duty Sprayer Model 190082) with a modified brass nozzle that was fitted to a 30.4 x 0.6 cm segment of polyethylene aquarium tubing. The apparatus was mounted to an angled piece of horizontally sectioned 15.2 cm polyvinyl chloride (PVC) piping, which had a fixed collection cup with 500 µm mesh lining (Foster 1977; Light et al. 1983; Culp et al. 1988; Hartleb and Moring 1995; Haley 1998). In addition to the gastric lavage technique, stomachs of *I. punctatus*, *L. auritus*, and *M. dolomieu* were removed by dissection, so that removal efficiency of the gastric lavage technique could be evaluated. Stomach and intestine samples were preserved in 10% formalin (Bowen 1996). Removal efficiency (%) was calculated using the following equation:

$$\%RE = (W_1/W_2)*100$$

where %RE is the removal efficiency, W_1 is the wet weight of flushed stomach contents, and W_2 is the total wet weight of stomach contents (Light et al. 1983). The gastric lavage technique had an average removal efficiency (\pm SE) of 94% (\pm 3%) for *L. auritus* and *M. dolomieu* (Table 1.2). Because of difficulty collecting *I. punctatus* during spring, the gastric lavage procedure was only performed once on this species, which was ineffective. Although the gastric lavage technique was generally successful for *L. auritus* and *M. dolomieu*, problems with the technique included variable removal efficiency due to difficulty removing larger prey items, such as crayfish and spiny-rayed fish (e.g., *Noturus insignis*), and lengthy fish processing time. After discussion with various stakeholders involved in this study, the gastric lavage technique was deemed unnecessary for subsequent sampling events. Therefore, stomachs of *I. punctatus*, *L. auritus*, and *M. dolomieu* were removed by dissection during summer, fall, and winter sampling events.

Items observed in the stomachs of *I. punctatus*, *L. auritus*, and *M. dolomieu* and in the anterior fifth of intestinal tracts of *C. commersoni* (Coomer et al. 1977) were identified to species (fish) and order (invertebrates) or the lowest taxonomic level practical using a dissection scope (Cambridge Instruments® Model Z30L with magnification range 7x-30x) and pertinent references (Thorp and Covich 1991; Jenkins and Burkhead 1993; Merritt and Cummins 1996). Partially digested unidentifiable insect and fish matter were categorized as PDUI and PDUF, respectively. Non-biological items (i.e., rocks, sand, fishing lures, and soybean and cheese bait)

were excluded from diet analyses. Hydracarina, banded water snake *Nerodia fasciata fasciata*, and fish eggs were categorized as miscellaneous diet items. Following identification, diet items were grouped taxonomically, blotted dry, weighed to the nearest 0.001 g, and preserved in 70% EtOH for archival purposes (Bowen 1996).

Data Analysis

Because of likely ontogenetic differences in diet, *L. auritus* and *M. dolomieu* were categorized into size classes prior to diet analyses. *Lepomis auritus* were grouped into three size classes (<100, 100-150, and >150 mm) and *M. dolomieu* were grouped into four size classes (<100, 100-199, 200-299, and >299 mm). *Ictalurus punctatus* and *C. commersoni* were not grouped into size classes for diet analyses because of difficulty collecting juveniles. The percent contribution by wet weight of each diet item was calculated using the following equation:

$$\%WTP_i = \Sigma(WTP_i/WT)/N$$

where %WTP_i is the average percent contribution by wet weight for diet item i, WTP_i is the wet weight of diet item i consumed by each fish, WT is the total wet weight of all diet items consumed by each fish, and N is the total number of fish sampled. Percent contribution by weight allows diet items to be quantified in comparable mass units to estimate relative importance of diet items in terms of approximate nutrition gained by the fish (Bowen 1996).

The Schoener (1970) overlap index was used to evaluate diet overlap between size classes, seasons, rivers, and species. The overlap index was calculated using the following equation:

$$C_{xy} = 1 - 0.5(\Sigma|p_{xi} - p_{yi}|)$$

where C_{xy} is the overlap index value, p_{xi} is the proportion of diet item i used by species x, and p_{yi} is the proportion of diet item i used by species y (Bowen 1996). The overlap index ranges from 0 (no overlap) to 1 (complete overlap) with biologically significant values defined as those exceeding 0.60 (Mathur 1977). Diet items remained in original categories for diet overlap analysis to avoid inflation of overlap estimates. PDUI and PDUF were distributed among the aquatic insect and fish taxa observed in the fish's diet relative to their proportions in the diet. Forage fish were categorized by family.

RESULTS

The collection goal was achieved 31 of 40 attempts and 1,276 fish were collected for diet analyses (Table 1.3). Mean total lengths (\pm SE) of *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* collected were 401 (\pm 4), 570 (\pm 16), 144 (\pm 2), and 222 (\pm 4) mm and ranged from 105-531, 197-827, 35-226, and 46-476 mm, respectively.

Principal Diet Items

Detritus and aquatic insects, mainly Diptera, Ephemeroptera, and Trichoptera, were the principal diet items (90-93%) of *C. commersoni* in the South River (Figure 1.2; Appendix A. Table 1.1), South Fork of the Shenandoah River (Figure 1.3; Appendix A. Table 1.2), and North River (Figure 1.4; Appendix A. Table 1.3). Sizeable proportions of Bivalvia, Cladocera, and filamentous green algae were also consumed.

Filamentous green algae and fish, mainly *Lepomis spp.* and *M. dolomieu*, were the principal diet items (84%) of *I. punctatus* in the South Fork of the Shenandoah River (Figure 1.5; Appendix A. Table 1.4). Sizeable proportions of aquatic insects, crayfish, and detritus were also consumed. Stomachs of the two *I. punctatus* collected in winter were empty.

Aquatic insects, particularly Coleoptera, Diptera, Ephemeroptera, Odonata, and Trichoptera, were the principal diet item (75-87%) of *L. auritus* in the South River (Figure 1.6; Appendix A. Table 1.5), South Fork of the Shenandoah River (Figure 1.7; Appendix A. Table 1.6), and North River (Figure 1.8; Appendix A. Table 1.7). Sizeable proportions of Annelida, crayfish, detritus, Gastropoda, terrestrial insects, and vegetation were also consumed.

Aquatic insects, crayfish, and fish were the principal diet items (87-97%) of *M. dolomieu* in the South River (Figure 1.9; Appendix A. Table 1.8), South Fork of the Shenandoah River (Figure 1.10; Appendix A. Table 1.9), and North River (Figure 1.11; Appendix A. Table 1.10). Diptera, Ephemeroptera, Megaloptera, Odonata, and Trichoptera were the principal taxa of aquatic insects consumed by *M. dolomieu*, while Centrarchidae, mainly *Lepomis spp.* and *M. dolomieu*, Cyprinidae, *Etheostoma spp.*, and *N. insignis* were the principal taxa of fish consumed. Sizeable proportions of Annelida, detritus, terrestrial insects, and vegetation were also consumed.

Size Dependent, Seasonal, Spatial, and Interspecific Dietary Patterns

Size dependent dietary shifts were exhibited by *L. auritus* and *M. dolomieu*. Although aquatic insects were the principal diet item of *L. auritus* for all size classes, *L. auritus* consumed a wider array of diet items as they increased in size, which often included larger diet items, such as crayfish, Gastropoda, terrestrial Coleoptera, and occasionally fish. *Lepomis auritus* diet overlap

between size classes was consistently higher between the two smallest (<100 and 100-150 mm) and largest size classes (100-150 and >150 mm), emphasizing the observed size dependent dietary shift (Table 1.4). As *M. dolomieu* increased in size, they shifted from a diet mainly composed of aquatic insects to one primarily composed of crayfish and fish. Crayfish and fish were not observed in the diet of *M. dolomieu* until they attained sizes >100 mm, with the exception of *M. dolomieu* in the South River which were piscivorous at all sizes. *Micropterus dolomieu* diet overlap between size classes was consistently higher between the two smallest (<100 and 100-199 mm) and largest size classes (200-299 and >299 mm), emphasizing the observed size dependent dietary shift (Table 1.5).

The percentage of empty stomachs observed for *I. punctatus*, *L. auritus*, and *M. dolomieu* increased substantially from spring to winter, but remained consistent among seasons for *C. commersoni* (Figure 1.12). The proportion of aquatic insects consumed by *C. commersoni* in the South River and South Fork of the Shenandoah River decreased from spring to winter but remained consistent between seasons in the North River. However, the proportion of Bivalvia consumed by *C. commersoni* in the North River increased in fall and winter. *Catostomus commersoni* diet overlap between seasons was consistently high (0.58-0.87), which was caused by their common dependence on detritus and aquatic insects, particularly Diptera, Ephemeroptera, and Trichoptera (Table 1.6). *Ictalurus punctatus* diet overlap between seasons was high between summer and fall (0.81) in the South Fork of the Shenandoah River, which were the only comparable seasons. High seasonal diet overlap by *I. punctatus* was caused by their dependence on filamentous green algae and fish. Larger *L. auritus*, particularly those >150 mm, consumed sizeable proportions of terrestrial insects, including Coleoptera and Hymenoptera, during summer and fall. *Lepomis auritus* diet overlap between seasons was highest between summer and fall in the South River (0.59) and South Fork of the Shenandoah River (0.58), and spring and summer (0.57) in the North River (Table 1.7). *Micropterus dolomieu* also consumed sizeable proportions of terrestrial insects, including Coleoptera and Hymenoptera, during summer and fall in the South River and summer in the North River. The proportion of aquatic insects consumed by *M. dolomieu* normally decreased from spring to winter, while the proportion of crayfish and fish consumed increased, particularly for larger size classes. *Micropterus dolomieu* diet overlap between seasons was highest between summer and fall in the South River (0.61), South Fork of the Shenandoah River (0.55), and North River (0.68), which was caused by their dependence on crayfish and fish (Table 1.8).

Catostomus commersoni diet overlap between rivers was consistently high, which was caused by their common dependence on detritus and aquatic insects, particularly Diptera,

Ephemeroptera, and Trichoptera (Table 1.9). *Catostomus commersoni* diet overlap between rivers was highest between *C. commersoni* in the South River and North River. *Lepomis auritus* diet overlap between rivers was also high, which was caused by their common dependence on aquatic insects, particularly Coleoptera, Diptera, Ephemeroptera, Odonata, and Trichoptera (Table 1.10). *Lepomis auritus* diet overlap between rivers was highest between *L. auritus* in the South Fork of the Shenandoah River and North River. *Micropterus dolomieu* diet overlap between rivers was variable, which was caused by differences in the composition and proportions of diet components consumed (Table 1.11). *Micropterus dolomieu* in the South Fork of the Shenandoah River were more dependent on aquatic insects at larger sizes and for longer periods than *M. dolomieu* in the South River and North River. In addition, *M. dolomieu* in the South River and North River consumed greater proportions of crayfish than *M. dolomieu* in the South Fork of the Shenandoah River. Although *M. dolomieu* in the South River were piscivorous at all sizes, fish were not observed in the diet of *M. dolomieu* in the South Fork of the Shenandoah River and North River until they attained sizes >100 mm. Differences were also observed in the composition of forage fish consumed by *M. dolomieu* between rivers. *Micropterus dolomieu* in the South River primarily consumed Centrarchidae, Cyprinidae, and *Etheostoma spp.*, while *M. dolomieu* in the South Fork of the Shenandoah River and North River primarily consumed Centrarchidae, Cyprinidae, and *N. insignis*. *Micropterus dolomieu* diet overlap was highest between the South Fork of the Shenandoah River and North River.

Interspecific diet overlap was consistently low between species in the South River (Table 1.12), South Fork of the Shenandoah River (Table 1.13), and North River (Table 1.14), with the exception of *L. auritus* and juvenile *M. dolomieu* in the South River and South Fork of the Shenandoah River on several occasions. High diet overlap between *L. auritus* and *M. dolomieu* was caused by their common dependence on aquatic insects, particularly Diptera, Ephemeroptera, and Trichoptera.

DISCUSSION

Principal Diet Items

Dietary pathways are the most important source of mercury uptake by fish (Jernelöv and Lann 1971; Phillips and Buhler 1978; Rodgers and Beamish 1981; Harris and Snodgrass 1993; Hall et al. 1997). Piscivorous fish species normally accumulate mercury at faster rates than similarly sized omnivorous, planktivorous, or benthivorous species (Phillips et al. 1980; Brouard et al. 1994; Olivero et al. 1998; Neumann and Ward 1999; Mueller and Serdar 2002). Phillips et al. (1980) found that piscivorous *Esox lucius* and *Stizostedion canadense* and *vitreum*

accumulated mercury at nearly twice the rate of zooplanktivorous *Pomoxis annularis* and *nigromaculatus* in Tongue River Reservoir, Montana. Differences in mercury uptake were directly related to the quantity of mercury consumed (Phillips et al. 1980). Mueller and Serdar (2002) found that concentrations of total mercury were highest in predaceous *M. dolomieu*, followed by omnivorous *Perca flavescens* and *Ameiurus nebulosus*, zooplanktivorous *Oncorhynchus nerka*, and benthivorous *Lepomis gibbosus* in Lake Whatcom, Washington.

There were substantial differences between the principal diet items consumed by *C. commersoni*, *L. auritus*, *I. punctatus*, and *M. dolomieu* in the Shenandoah River basin, which was emphasized by interspecific comparisons. *Micropterus dolomieu* had the highest proportion of piscivory, indicating that they are feeding at a higher trophic level than *C. commersoni*, *I. punctatus*, and *L. auritus* and are presumably being exposed to greater concentrations of mercury. Results of the mercury monitoring program in the Shenandoah River basin support this inference, indicating that concentrations of total mercury are consistently higher in *M. dolomieu* than *C. commersoni*, *I. punctatus*, and *L. auritus* (VDEQ 2000, 2001, 2003). For instance, the most recent monitoring data from the South River indicates that the mean concentration of total mercury wet weight in *M. dolomieu* (1.98 µg/g) is 92 and 98% greater than mean concentrations of total mercury in *C. commersoni* (1.03 µg/g) and *L. auritus* (1.00 µg/g), respectively (VDEQ 2003). Although *I. punctatus* were also piscivorous, filamentous green alga was the principal diet item consumed, which is not uncommon (Menzel 1943; Perry 1969; Hubert 1999). Menzel (1943) reported that filamentous green alga was the principal diet item of *I. punctatus* during August in the Chickahominy River, Virginia. Concentrations of total mercury in filamentous green alga in the South Fork of the Shenandoah River are negligible (Chapter 2), which may partly explain why concentrations of mercury in *I. punctatus* are typically lower than in *M. dolomieu* (VDEQ 2003). Although aquatic insects were important in the diet of *C. commersoni* and *L. auritus*, detritus was the principal diet item of *C. commersoni* while aquatic insects were the principal diet item of *L. auritus*. Observing large proportions of detritus in the diet of *C. commersoni* is not uncommon (Elder and Carlson 1977; Lalancette 1977; Ahlgren 1990a). Elder and Carlson (1977) reported that detritus accounted for 70% of the diet by volume of *C. commersoni* in the South Platte River, Colorado. Detritus is normally ingested by *C. commersoni* intentionally (i.e., the proportion of detritus in the diet varies inversely with aquatic invertebrate abundance) and is a nutritionally significant component of their diet (Ahlgren 1990a, 1990b). Even though the principal diet items of *C. commersoni* and *L. auritus* in the Shenandoah River basin are different, mean concentrations of total mercury in the two species are comparable and often higher in *C. commersoni* (VDEQ 2003), indicating that mercury uptake through detrital

pathways may be important. Snyder and Hendricks (1995) found a significant relationship between whole-animal concentrations of total mercury and the relative amount of detritus consumed by *Hydropsyche morose* in the South River.

Size Dependent, Seasonal, and Spatial Dietary Patterns

Mercury uptake by fish through dietary pathways is highly affected by dietary shifts (MacCrimmon et al. 1983; Mathers and Johansen 1985; Driscoll et al. 1994). MacCrimmon et al. (1983) found that when *Salvelinus namaycush* in Tadenac Lake, Canada switched from a diet mainly composed of benthic macroinvertebrates to one primarily composed of smelt, they exhibited an abrupt increase in concentration of total mercury, which was apparently caused by the increased length of the food web. Driscoll et al. (1994) found that concentrations of total mercury in *P. flavescens* in Adirondack lakes increased sharply after age-5, which corresponded to the size at which they became predominately piscivorous (200 mm).

Catostomus commersoni, *L. auritus*, *I. punctatus*, and *M. dolomieu* in the Shenandoah River basin had important dietary patterns between sizes classes, seasons, and rivers, which may be critical to understanding mercury uptake. Food habits of fish are normally relative to their size. As fish grow larger, they may switch from one food type to another or select larger individuals of the same food type (Wallace 1984; Bowen 1996). Use of different food resources through ontogeny presumably reduces intraspecific competition among size classes of fish (Ebenman 1988). Size related dietary shifts exhibited by *L. auritus* and *M. dolomieu* in the Shenandoah River basin were comparable to the results of similar studies in other systems (Surber 1941; Sandow et al. 1974; Coomer et al. 1977; Buynak et al. 1982; Cooner and Bayne 1982; Wallace 1984; Austen and Orth 1985; Roell 1989; Stephenson and Momot 1991; Easton and Orth 1992; Pert 1997). Mercury exposure through dietary pathways most likely differs little as *L. auritus* in the Shenandoah River basin increase in size, because aquatic insects remain the principal diet item and concentrations of total mercury in larger aquatic invertebrates (e.g., crayfish and Gastropoda) are normally comparable or less than concentrations of total mercury in aquatic insects (Chapter 2). Conversely, as *M. dolomieu* in the Shenandoah River basin increase in size and shift to a more piscivorous diet, they are almost certainly being exposed to higher concentrations of mercury. Size dependent dietary shifts have also been observed in *C. commersoni* (Stewart 1926; Lalancette 1977; Twomey et al. 1984) and *I. punctatus* (Perry 1969; Starostka and Nelson 1974; McMahan and Terrell 1982; Zuerlein 1982), but this study did not permit this finding because of difficulty collecting juveniles.

Fish are highly responsive to seasonal changes in food availability. Dietary shifts within trophic categories are common as invertebrate populations mature and emerge. Dietary shifts from one trophic category to another as also known to occur (Wallace 1984; Bowen 1996). *Catostomus commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the Shenandoah River basin had important seasonal dietary shifts that may be affecting mercury uptake, including decreased consumption of aquatic insects from spring to fall by *C. commersoni* and *M. dolomieu*, increased consumption of terrestrial insects during summer and fall by *L. auritus* and *M. dolomieu*, and decreased feeding during winter by *I. punctatus*, *L. auritus*, and *M. dolomieu*. Decreased consumption of aquatic insects by *C. commersoni* and *M. dolomieu* may have been related to an actual variation in the abundance of diet items and their varying relative availability. However, it is possible that the types and relative numbers of diet items consumed by fish in this study were not representative of the types and numbers present in the habitat due to influences such as preference, but this is doubtful since these species are generally less selective (Wallace 1984; Austen and Orth 1985). *Lepomis auritus* and *M. dolomieu* in the Shenandoah River basin consumed substantial proportions of terrestrial insects during summer and fall, particularly in the South River. This finding identifies an important relationship between floodplain and aquatic ecosystems on the South River that was previously overlooked. The percentage of empty stomachs observed for *I. punctatus*, *L. auritus*, and *M. dolomieu* in the Shenandoah River basin was exceptionally high during winter, which presumably indicates a reduction in consumption. Reduced consumption during winter was probably caused by frigid water temperatures, which had means of 5.5, 4.5, and 4.0°C during the winter sampling period in the South River, South Fork of the Shenandoah River, and North River, respectively. Water temperatures below 10°C normally reduce metabolic demands, causing fish to become inactive and seek shelter (Edwards et al. 1983; Aho et al. 1986). Because dietary pathways account for the majority of mercury uptake by fish, reduced consumption during winter almost certainly decreases mercury exposure. Conversely, *C. commersoni* fed actively throughout the year, which is consistent with previous reports (Twomey et al. 1984).

For reasons relatively unknown, food habits of fish can vary spatially between reaches, rivers, and basins (Surber 1941; Buynak et al. 1982; Austen and Orth 1985). Differences in the composition and proportions of diet components consumed by *M. dolomieu* in the Shenandoah River basin were comparable to differences typically observed in other systems observed (Surber 1941; Buynak et al. 1982; Austen and Orth 1985). Factors potentially influencing differences in food habits between rivers include differences in habitat and forage abundance, composition, and availability (Buynak et al. 1982; Austen and Orth 1985). Food habits of *C. commersoni* and *L.*

auritus were similar between rivers in the Shenandoah River basin. Therefore, one may expect to observe similar concentrations of mercury in *C. commersoni* and *L. auritus* among rivers if ambient environmental concentrations of mercury were similar.

Conclusions

Results of this study have identified the dietary pathways and patterns affecting mercury uptake by *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the Shenandoah River basin and clearly indicate that disregarding system- and species-specific dietary information may hamper the results of mercury bioaccumulation studies and ultimately remediation efforts. There were substantial differences between the principal diet items of the selected fish species. *Micropterus dolomieu* had the highest proportion of piscivory, indicating that they are feeding at the highest trophic level and presumably have the highest exposure to mercury. Additionally, as *M. dolomieu* increase in size and shift to a more piscivorous diet, they are almost certainly being exposed to higher concentrations of mercury. Based on food habits and results of the mercury monitoring program for *C. commersoni* in the Shenandoah River basin, it appears that detritus may be an important source of mercury uptake by *C. commersoni*. Large proportions of terrestrial insects consumed by *L. auritus* and *M. dolomieu* during summer and fall indicates an important relationship between floodplain and aquatic ecosystems that may have been overlooked previously. Reduced consumption during winter presumably decreases mercury exposure through dietary pathways.

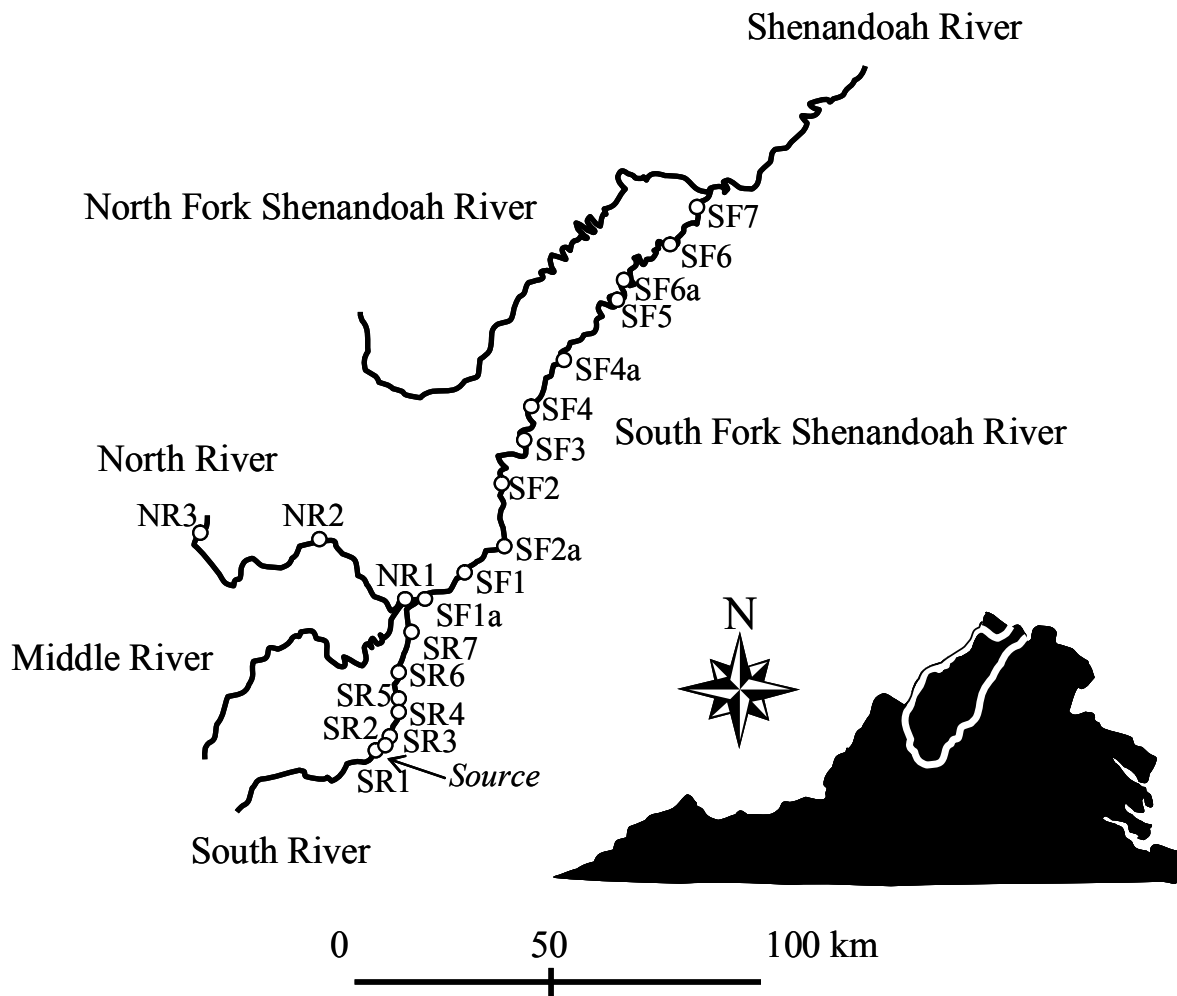


Figure 1.1. Study area and sites in the Shenandoah River basin, Virginia used to collect fish for diet analyses.

Table 1.1. Description of study sites in the Shenandoah River basin, Virginia used to collect fish for diet analyses, including distance downriver from historic source of mercury.

Site	Distance (rkm)	Latitude	Longitude	Study Site Description
<u>SOUTH RIVER</u>				
SR1	*	N38°03'37"	W78°53'59"	Waynesboro-Rife Loth Park
SR2	0.0	N38°03'48"	W78°53'05"	Waynesboro-Constitution Park
SR3	2.1	N38°04'40"	W78°52'45"	Waynesboro-North Park
SR4	3.7	N38°05'25"	W78°52'35"	Waynesboro-Hopeman Parkway
SR5	8.7	N38°06'21"	W78°51'55"	Dooms-Rt. 611 above dam
SR6	16.9	N38°09'30"	W78°51'10"	Crimora-Department of Forestry
SR7	33.5	N38°17'15"	W78°50'00"	Grottoes-Town Park
<u>SOUTH FORK SHENANDOAH RIVER</u>				
SF1a	40.2	N38°18'00"	W78°48'25"	Port Republic-boat launch
SF1	44.9	N38°18'50"	W78°46'16"	Lynwood-Rt. 708 bridge
SF2a	56.2	N38°21'25"	W78°41'45"	Island Ford-boat launch
SF2	80.0	N38°28'30"	W78°37'30"	Shenandoah-boat launch above dam
SF3	104.6	N38°35'00"	W78°35'40"	Newport-Rt. 340 boat launch
SF4	124.7	N38°38'45"	W78°32'00"	Hamburg-Rt. 340 bridge boat launch
SF4a	144.0	N38°44'45"	W78°26'15"	Massanutten-boat launch
SF5	149.7	N38°47'15"	W78°23'20"	Fosters-boat launch
SF6a	152.1	N38°47'00"	W78°22'10"	Compton-Compton's Rapids
SF6	174.9	N38°50'23"	W78°19'44"	Bentonville-Rt. 613 bridge boat launch
SF7	199.2	N38°54'45"	W78°12'45"	Front Royal-boat launch
<u>NORTH RIVER</u>				
NR1	*	N38°17'07"	W78°51'02"	Grottoes-Rt. 668 bridge
NR2	*	N38°20'40"	W78°55'00"	Burketown-USGS gage station
NR3	*	N38°22'30"	W78°58'45"	Bridgewater-Rt. 42 bridge

*Reference site, not located downriver from the historic mercury source.

Table 1.2. Removal efficiency (RE%) of gastric lavage technique on *Lepomis auritus* and *Micropterus dolomieu* collected in the Shenandoah River basin, Virginia.

Species	<i>N</i>	Mean RE	±SE	Range
<u>SOUTH RIVER</u>				
<i>Lepomis auritus</i>	25	97%	2%	54-100%
<i>Micropterus dolomieu</i>	32	93%	3%	28-100%
<u>SOUTH FORK SHENANDOAH RIVER</u>				
<i>Lepomis auritus</i>	28	99%	<1%	90-100%
<i>Micropterus dolomieu</i>	27	87%	6%	2-100%
<u>NORTH RIVER</u>				
<i>Lepomis auritus</i>	33	96%	3%	0-100%
<i>Micropterus dolomieu</i>	36	91%	4%	2-100%

Table 1.3. Total number of fish collected in the Shenandoah River basin, Virginia for diet analyses, where TL = total length (mm).

Species	Spring	Summer	Fall	Winter	Total	Mean TL	±SE	TL Range
	<u>SOUTH RIVER</u>							
<i>Catostomus commersoni</i>	35	35	32	35	137	353	8	169-497
<i>Lepomis auritus</i>	34	32	34	31	131	140	3	45-206
<i>Micropterus dolomieu</i>	35	42	44	20	141	199	8	46-476
	<u>SOUTH FORK SHENANDOAH RIVER</u>							
<i>Catostomus commersoni</i>	30	30	27	18	105	441	3	310-510
<i>Ictalurus punctatus</i>	1	38	26	2	67	566	17	179-827
<i>Lepomis auritus</i>	39	35	42	30	146	143	3	35-226
<i>Micropterus dolomieu</i>	56	58	49	37	200	241	6	59-466
	<u>NORTH RIVER</u>							
<i>Catostomus commersoni</i>	30	30	32	30	122	401	6	186-531
<i>Lepomis auritus</i>	30	24	31	23	108	127	3	54-210
<i>Micropterus dolomieu</i>	30	31	37	21	119	218	7	61-408

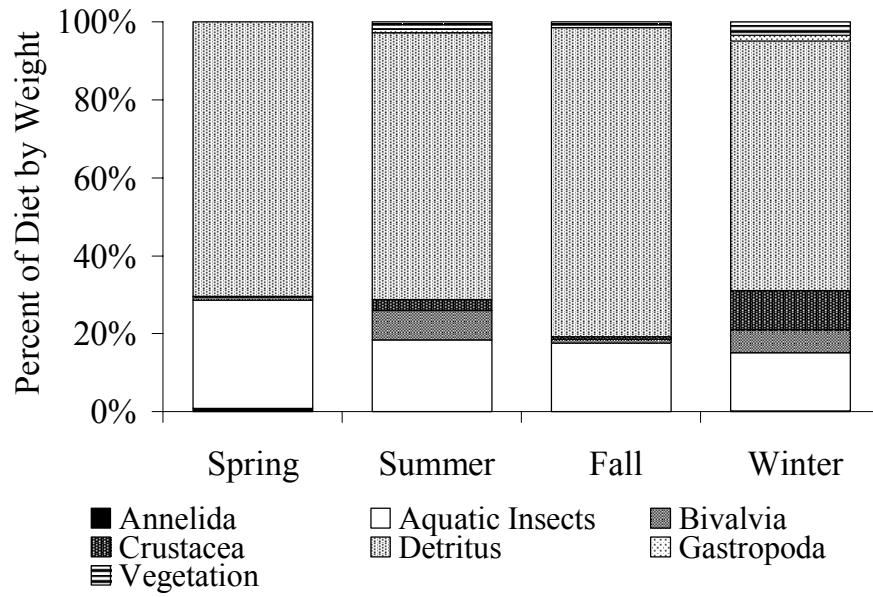


Figure 1.2. Diet composition of *Catostomus commersoni* in the South River, Virginia.

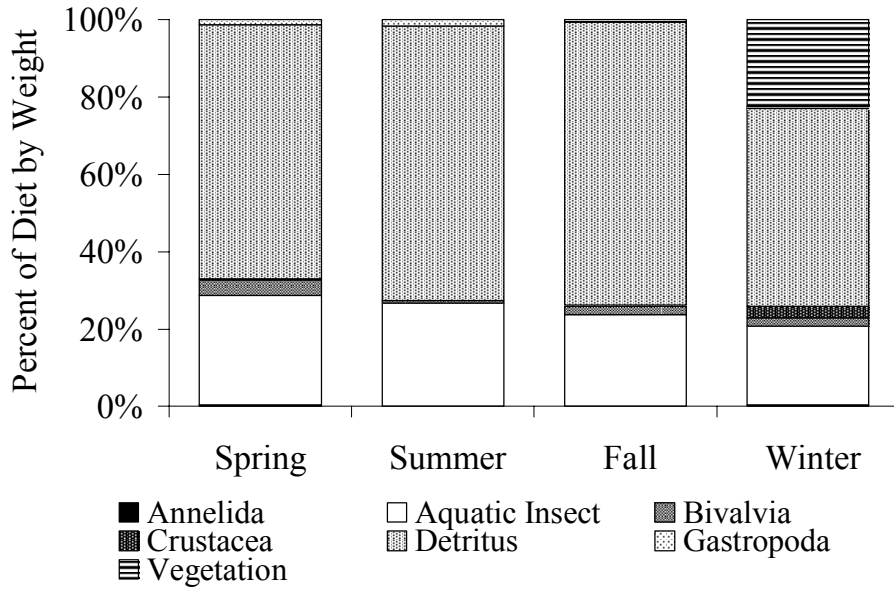


Figure 1.3. Diet composition of *Catostomus commersoni* in the South Fork of the Shenandoah River, Virginia.

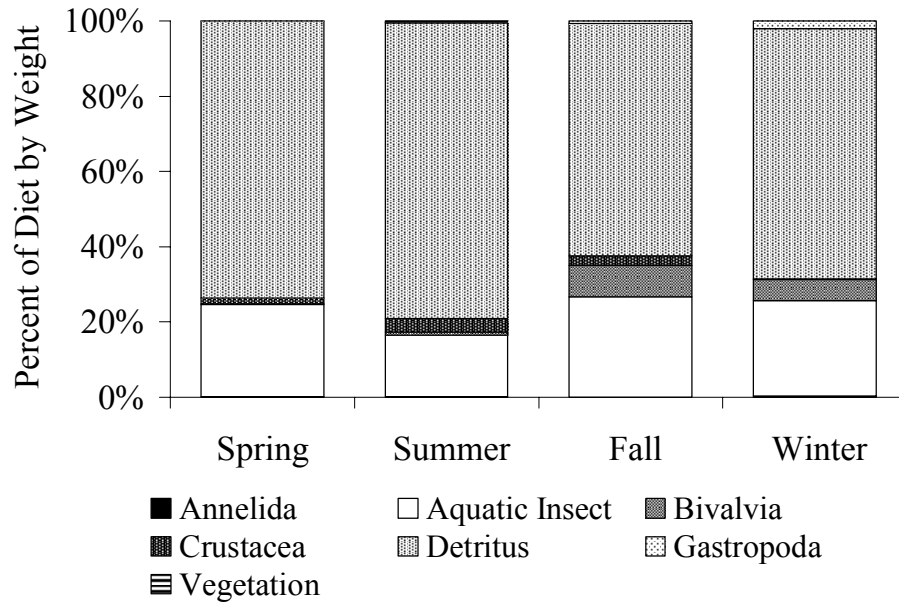


Figure 1.4. Diet composition of *Catostomus commersoni* in the North River, Virginia.

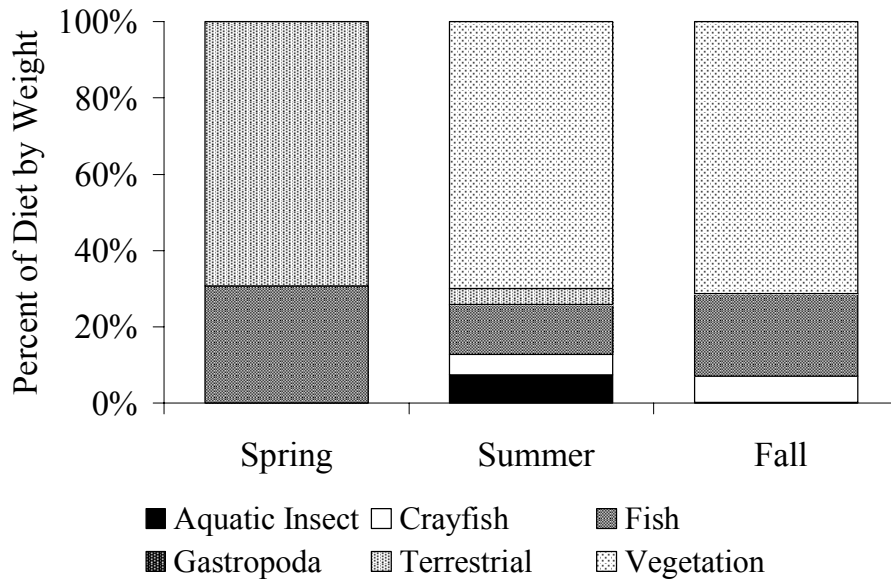


Figure 1.5. Diet composition of *Ictalurus punctatus* in the South Fork of the Shenandoah River, Virginia

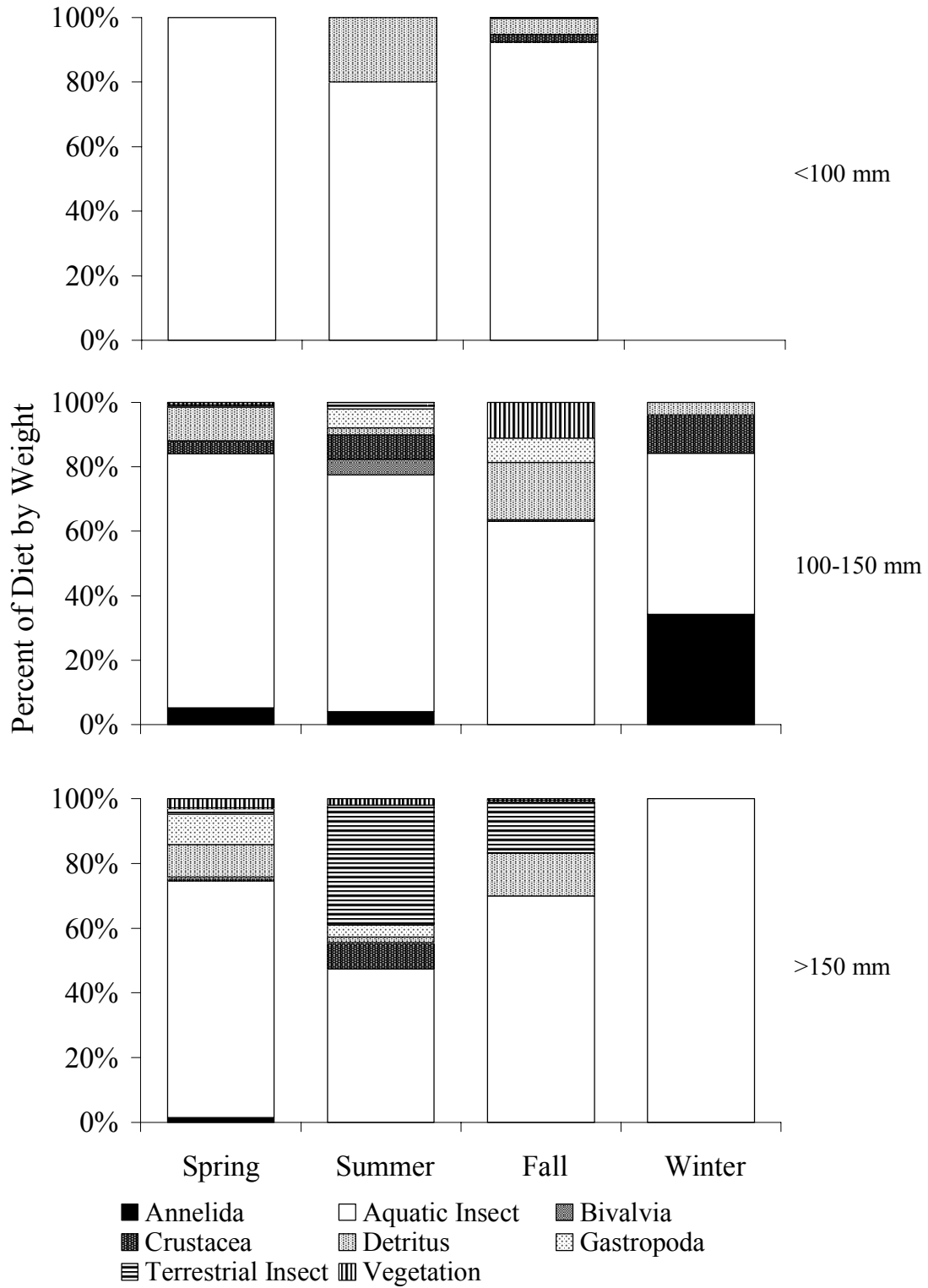


Figure 1.6. Diet composition of *Lepomis auritus* in the South River, Virginia.

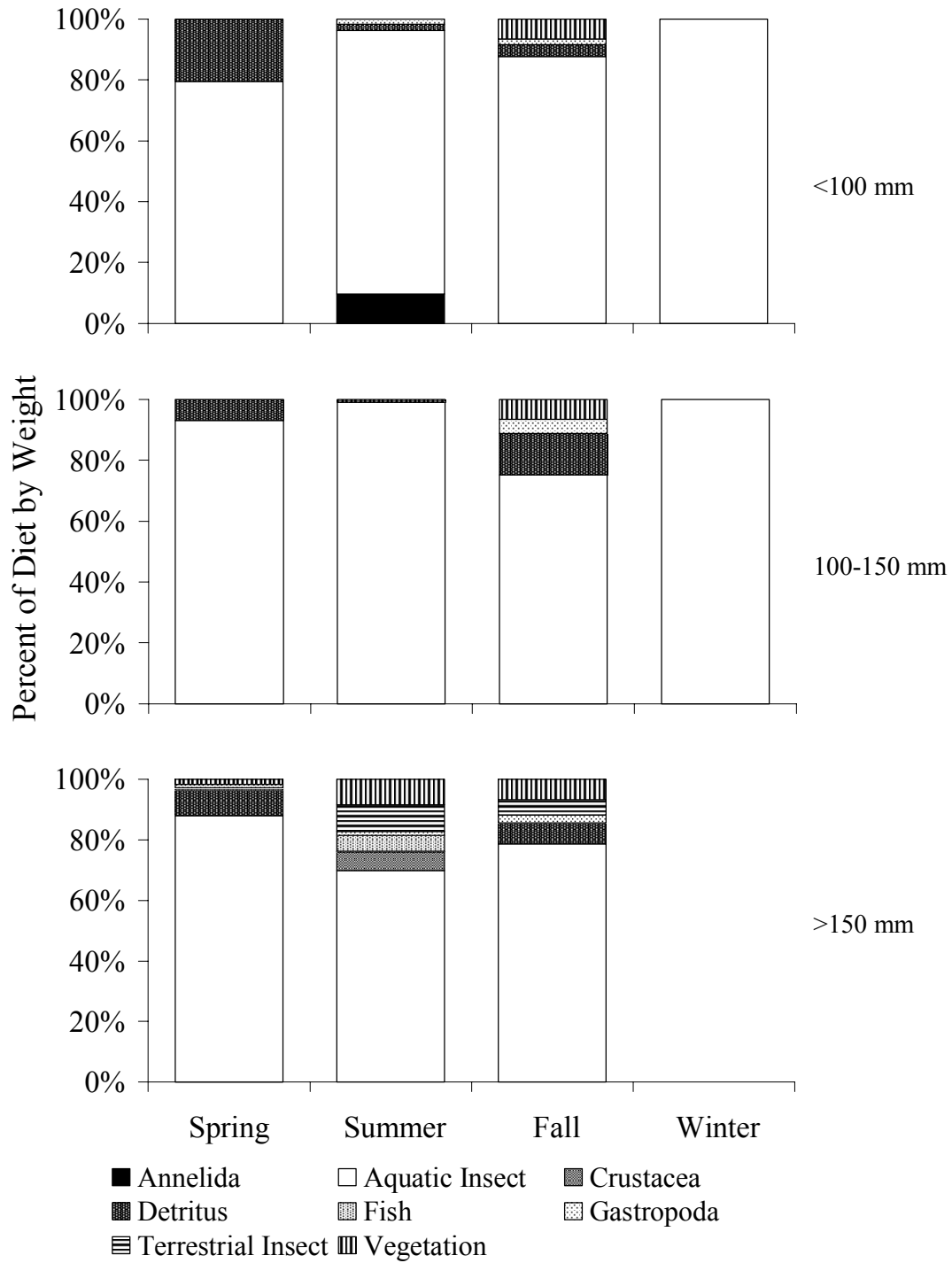


Figure 1.7. Diet composition of *Lepomis auritus* in the South Fork of the Shenandoah River, Virginia.

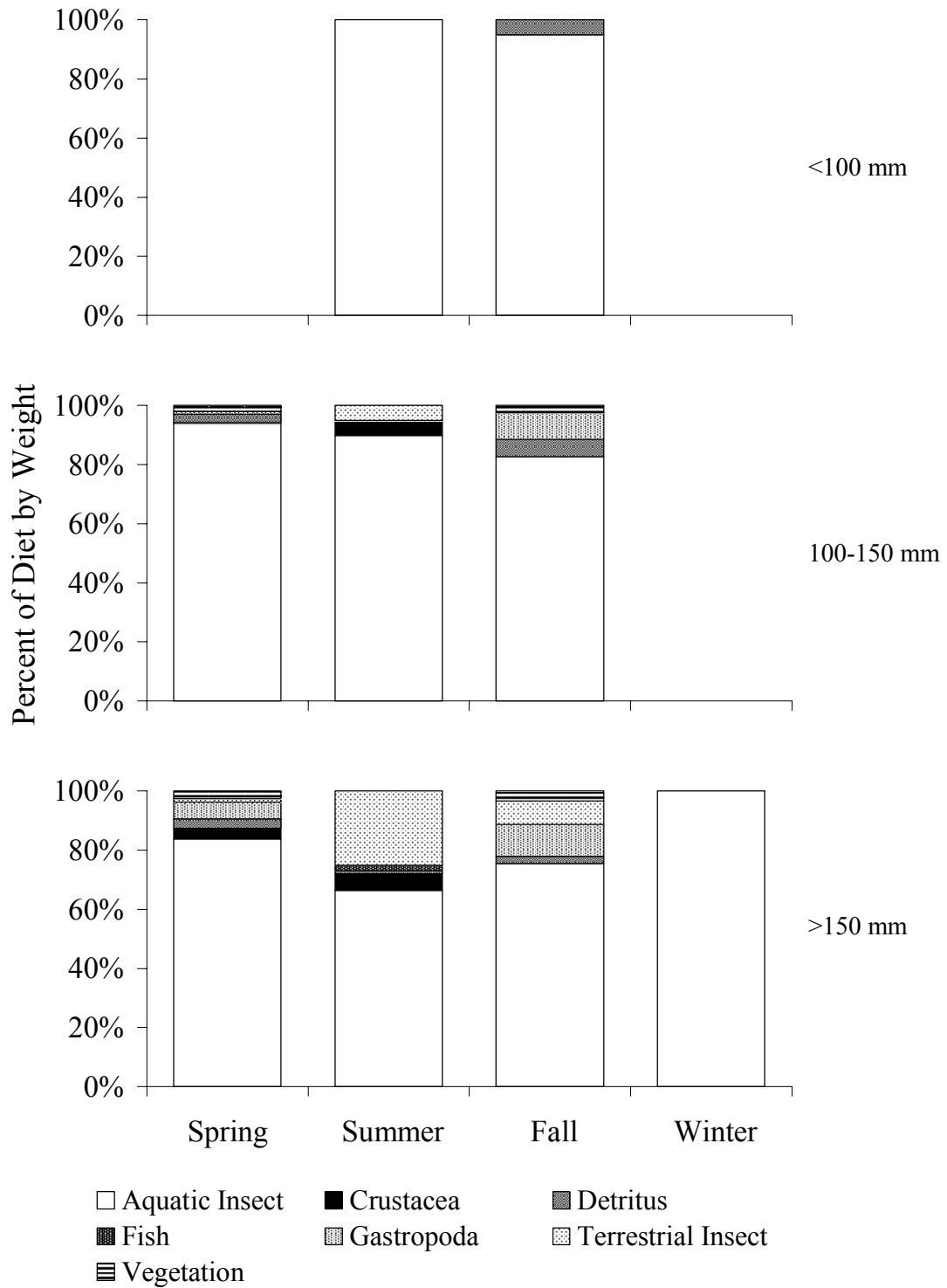


Figure 1.8. Diet composition of *Lepomis auritus* in the North River, Virginia.

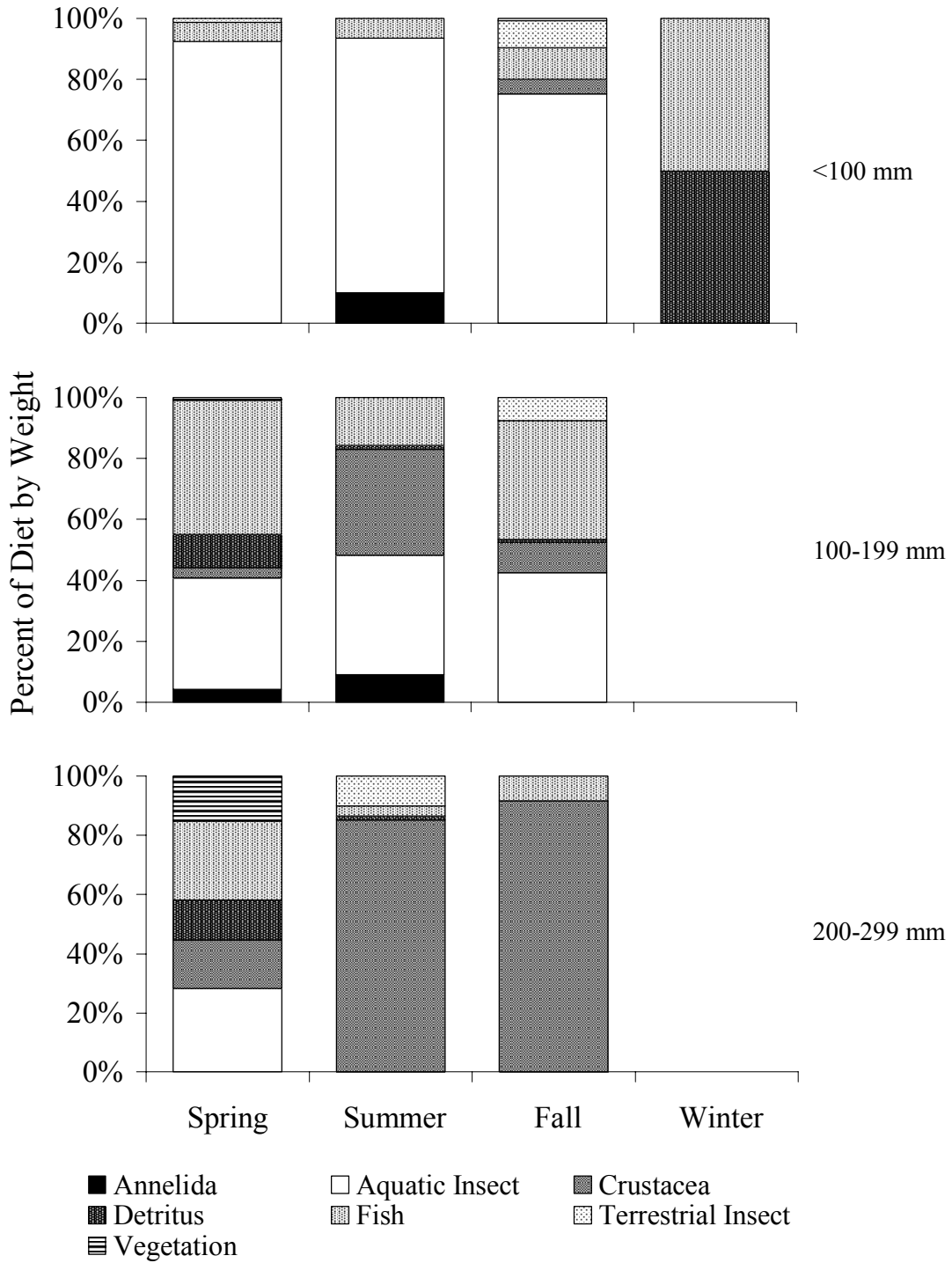


Figure 1.9. Diet composition of *Micropterus dolomieu* in the South River, Virginia.

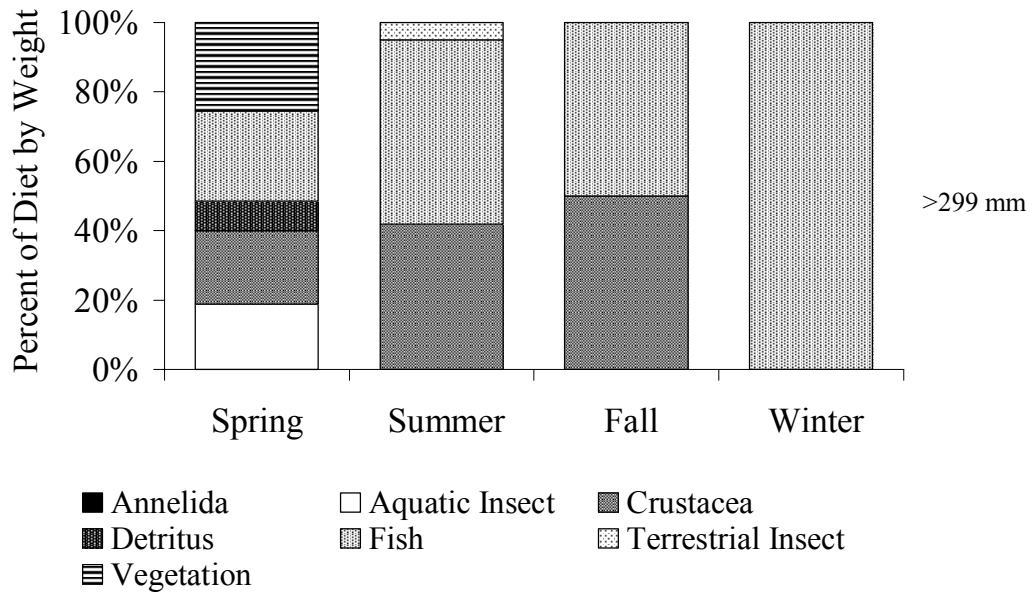


Figure 1.9. (continued) Diet composition of *Micropterus dolomieu* in the South River, Virginia.

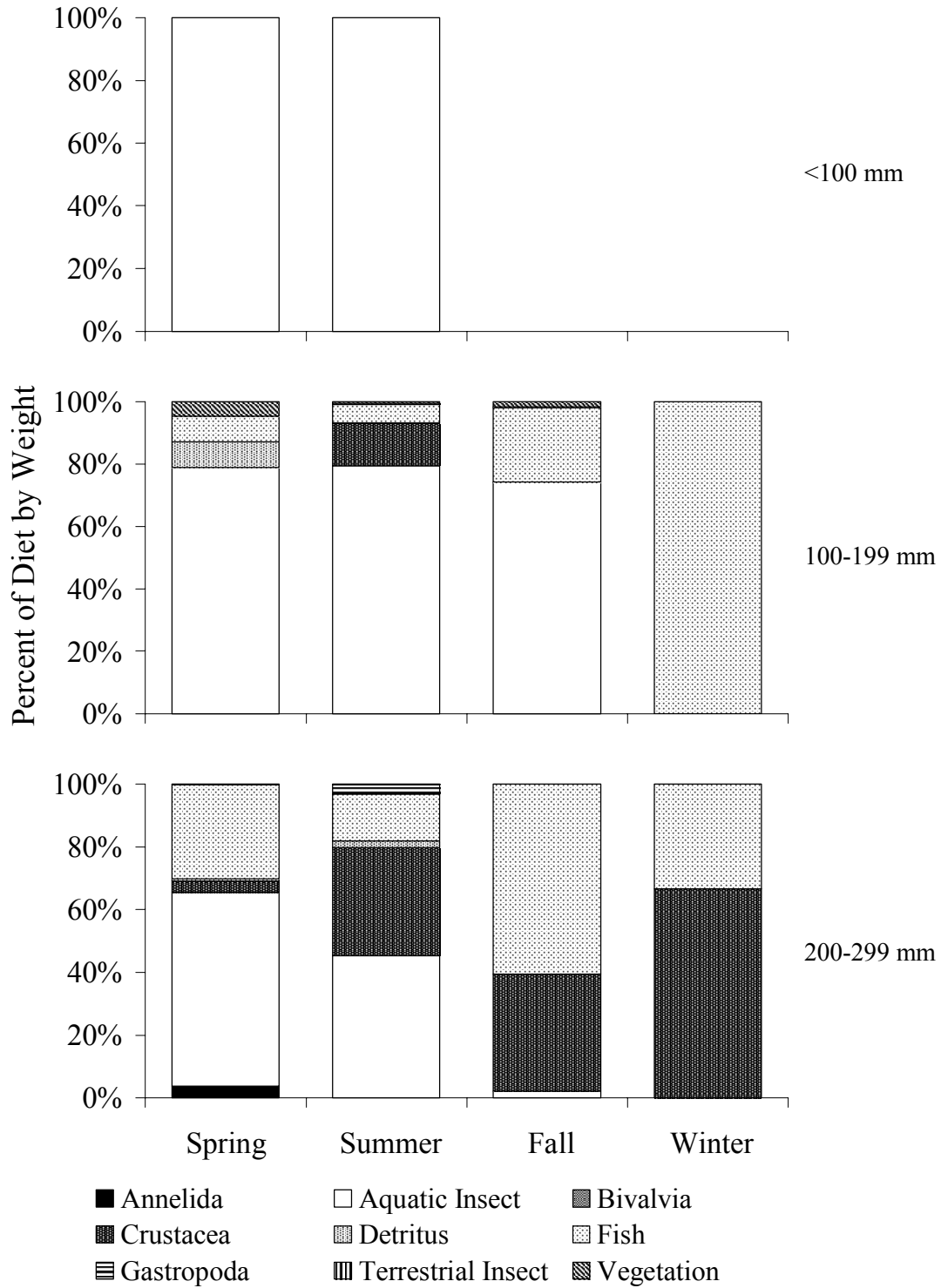


Figure 1.10. Diet composition of *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia.

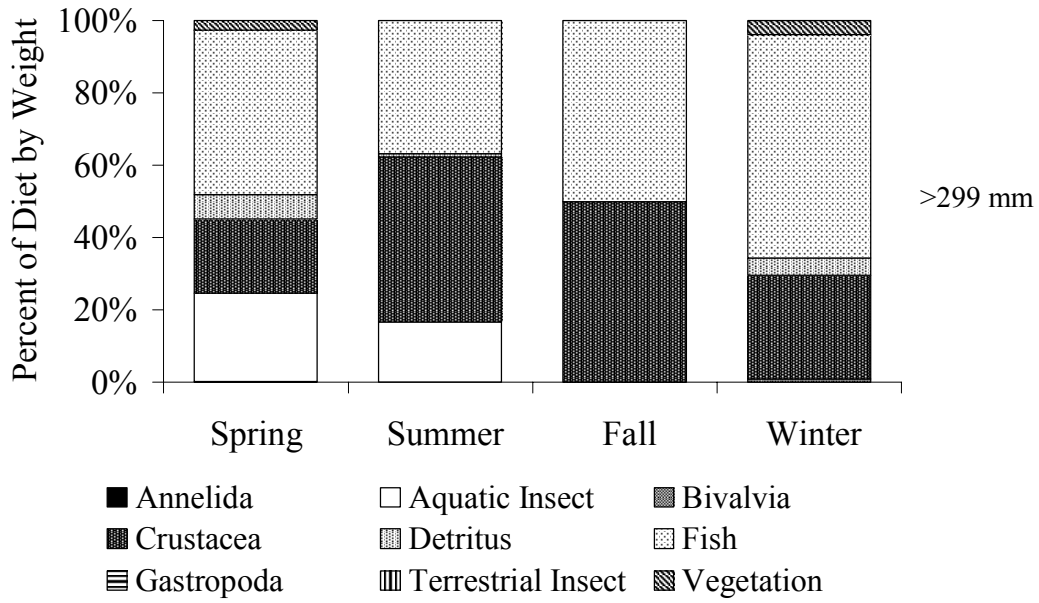


Figure 1.10. (continued) Diet composition of *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia.

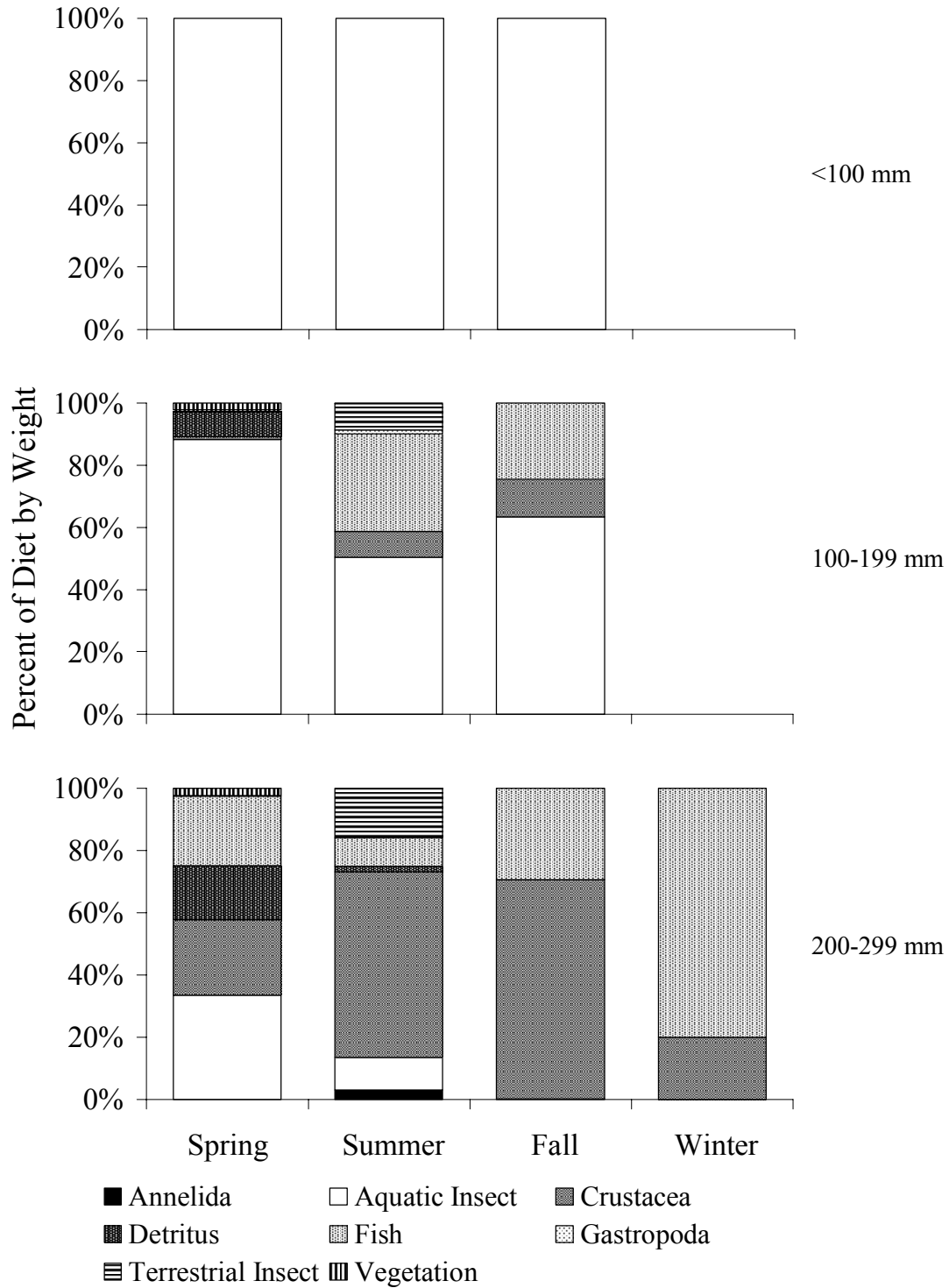


Figure 1.11. Diet composition of *Micropterus dolomieu* in the North River, Virginia.

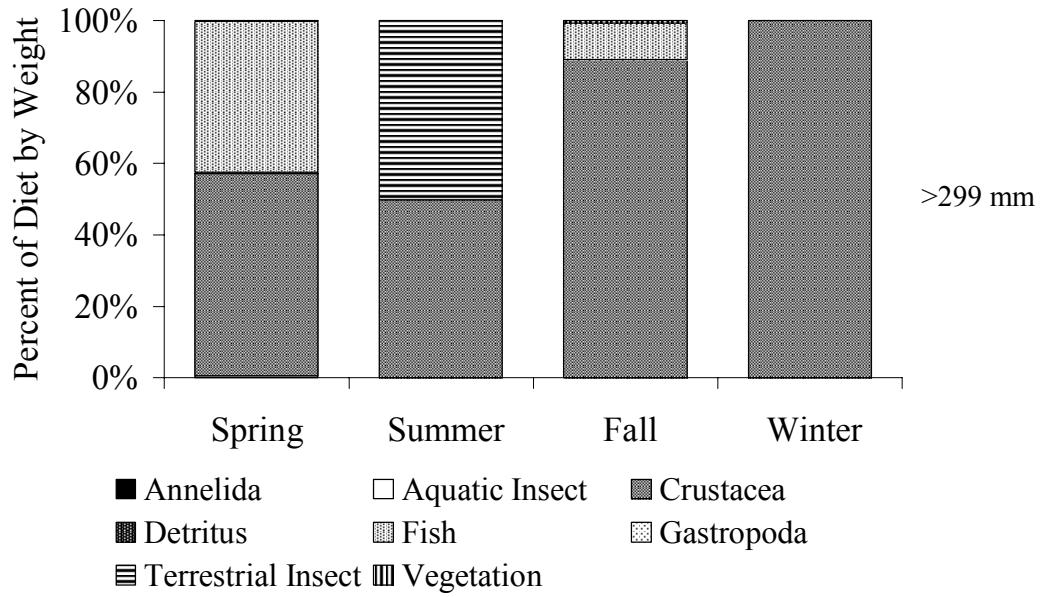


Figure 1.11. (continued) Diet composition of *Micropterus dolomieu* in the North River, Virginia.

Table 1.4. *Lepomis auritus* diet overlap between length classes (mm) in the Shenandoah River basin, Virginia. Biologically significant values are highlighted.

Season	<100*100-150	<100*>150	100-150*>150
<u>SOUTH RIVER</u>			
Spring	0.63	0.52	0.64
Summer	0.58	0.37	0.47
Fall	0.54	0.48	0.51
Winter	-	-	0.50
<u>SOUTH FORK SHENANDOAH RIVER</u>			
Spring	0.22	0.44	0.70
Summer	0.67	0.46	0.57
Fall	0.83	0.52	0.57
Winter	1.00	-	-
<u>NORTH RIVER</u>			
Spring	-	-	0.66
Summer	0.82	0.55	0.61
Fall	0.58	0.31	0.45
Winter	-	-	-

Table 1.5. *Micropterus dolomieu* diet overlap between length classes (mm) in the Shenandoah River basin, Virginia. Biologically significant values are highlighted.

Season	<100*100-199	<100*200-299	<100*>299	100-199*200-299	100-199*>299	200-299*>299
<u>SOUTH RIVER</u>						
Spring	0.13	0.10	0.20	0.61	0.25	0.49
Summer	0.39	0.03	0.02	0.39	0.41	0.48
Fall	0.51	0.08	0.03	0.12	0.10	0.52
Winter	-	-	0.00	-	-	-
<u>SOUTH FORK SHENANDOAH RIVER</u>						
Spring	0.24	0.31	0.18	0.46	0.42	0.53
Summer	0.71	0.32	0.00	0.59	0.26	0.51
Fall	-	-	-	0.26	0.16	0.84
Winter	-	-	-	0.33	0.57	0.62
<u>NORTH RIVER</u>						
Spring	0.15	0.05	0.00	0.37	0.01	0.40
Summer	0.44	0.00	0.00	0.25	0.16	0.66
Fall	0.50	0.00	0.00	0.37	0.15	0.74
Winter	-	-	-	-	-	0.20

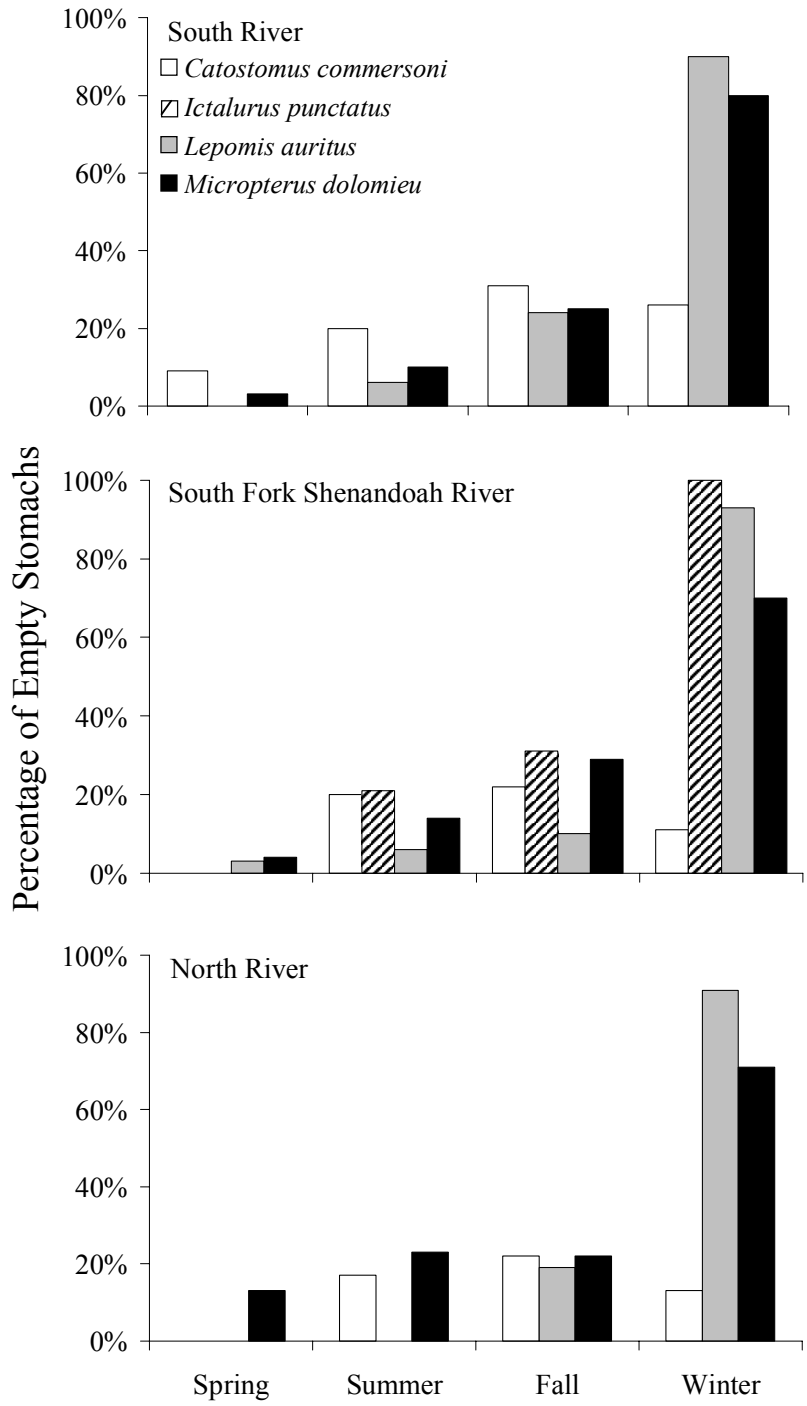


Figure 1.12. Percentage of empty fish stomachs collected in the Shenandoah River basin, Virginia.

Table 1.6. *Catostomus commersoni* diet overlap between seasons in the Shenandoah River basin, Virginia. Biologically significant values are highlighted.

River	Spring*Summer	Spring*Fall	Spring*Winter	Summer*Fall	Summer*Winter	Fall*Winter
South River	0.87	0.82	0.78	0.81	0.87	0.73
S. F. Shenandoah River	0.86	0.85	0.67	0.78	0.65	0.58
North River	0.86	0.86	0.80	0.76	0.75	0.85

Table 1.7. *Lepomis auritus* diet overlap between seasons in the Shenandoah River basin, Virginia. Biologically significant values are highlighted.

Length class (mm)	Spring*Summer	Spring*Fall	Spring*Winter	Summer*Fall	Summer*Winter	Fall*Winter
<100	0.50	0.47	-	0.75	-	-
100-150	0.50	0.69	0.15	0.50	0.06	0.04
>150	0.44	0.58	0.05	0.52	0.00	0.00
<u>SOUTH FORK SHENANDOAH RIVER</u>						
<100	0.51	0.31	0.00	0.68	0.01	0.13
100-150	0.45	0.69	0.09	0.52	0.00	0.03
>150	0.52	0.60	-	0.54	-	-
<u>NORTH RIVER</u>						
<100	-	-	-	0.80	-	-
100-150	0.65	0.53	-	0.65	-	-
>150	0.49	0.41	0.03	0.19	0.00	0.14

Table 1.8. *Micropterus dolomieu* diet overlap between seasons in the Shenandoah River basin, Virginia. Biologically significant values are highlighted.

Length class (mm)	Spring*Summer	Spring*Fall	Spring*Winter	Summer*Fall	Summer*Winter	Fall*Winter
<u>SOUTH RIVER</u>						
<100	0.25	0.11	0.02	0.75	0.02	0.03
100-199	0.22	0.55	-	0.35	-	-
200-299	0.19	0.18	-	0.89	-	-
>299	0.47	0.21	0.26	0.42	0.53	0.00
<u>SOUTH FORK SHENANDOAH RIVER</u>						
<100	0.87	-	-	-	-	-
100-199	0.26	0.31	0.08	0.53	0.00	0.16
200-299	0.48	0.23	0.21	0.46	0.35	0.71
>299	0.38	0.37	0.49	0.66	0.50	0.79
<u>NORTH RIVER</u>						
<100	0.00	0.11	-	0.74	-	-
100-199	0.46	0.51	-	0.82	-	-
200-299	0.32	0.34	0.42	0.64	0.24	0.49
>299	0.50	0.67	0.57	0.50	0.50	0.89

Table 1.9. *Catostomus commersoni* diet overlap between rivers in the Shenandoah River basin Virginia, including the South River (SR), South Fork of the Shenandoah River (SFSR), and North River (NR). Biologically significant values are highlighted.

Season	SR*SFSR	SR*NR	SFSR*NR
Spring	0.86	0.92	0.87
Summer	0.81	0.84	0.86
Fall	0.91	0.75	0.82
Winter	0.65	0.85	0.62

Table 1.10. *Lepomis auritus* diet overlap between rivers in the Shenandoah River basin, Virginia, including the South River (SR), South Fork of the Shenandoah River (SFSR), and North River (NR). Biologically significant values are highlighted.

Season	SR*SFSR	SR*NR	SFSR*NR
<u>≤100 mm</u>			
Spring	0.48	-	-
Summer	0.59	0.67	0.82
Fall	0.82	0.82	0.78
Winter	-	-	-
<u>100-150 mm</u>			
Spring	0.52	0.70	0.46
Summer	0.62	0.70	0.75
Fall	0.67	0.57	0.54
Winter	0.50	-	-
<u>>150 mm</u>			
Spring	0.65	0.69	0.78
Summer	0.49	0.79	0.64
Fall	0.44	0.33	0.46
Winter	-	0.50	-

Table 1.11. *Micropterus dolomieu* diet overlap between rivers in the Shenandoah River basin, Virginia, including the South River (SR), South Fork of the Shenandoah River (SFSR), and North River (NR). Biologically significant values are highlighted.

Season	SR*SFSR	SR*NR	SFSR*NR
<u>≤100 mm</u>			
Spring	0.13	0.18	0.13
Summer	0.67	0.60	0.84
Fall	-	0.67	-
Winter	-	-	-
<u>100-199 mm</u>			
Spring	0.43	0.35	0.40
Summer	0.46	0.34	0.55
Fall	0.43	0.50	0.67
Winter	-	-	-
<u>200-299 mm</u>			
Spring	0.28	0.43	0.47
Summer	0.38	0.73	0.49
Fall	0.42	0.73	0.67
Winter	-	-	0.53
<u>>299 mm</u>			
Spring	0.38	0.32	0.53
Summer	0.58	0.47	0.46
Fall	1.00	0.53	0.53
Winter	0.00	0.00	0.29

Table 1.12. Interspecific diet overlap between *Micropterus dolomieu* <100, 100-199, 200-299, and >299 mm (S1-S4), *Lepomis auritus* <100, 100-150, and >150 mm (R1-R3), and *Catostomus commersoni* (W) in the South River, Virginia. Biologically significant values are highlighted.

Season	S1	S1	S1	S2	S2	S2	S2	S3	S3	S3	S3	S4	S4	S4	S4	R1	R2	R3	
	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
Spring	0.51	0.33	0.15	0.15	0.24	0.49	0.47	0.37	0.13	0.35	0.35	0.33	0.18	0.29	0.24	0.24	0.21	0.39	0.35
Summer	0.62	0.51	0.20	0.16	0.31	0.42	0.27	0.08	0.01	0.11	0.19	0.01	0.00	0.10	0.13	0.00	0.38	0.24	0.16
Fall	0.72	0.40	0.52	0.17	0.42	0.30	0.47	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.36	0.27
Winter	-	0.04	0.00	0.50	-	-	-	-	-	-	-	-	-	0.00	0.00	0.00	-	0.06	0.02

Table 1.13. Interspecific diet overlap between *Micropterus dolomieu* <100, 100-199, 200-299, and >299 mm (S1-S4), *Lepomis auritus* <100, 100-150, and >150 mm (R1-R3), *Catostomus commersoni* (W), and *Ictalurus punctatus* (C) in the South Fork of the Shenandoah River, Virginia. Biologically significant values are highlighted.

Season	S1	S1	S1	S1	S2	S2	S2	S2	S2	S3	S3	S3	S3	S3	S3	S3	S4	S4	S4	S4	S4	S4			
	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		
	R1	R2	R3	W	C	R1	R2	R3	W	C	R1	R2	R3	W	C	R1	R2	R3	W	C	R1	R2	R3	W	C
Spring	0.13	0.63	0.48	0.14	0.00	0.40	0.58	0.63	0.37	0.08	0.19	0.42	0.50	0.27	0.17	0.18	0.31	0.33	0.26	0.17					
Summer	0.50	0.43	0.28	0.15	0.03	0.47	0.39	0.40	0.13	0.13	0.37	0.28	0.36	0.06	0.12	0.01	0.00	0.18	0.01	0.22					
Fall	-	-	-	-	-	0.53	0.51	0.32	0.14	0.18	0.02	0.02	0.02	0.00	0.28	0.00	0.00	0.00	0.00	0.28					
Winter	-	-	-	-	-	0.00	0.00	-	0.00	-	0.00	0.00	-	0.00	-	0.00	0.00	-	-	0.10					

Table 1.13. (continued) Interspecific diet overlap between *Micropterus dolomieu* <100, 100-199, 200-299, and >299 mm (S1-S4), *Lepomis auritus* <100, 100-150, and >150 mm (R1-R3), *Catostomus commersoni* (W), and *Ictalurus punctatus* (C) in the South Fork of the Shenandoah River, Virginia. Biologically significant values are highlighted.

Season	R1	R1	R2	R2	R3	R3	W
	*	*	*	*	*	*	*
	W	C	W	C	W	C	C
Spring	0.39	0.00	0.27	0.00	0.38	0.00	0.00
Summer	0.30	0.05	0.27	0.04	0.28	0.30	0.12
Fall	0.27	0.07	0.34	0.07	0.29	0.07	0.01
Winter	0.07	-	0.07	-	-	-	-

Table 1.14. Interspecific diet overlap between *Micropterus dolomieu* <100, 100-199, 200-299, and >299 mm (S1-S4), *Lepomis auritus* <100, 100-150, and >150 mm (R1-R3), and *Catostomus commersoni* (W) in the North River, Virginia.

Season	S1	S1	S1	S1	S2	S2	S2	S2	S2	S3	S3	S3	S3	S3	S4	S4	S4	S4	R1	R2	R3	
	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	R1	R2	R3	W	R1	R2	R3	W	R1	R2	R3	W	R1	R2	R3	W	R1	R2	W	W	W	
Spring	-	0.36	0.44	0.15	-	0.41	0.59	0.30	-	0.33	0.37	0.32	-	0.01	0.03	0.01	-	0.28	0.28	0.28	0.28	0.28
Summer	0.35	0.29	0.16	0.02	0.36	0.39	0.33	0.02	0.01	0.11	0.25	0.03	0.00	0.10	0.31	0.00	0.16	0.16	0.16	0.16	0.16	0.14
Fall	0.56	0.29	0.16	0.17	0.49	0.19	0.18	0.12	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.31	0.31	0.31	0.31	0.24	0.24
Winter	-	-	-	-	-	-	-	-	-	-	0.00	0.00	-	-	0.00	0.00	-	-	-	-	-	0.03

CHAPTER 2: Total Mercury and Methylmercury in Common Prey Items of Selected Fish Species in the Shenandoah River Basin, Virginia

ABSTRACT

Despite the obvious importance of lower trophic levels as critical intermediaries in the movement and biomagnification of mercury from the physical environment to larger fishes, relatively few researchers have thoroughly assessed concentrations of mercury in prey items of larger fishes. Concentrations of total mercury and methylmercury in common prey items of *Catostomus commersoni*, *Ictalurus punctatus*, *Lepomis auritus*, and *Micropterus dolomieu* were assessed during spring, summer, and fall 2002 in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia. Mean concentrations of total mercury in aquatic invertebrates and forage fish in contaminated rivers ranged from 66.7-398.3 and 198.0-594.9 ng/g wet weight, while mean concentrations of total mercury in aquatic invertebrates and forage fish in the reference river were 4.4 and 29.3 ng/g. Mean percentages of methylmercury in crayfish, forage fish, Gastropoda, and terrestrial Coleoptera were 78.0, 97.9, 55.3, and 5.2%, respectively. Mean percentages of methylmercury in aquatic insect larvae were 34.5% in detritivores-grazers (Ephemeroptera) and 75.6% in predators (Anisoptera and Zygoptera). Aquatic and terrestrial invertebrates closely associated with river and floodplain sediments had the highest concentrations of total mercury. Concentrations of total mercury in aquatic insects, crayfish, and forage fish were significantly different among sites ($P < 0.05$) and were consistently higher in the South River, particularly at site SR6. Concentrations of total mercury in prey items were significantly different among prey taxa ($P < 0.05$) and were consistently higher in forage fish. Predacious aquatic invertebrates (e.g., Odonata) normally had higher concentrations of total mercury than herbivorous and detritivorous invertebrates, while juvenile Centrarchidae (*L. auritus* and *M. dolomieu*), juvenile Ictaluridae (*Ameiurus natalis*), and Percidae (*Etheostoma spp.*) had the highest concentrations of total mercury among forage fish. No consistent seasonal patterns were found. Results of this study have established baseline concentrations of total mercury and methylmercury in common prey items of the selected fish species in the Shenandoah River basin, which is critical to mapping the flow of mercury through aquatic food webs and ultimately remediation efforts.

INTRODUCTION

Many researchers have studied accumulation rates and concentrations of mercury in common sport fishes, such as *Micropterus salmoides*, *Perca flavescens*, and *Stizostedion vitreum*, because of the human health risks (Kelso and Frank 1974; Scott 1974; Phillips et al. 1980; Grieb et al. 1990; Lange et al. 1994; Neumann and Ward 1999; Ward and Neumann 1999; Foster et al. 2000). Results of these studies indicate that piscivorous fish species normally accumulate mercury at faster rates than similarly sized omnivorous, planktivorous, or benthivorous species (Phillips et al. 1980; Brouard et al. 1994; Olivero et al. 1998; Neumann and Ward 1999; Mueller and Serdar 2002). Although some direct aqueous uptake of mercury is possible, fish mainly accumulate mercury through dietary pathways (Jernelöv and Lann 1971; Phillips and Buhler 1978; Rodgers and Beamish 1981; Harris and Snodgrass 1993; Hall et al. 1997).

Despite the obvious importance of lower trophic levels as critical intermediaries in the movement and biomagnification of mercury from the physical environment to larger fishes, relatively little is known about concentrations of mercury in prey items of larger fishes, largely because of the costly expenditures involved. Information on concentrations of mercury in lower trophic levels, can be of great utility, particularly for mapping the flow of mercury through aquatic food webs, determining dietary exposures to piscivorous and insectivorous wildlife, monitoring short- and long-term trends, uncovering potential bioindicator species, and identifying local sources of contamination. The objective of this study was to assess concentrations of total mercury and methylmercury in common prey items of *Catostomus commersoni*, *Ictalurus punctatus*, *Lepomis auritus*, and *Micropterus dolomieu* in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia. Tasks of this objective were to:

1. Establish baseline concentrations of total mercury and methylmercury in prey items.
2. Determine the relationship between methylmercury and total mercury in prey items.
3. Identify spatial, trophic, and temporal patterns in concentrations of total mercury in prey items.

MATERIALS AND METHODS

Description of Study Sites

This study was conducted in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia (Figure 2.1). The South River is a fourth-order stream that originates on the western slope of the Blue Ridge Mountains, drains an area of 373 km², and has an average annual

discharge of 7.1 m³/s. The North River is a fifth-order stream that originates in the Allegheny foothills, drains an area of 1140 km², and has an average annual discharge of 10.2 m³/s. The South River and North River converge at Port Republic to form the South Fork of the Shenandoah River. The South Fork of the Shenandoah River is a sixth-order stream that flows for 160 rkm and drains an area of 4,144 km² before joining the North Fork of the Shenandoah River at Front Royal to form the main stem of the Shenandoah River, approximately 290 rkm from the Chesapeake Bay. Because of the high cost of total mercury and methylmercury analyses, prey item sampling was limited to three sites on the South River (SR3, SR4, and SR6), one site on the South Fork of the River (SF5), and one site on the North River (NR2) (Table 2.1).

Data Collection

Food habits of *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the South River, South Fork of the Shenandoah River, and North River documented in this study were used to select target prey items for collection and analysis of total mercury and methylmercury (Chapter 1). Within each river, target prey items were selected based on rank across the diets of all species (Table 2.2). Forage fish were also selected based on field observations and discussion with district fishery biologist of the Virginia Department of Game and Inland Fisheries. Because of inherent variability in the composition and abundance of aquatic invertebrates and forage fish, suitable alternates were collected when target taxa were not found.

Standard operating procedures, which included clean methods, were drafted and followed during each prey sampling event to assure consistent sampling methods among sites and seasons. Sampling equipment in contact with study organisms was thoroughly washed with detergent, rinsed with 5% HNO₃, tap water (3x), and de-ionized water (3x), and sealed (when practical) prior to sampling. Sampling equipment was cleaned between sites. Personnel handling study organisms wore talc-free rubber gloves to eliminate the potential for additional contamination.

Prey items were collected in the South River and South Fork of the Shenandoah River during spring (April 21-May 1), summer (July 6-24), and fall (October 1-6) 2003. Prey items were only collected in North River during spring (April 23-24) to establish background concentrations. During each season, water samples were collected at each study site to document water chemistry as potential explanatory parameters.

Forage fish were collected using backpack electrofishers and seines. Fish were held in clean collection containers filled with ambient river water, measured for total length (mm), rinsed with de-ionized water (3x), separated into three composite samples of ten individuals (when practical), and double sealed in clean polyethylene bags. Composites, rather than individuals,

were analyzed to attain greater resolution in estimating concentrations of mercury at the population level. Two composite samples were designated for analysis of total mercury (and a subset for methylmercury), while the third sample was saved for archival purposes (when practical). Dorsal and pectoral spines of fish (e.g., *Noturus insignis*) were sheared to avoid bag punctures.

Invertebrates were primarily collected by physically disrupting the river substrate upstream from D-frame kick nets and Surber samplers. Invertebrates were also collected by hand picking (e.g., Bivalvia, crayfish, and Gastropoda), sifting river sediment (e.g., Oligochaeta), sweep netting (e.g., adult terrestrial Coleoptera), and using backpack electrofishers (e.g., crayfish). Aquatic invertebrates were held in clean collection containers filled with ambient river water, picked from debris, and identified to the lowest taxonomic level practical (normally family). Identified organisms were held in clean containers filled with de-ionized water until picking was completed. Within each target order of aquatic insect larvae, abundant families were evenly divided by wet weight and combined to form three composite samples. Annelida were also divided by wet weight to form three composite samples. Crayfish and Bivalvia were measured for carapace length and shell width (mm) and separated into three composite samples of ten individuals. Adult terrestrial Coleoptera were separated into three composite samples of just five individuals because of collection difficulties. Two composite samples of each invertebrate taxa were designated for analysis of total mercury (and a subset for methylmercury), while the third sample was saved for archival purposes (when practical).

Prey samples were stored on wet ice until frozen, which was normally within eight hours of collection. Frozen samples were packed in clean coolers with liberal amounts of dry ice, sealed with tape, and shipped overnight with a chain of custody to the analytical laboratory conducting total mercury and methylmercury analyses.

Analytical Analyses

Total mercury and methylmercury analyses were conducted by Frontier Geosciences Inc. in Seattle, Washington. Total mercury analysis cost \$122.50 per sample and methylmercury analysis cost \$220.00 per sample. Study organisms were analyzed whole, including unpurged guts, to represent that which is normally consumed by fish. Samples were homogenized and centrifuged prior to digestion to improve reproducibility during analysis. For analysis of total mercury, approximately 0.1-0.9 grams of sample was digested in a 70:30 HNO₃/H₂SO₄ solution. Aliquots of each digest (100 mL for whole water) were reduced in pre-purged double-distilled water to mercury with SnCl₂, and then the mercury purged onto gold traps as a preconcentration

step. Mercury contained on gold traps was analyzed by thermal desorption into a cold vapor atomic fluorescence detector (CVAFS) using the dual amalgamation technique. For methylmercury analysis, samples were digested in KOH/CH₃OH and determined by aqueous phase ethylation, isothermal GC separation, and CVAFS detection (EPA draft method 1630 modified) (Frontier Geosciences, Inc. unpublished). Methylmercury analysis was conducted for 20% of samples.

Water chemistry analyses were conducted by the Water Quality Laboratory at Virginia Polytechnic Institute and State University. Water samples were analyzed for alkalinity, chloride, cations (Ca⁺, Mg⁺, K⁺, and Na⁺), nitrate-nitrogen (NO₃-N), total phosphate (total-P), sulfate, total suspended solids (TSS), dissolved organic carbon (DOC), and total organic carbon (TOC).

Quality Assurance/Quality Control

Precision (relative % difference) and accuracy (% recovery) of the analytical methods used by Frontier Geosciences, Inc. were assessed through analysis of matrix spikes, matrix spike duplicates, and replicate analysis of 5% of samples. Standard reference materials, including dogfish muscle (DORM-2) and liver tissue (DOLT-2), were also analyzed.

Field sampling methodologies were assessed during spring to determine if the selected fish sampling methods introduced additional contamination to samples. The quality assurance/quality control experiment was conducted using hatchery reared juvenile *Salvelinus fontinalis* obtained from the Montebello Fish Cultural Station of the Virginia Department of Game and Inland Fisheries. Fish obtained from the hatchery were separated into four composite samples of five individuals, sealed in clean polyethylene bags, and frozen until the experiment. Prior to the experiment, fish were partially thawed and measured for total length (mm) while remaining in polyethylene bags to avoid excess handling exposure. Each sample was randomly exposed to a different step of fish sampling activities, including electrofishing exposure, processing exposure, and no exposure. The remaining sample was saved for archival purposes.

Data Analysis

The Kruskal-Wallis nonparametric one-way analysis of variance, which is a generalization of the rank sum test, was used to test whether mean concentrations of total mercury in prey items differed spatially between sites, trophically between taxa, and temporally between seasons. The Kruskal-Wallis test was performed using Statistix® version 1.0. If significant differences were found overall ($\alpha = 0.05$), pairwise comparisons between mean ranks were performed using the comparison of mean ranks procedure, which identifies subsets of similar

(homogeneous) means. Similar to the Bonferroni procedure for the parametric analysis of variance, the comparison of mean ranks procedure controls the experimentalwise error rate and becomes increasingly conservative as the number of means increases. Treatments with sample sizes of less than two were excluded from analyses.

RESULTS

Precision and accuracy of total mercury and methylmercury analyses conducted by Frontier Geosciences, Inc. were within acceptable control limits (Table 2.3). Reported detection limits for total mercury and methylmercury analyses were 0.45 and 1.50 ng/g wet weight, respectively (Frontier Geosciences, Inc. unpublished). There were no differences between concentrations of total mercury in juvenile *S. fontinalis* used for quality assurance/quality control testing during spring (Table 2.4). Therefore, fish sampling methods were deemed appropriate for summer and fall sampling events. Water chemistry was within normal limits during each sampling period (Table 2.5).

Total Mercury in Prey Items

Total mercury analysis was conducted on 254 composite samples of prey items collected in the Shenandoah River basin, which included Annelida (Oligochaeta), eight orders of aquatic insect larvae (Anisoptera, Coleoptera, Diptera, Ephemeroptera, Megaloptera, Plecoptera, Trichoptera, and Zygoptera), Bivalvia (*C. fluminea*), crayfish, filamentous green alga, 13 species of forage fish (juvenile *Ameiurus natalis*, *Cottus bairdi* and *carolinae*, *Cyprinella analostana*, *Etheostoma flabellare* and *olmstedii*, juvenile *L. auritus*, *Luxilus cornutus*, juvenile *M. dolomieu*, *Notropis amoenus* and *hudsonius*, *N. insignis*, and *Rhinichthys cataractae*), Gastropoda (Pleuroceridae), and adult terrestrial Coleoptera (*Cotinis nitida*).

Mean concentrations of total mercury (\pm SE) in aquatic invertebrates and forage fish at sites SR3, SR4, and SR6 on the South River were 105.4 (\pm 19.0) and 213.2 (\pm 25.9) (Table 2.6), 191.2 (\pm 12.2) and 378.2 (\pm 41.3) (Table 2.7), and 398.3 (\pm 65.5) and 594.9 (\pm 45.7) ng/g wet weight (Table 2.8), respectively. Mean concentrations of total mercury (\pm SE) in aquatic invertebrates and forage fish collected at site SF5 on the South Fork of the Shenandoah River were 66.7 (\pm 4.7) and 198.0 (\pm 10.2) ng/g wet weight, respectively (Table 2.9). Mean concentrations of total mercury (\pm SE) in aquatic invertebrates and forage fish collected at site NR2 on the North River were 4.4 (\pm 1.1) and 29.3 (\pm 2.2) ng/g wet weight, respectively (Table 2.10).

Methylmercury in Prey Items

Methylmercury analysis was conducted on 51 composite samples of prey items collected in the Shenandoah River basin, which included three orders of aquatic insect larvae (Anisoptera, Ephemeroptera, and Zygoptera), crayfish, eight species of forage fish (juvenile *A. natalis*, *C. analostana*, *E. flabellare* and *olmstedii*, juvenile *M. dolomieu*, *N. amoenus*, *N. insignis*, and *R. cataractae*), Gastropoda, and adult terrestrial Coleoptera (*C. nitida*). Mean percentages of methylmercury (\pm SE) in crayfish, forage fish, Gastropoda, and adult terrestrial Coleoptera were 78.0% (\pm 5.1%), 97.9% (\pm 1.0%), 55.3% (\pm 5.4%), and 5.2% (\pm 2.3%), respectively (Table 2.11). Mean percentages of methylmercury (\pm SE) in aquatic insect larvae were 34.5% (\pm 5.0%) in detritivores-grazers (Ephemeroptera) and 75.6% (\pm 13.3%) in predators (Anisoptera and Zygoptera).

Spatial, Trophic, and Temporal Patterns of Total Mercury in Prey Items

Concentrations of total mercury in aquatic insects ($P < 0.0001$), crayfish ($P = 0.0003$), and forage fish ($P < 0.0001$) were significantly different between sites in the South River, South Fork of the Shenandoah River, and North River (Table 2.12). Mean concentrations of total mercury in aquatic insects, crayfish, and forage fish were consistently higher in the South River than South Fork of the Shenandoah River and North River, particularly at site SR6 (Figure 2.2). For instance, the mean concentration of total mercury in crayfish at site SR6 on the South River was 254 and 3,175% higher than mean concentrations of total mercury in crayfish in the South Fork of the Shenandoah River and North River, respectively. Although concentrations of total mercury in Bivalvia and Gastropoda were not significantly different between sites, mean concentrations of total mercury were consistently higher in the South River than South Fork of the Shenandoah River and North River and followed the same spatial pattern to that observed for aquatic insects, crayfish, and forage fish.

Concentrations of total mercury were significantly different between groups of prey taxa in the South River at sites SR3 ($P = 0.0001$), SR4 ($P = 0.0001$), and SR6 ($P = 0.0001$), South Fork of the Shenandoah River ($P < 0.0001$), and North River ($P = 0.0056$) (Table 2.13). Mean concentrations of total mercury were consistently higher in forage fish (Figure 2.2). For instance, the mean concentration of total mercury in forage fish at site SR6 on the South River was 72-721% higher than mean concentrations of total mercury in aquatic insects, Bivalvia, crayfish, and Gastropoda. Mean concentrations of total mercury in aquatic insect larvae and crayfish were comparable at all sites, while mean concentrations of total mercury were consistently lowest in Bivalvia and Gastropoda at all sites.

Concentrations of total mercury in aquatic insects were significantly different between taxa in the South River at sites SR3 ($P = 0.0051$) and SR6 ($P = 0.0052$) and South Fork of the Shenandoah River ($P = 0.0057$) (Table 2.14). Mean concentrations of total mercury were normally higher in Diptera, Megaloptera, Odonata, Plecoptera, and Trichoptera than Coleoptera and Ephemeroptera (Figure 2.3). For instance, the mean concentration of total mercury in Odonata at site SR4 on the South River was 86 and 287% higher than mean concentrations of total mercury in Coleoptera and Ephemeroptera.

Concentrations of total mercury in forage fish were significantly different between taxa in the South River at sites SR3 ($P = 0.0066$) and SR4 ($P = 0.0020$) (Table 2.15). Concentrations of total mercury in forage fish in the South River were consistently higher in juvenile Centrarchidae (*L. auritus* and *M. dolomieu*), juvenile Ictaluridae (*A. natalis*), and Percidae (*E. flabellare* and *olmstedii*) than Cottidae (*C. bairdi* and *carolinae*) and Cyprinidae (*C. analostana*, *L. cornutus*, *N. hudsonius*, and *R. cataractae*) (Figure 2.4). For instance, the mean concentration of total mercury in juvenile *L. auritus* collected at site SR3 on the South River was 143 and 169% higher than mean concentrations of total mercury in *C. bairdi* and *L. cornutus*. Despite the patterns observed in the South River, mean concentrations of total mercury in forage fish were similar between taxa in the South Fork the Shenandoah River and North River.

There were no consistent differences in concentrations of total mercury in prey items between seasons in the South River or South Fork of the Shenandoah River (Table 2.16). Concentrations of total mercury in aquatic insects were significantly different between seasons in the South River at site SR4 ($P = 0.0210$).

DISCUSSION

Total Mercury in Prey Items

Concentrations of total mercury in aquatic insect larvae (Bolgiano 1980; Hildebrand et al. 1980; Powell 1983; Hendricks et al. 1989; Becker and Bigham 1995; Snyder and Hendricks 1995; Tremblay et al. 1996b, 1998; Tremblay and Lucotte 1997; Wong et al. 1997; Fischer and Gustin 2002), crayfish (Bolgiano 1980; Hildebrand et al. 1980; Allard and Stokes 1989; Hendricks et al. 1989; Scheuhammer and Graham 1999; Mason et al. 2000; Mueller and Serdar 2002), forage fish (LMS 1982; Weis et al. 1986; Hendricks et al. 1989; Hill et al. 1996; Peterson et al. 1996; Hall et al. 1997; Brazner and DeVita 1998; Frederick et al. 1999; Gorski et al. 1999; Scheuhammer and Graham 1999; Mason et al. 2000), and Gastropoda (Filion 1997; Wong et al. 1997; Désy et al. 2000; Callil and Junk 2001; Liang et al. 2003) collected in the South River and

South Fork of the Shenandoah River were comparable to the results of similar investigations in other mercury contaminated systems. These studies are presented in brief in Table 2.17.

Concentrations of total mercury in aquatic insect larvae, crayfish, and forage fish collected in the South River and South Fork of the Shenandoah River during this study were consistently lower than those reported previously for the South River and South Fork of the Shenandoah River, possibly signifying a decrease in the level of mercury contamination since the 1980s (Bolgiano 1980; LMS 1982; Hendricks et al. 1989; Snyder and Hendricks 1995). These studies are presented in brief in Table 2.17. For instance, concentrations of total mercury in Ephemeroptera (Ephemerellidae, Heptageniidae, and Isonychiidae) collected in the South River during this study ranged from 46-318 ng/g wet weight, while Hendricks et al. (1989) reported that concentrations of total mercury in Ephemeroptera (*Ephoron leukon* and *Isonychia bicolor*) in the South River ranged from 330-1,630 ng/g wet weight. This pattern was consistent for nearly all prey taxa. Caution is advised when comparing historical data, such as that for the South River and South Fork of the Shenandoah River, because of potential differences between analytical techniques and sample composition.

Aquatic Oligochaeta collected in the South River during this study exhibited concentrations of total mercury that were much higher than concentrations reported in other mercury contaminated systems (Wong et al. 1997; Ando et al. 2002). These studies are presented in brief in Table 2.17. Differences were most likely associated with the level of mercury contamination and/or sampling methodologies. Wong et al. (1997) conducted their study in Ranger Lake, Ontario, which has never been directly contaminated with mercury, unlike the South River. Therefore, one would naturally expect concentrations of mercury to be lower in aquatic organisms inhabiting this type of system. Aquatic Oligochaeta feed continuously in a conveyor-belt fashion, ingesting sediment and extracting nutrients from organic matter and bacteria (Thorp and Covich 1991). The gut cavities of aquatic Oligochaeta collected in this study were not purged prior to mercury analysis, unlike the study by Wong et al. (1997). Therefore, it seems reasonable to speculate that the high concentrations of total mercury found in aquatic Oligochaeta during this study were caused by contaminated sediment in the gut cavity rather than mercury accumulated in tissues.

Concentrations of total mercury in *C. fluminea* collected in the South River and South Fork of the Shenandoah River during this study were considerably lower than concentrations reported in previous studies in the South River and South Fork of the Shenandoah River (Graber-Neufeld 2002; Bowles 2003; Benzing 2004). These studies are presented in brief in Table 2.17. Size and age of *C. fluminea* collected in this study and previous studies were similar. For

instance, mean shell widths of *C. fluminea* collected in this study and in the study by Bowles (2003) were 20.8 and 20.6 mm, respectively. Therefore, differences were probably not associated with the size/age of study organisms, but were most likely associated with the types of matrices analyzed. *Corbicula fluminea* were analyzed whole in this study (including shell), while the previous studies only analyzed soft tissues (Graber-Neufeld 2002; Bowles 2003; Benzing 2004). Therefore, it seems reasonable to conjecture that concentrations of total mercury in *C. fluminea* in this study were diluted by the inclusion of calcified shells, which presumably have negligible concentrations of mercury.

Adult *C. nitida* collected from floodplain fields adjacent the South River in this study exhibited extraordinarily high concentrations of total mercury, which contradicts the results of Hayes (1986) who found that mean concentrations of total mercury in adult terrestrial Coleoptera *Popillia japonica* and *Tetraopes tetraophthalmus* collected from low and high level mercury contaminated sites along the floodplain of South River were negligible (<0.2 µg/g wet weight) or nondetectable. Differences were presumably associated with ecological differences between species and/or sample preparation methodologies. Although *P. japonica* and *C. nitida* are in the same taxonomic family (Scarabaeidae), ecological differences inherently exist between the two species. *Cotinis nitida* larvae inhabit shallow sediments (<10 cm) for one year prior to emergence where they feed heavily on organic matter within sediments around the roots of grasses (Brandhorst-Hubbard et al. 2001). Bolgiano (1981) reported that the mean concentration of total mercury in floodplain sediments adjacent the South River was 10.7 µg/g dry weight and ranged from <0.2-34.5 µg/g. Considering the ecology of *C. nitida* larvae and the high concentrations of total mercury in flood plain sediments adjacent the South River, concentrations of total mercury exhibited by adult *C. nitida* in this study seem logical. Although Hayes (1986) reported nondetectable or negligible concentrations of total mercury in adult *P. japonica*, he reported exceptionally high concentrations of total mercury in *P. japonica* larvae, which exceeded 5.5 µg/g wet weight. Even though study organisms were thoroughly rinsed with de-ionized water in both studies, adult *C. nitida* collected in this study were not rinsed with dilute HNO₃, unlike the study by Hayes (1986), which may have allowed fine sediment dust to adhere to the exterior surface study organisms. Thus, accounting for the exceptionally high concentrations of total mercury observed in this study (D. Cocking, South River Science Team, 10/20/2003). Regardless of the differences between sample preparation methodologies, fish consuming adult *C. nitida* in the South River are being exposed to concentrations of total mercury as measured in this study.

Aquatic and terrestrial invertebrates closely associated with river and floodplain sediments in and adjacent the South River exhibited the highest concentrations of total mercury in

this study. Adult *C. nitida* collected from floodplain fields adjacent the South River exhibited the highest concentrations of total mercury among the prey items analyzed (>14.5 µg/g wet weight). This finding indicates that *C. nitida* serve as a critical link between mercury stabilized in floodplain sediments and fish in the South River, particularly larger *L. auritus* (>150 mm), which consume substantial proportions of *C. nitida* during summer (Chapter 1). Aquatic Oligochaeta collected in the South River also had exceptionally high concentrations of total mercury. As discussed previously, high concentrations of total mercury in aquatic Oligochaeta were presumably caused by contaminated sediment in the gut cavity of study organisms rather than mercury accumulated in tissues. Whether mercury bound to sediment particles speculated to be in the gut cavity of aquatic Oligochaeta can be accumulated by fish remains unknown. Sediment dwelling larvae of aquatic insects, including Ephemeroptera (Ephemeridae) and Diptera (blood/red Chironomidae), collected in the South River, which were inadvertently discovered while sifting submerged sediments for aquatic Oligochaeta, also exhibited very high concentrations of total mercury. The mean concentration of total mercury in the larvae of Ephemeridae collected at site SR3 on the South River was 213 ng/g wet weight, which was 276% greater than the mean concentration of total mercury observed in the larvae of Ephemerellidae, Heptageniidae, and Isonychiidae. The concentration of total mercury in the larvae of blood/red Chironomidae collected at site SR4 on the South River was 836 ng/g wet weight, which was 1,047% greater than the concentration of total mercury in the larvae of green Chironomidae. These findings were not reported previously because these taxa were rarely observed in the diets of *C. commersoni*, *L. auritus*, and *M. dolomieu* in the South River and are probably not readily available to fish because of their sediment dwelling behavior. However, fish may feed heavily upon these taxa during their emergence period.

An accurate estimate of background concentrations of mercury in aquatic organisms is needed to determine the level of contamination and to assist in determining assessment and measurement endpoints that are essential for establishing restoration goals (Southworth et al. 1994). Site NR2 on the North River was selected as the reference site in this study because there are no reports of mercury contamination in this system. Therefore, concentrations of mercury present in aquatic organisms inhabiting the North River are almost certainly due to natural processes and/or atmospheric deposition (Porcella 1994). Aquatic invertebrates and forage fish collected in the North River had concentrations of total mercury that were comparable to the results of similar investigations in other uncontaminated systems (Hildebrand et al. 1980; Powell 1983; Southworth et al. 1994; Hill et al. 1996). These studies are presented in brief in Table 2.17. Even with 100% restoration of the South River and South Fork of the Shenandoah River,

concentrations of total mercury in aquatic organisms will probably not decrease below concentrations observed in the North River due to atmospheric deposition.

Methylmercury in Prey Items

Methylmercury composed a substantial percentage of the total mercury in prey items collected in the Shenandoah River basin, particularly in the predacious larvae of aquatic insects, crayfish, and forage fish. The percentage of methylmercury in aquatic insect larvae, (Hildebrand et al. 1980; Becker and Bigham 1995; Tremblay et al. 1996a, 1996b; Tremblay and Lucotte 1997; Tremblay et al. 1998; Mason et al. 2000; Fischer and Gustin 2002), crayfish (Hildebrand et al. 1980; Mason et al. 2000), and Gastropoda collected in the Shenandoah River basin during this study were comparable to the results of similar investigations in other mercury contaminated systems. These studies are presented in brief in Table 2.18. There were no published reports regarding the percentage of methylmercury in terrestrial Coleoptera or any comparable terrestrial insects.

The mean percentage of methylmercury in forage fish collected in the Shenandoah River basin during this study was higher than the mean percentage of methylmercury reported for adult/edible size fish in the Shenandoah River basin (Messing and Winfield 1998; VDEQ 2000, 2003). The most recent estimate indicates that methylmercury accounts for 85.5% of the total mercury in adult/edible size fish (i.e., *C. commersoni*, *H. nigricans*, *I. punctatus*, *L. auritus*, *M. dolomieu* and *salmoides*, and *Oncorhynchus mykiss*) in the Shenandoah River basin (VDEQ 2003). Although the percentage of methylmercury in forage fish was higher than that reported for adult/edible size fish, it was similar to that reported for fish in other mercury contaminated systems, which indicate that methylmercury normally accounts for 90-99% of the total mercury in fish muscle tissue (Hildebrand et al. 1980; Grieb et al. 1990; Bloom 1992). These studies are presented in brief in Table 2.18. Differences between the percentage of methylmercury in forage fish and adults may be associated with ecological differences between species, differences in analytical techniques, and/or sample composition. In this study, samples were composed of multiple whole individuals (including unpurged guts), whereas samples analyzed by VDEQ (2003) are only muscle tissue fillets.

Spatial, Trophic, and Temporal Patterns of Total Mercury in Prey Items

Concentrations of total mercury in prey items collected in this study were consistently higher in the South River than South Fork of the Shenandoah River and North River, particularly at site SR6. Spatial patterns exhibited by prey items in this study were comparable to patterns

typically observed in adult fish (Messing and Winfield 1998; VDEQ 2000, 2001, 2003), sediment (AMRL 1998), and water (VDEQ unpublished) in the basin. Although Hildebrand et al. (1980) found that concentrations of total mercury in fish and benthic invertebrates in the North Fork of the Holston River, Virginia were highest immediately below the mercury source and decreased downriver, concentrations of total mercury in prey items in this study were much higher at site SR6 than sites SR3 and SR4 on the South River, even though sites SR3 and SR4 are closer to the historic mercury source. Site SR6 is 14.8 and 13.2 rkm downriver from sites SR3 and SR4, respectively. Spatial patterns observed in aquatic biota in the South River indicate that there may be ongoing sources of mercury contamination, such as sediment deposits, near site SR6.

Forage fish consistently exhibited higher concentrations of total mercury than aquatic invertebrates in the Shenandoah River basin (with the exception of those invertebrates closely associated river sediments). Considering that dietary pathways account for the majority of mercury uptake by fish (Jernelöv and Lann 1971; Phillips and Buhler 1978; Rodgers and Beamish 1981; Harris and Snodgrass 1993; Hall et al. 1997) and the species of forage fish collected in this study are known to consume aquatic invertebrates (Jenkins and Burkhead 1994), it seems logical to find higher concentrations of total mercury in forage fish than aquatic invertebrates. This finding indicates that piscivorous fish species (e.g., *M. dolomieu*) in the Shenandoah River basin are being exposed to higher concentrations of mercury than omnivorous and benthivorous species.

Although the larvae of predatory aquatic insects, particularly Megaloptera, Odonata, and Plecoptera, typically exhibited the highest concentrations of total mercury among the taxa of aquatic insects collected in this study, high concentrations of total mercury were also observed in Diptera and Trichoptera. Observing high concentrations of total mercury in nonpredacious aquatic insect larvae is not uncommon (Hildebrand et al. 1980; Hendricks et al. 1989; Snyder and Hendricks 1995). Observing high concentrations of total mercury in detritivorous insects may indicate that mercury uptake through detrital pathways is important. Snyder and Hendricks (1995) found a significant relationship between whole-animal concentrations of total mercury and the relative amount of detritus consumed by *Hydropsyche morose* in the South River.

Even though forage fish in the South Fork of the Shenandoah River and North River exhibited comparable concentrations of total mercury among species, concentrations of total mercury in forage fish in the South River were substantially higher in juvenile Centrarchidae (*L. auritus* and *M. dolomieu*), juvenile Ictaluridae (*A. natalis*), and Percidae (*Etheostoma spp.*) than Cottidae (*Cottus spp.*) and Cyprinidae (*C. analostana*, *L. cornutus*, and *N. hudsonius*). Forage fish are limited to similarly sized prey items because of morphological constraints, such as mouth

gape, but dietary differences inherently exist and may be partly responsible for differences of total mercury observed in this study.

Although consistent seasonal patterns were not found in this study, they may exist. This study was designed to track seasonal patterns of mercury in groups of prey items consumed by the selected fish species. Therefore, temporal differences among seasons for specific taxa were difficult to discern in this study due to inherent variability in sample composition.

Conclusions

Results of this study have established baseline concentrations of total mercury and methylmercury in common prey items of *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, which is critical to mapping the flow of mercury through aquatic food webs and ultimately remediation efforts. Concentrations of total mercury in aquatic invertebrates and forage fish in the South River and South Fork of the Shenandoah River reported in this study were consistently lower than those reported historically, possibly signifying a decrease in the level of mercury contamination since the 1980s. Adult *C. nitida* collected from floodplain fields adjacent the South River exhibited the highest concentrations of total mercury among prey items analyzed in this study, which indicates an important pathway of mercury to fish in the South River via floodplain ecosystems. Aquatic and terrestrial invertebrates closely associated with river and floodplain sediments along the South River exhibited the highest concentrations of total mercury in this study, providing evidence that river and floodplain sediments may be important sources of mercury to aquatic biota. Spatial patterns observed for prey items in the South River indicate that concentrations of mercury in prey items were highest at site SR6, suggesting that there may be mercury “hot spots”, such a sediment deposits, near this site. Given that mercury is mainly accumulated through dietary pathways, trophic related patterns observed in this study were presumably related to differences in food habits between prey taxa. Even with 100% restoration of the South River and South Fork of the Shenandoah River, concentrations of total mercury in aquatic organisms will probably not decrease below concentrations observed in the North River due to atmospheric deposition.

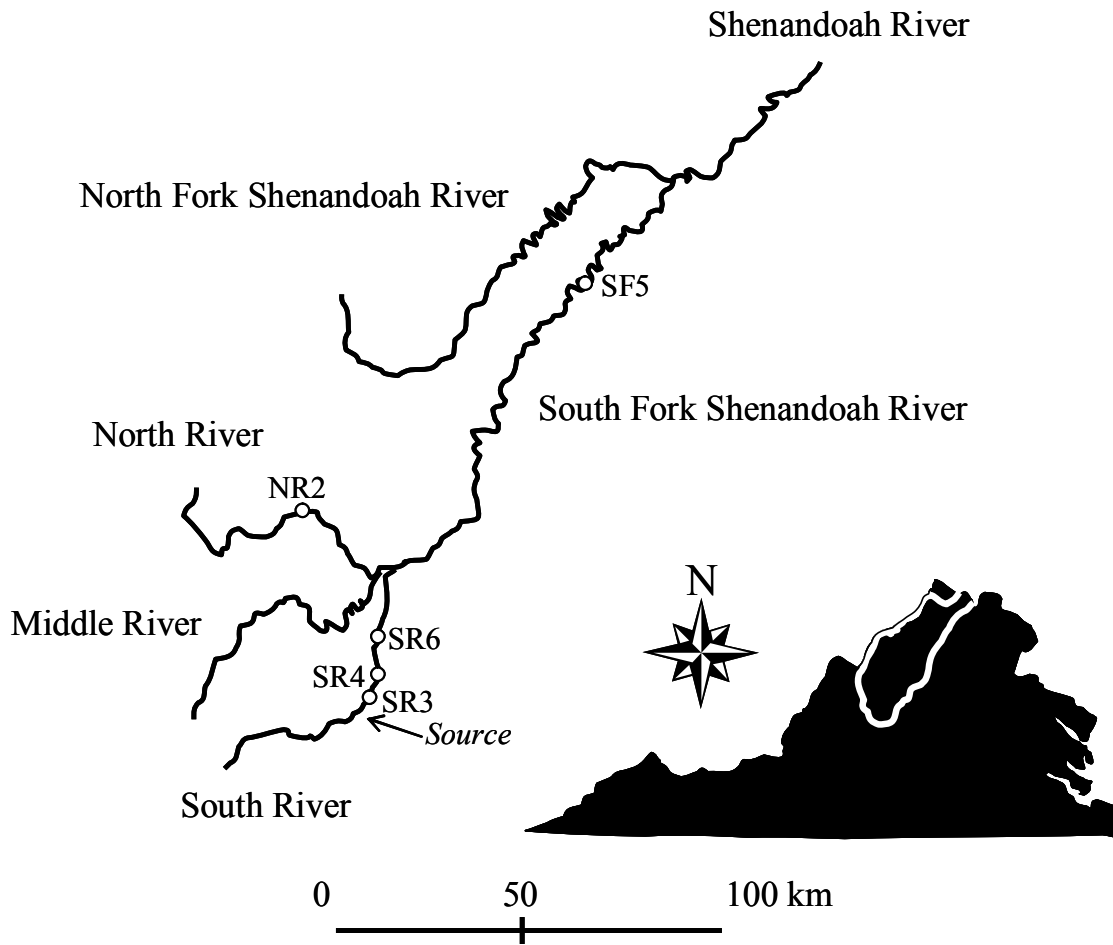


Figure 2.1. Study area and sites in the Shenandoah River basin, Virginia used to collect prey items for analysis of total mercury and methylmercury.

Table 2.1. Description of study sites in the Shenandoah River basin, Virginia used to collect prey items for analysis of total mercury and methylmercury, including distance downriver from the historic source of mercury.

Site	Distance (rkm)	Latitude	Longitude	Site Description
<u>SOUTH RIVER</u>				
SR3	2.1	N38°04'40"	W78°52'45"	Waynesboro-North Park
SR4	3.7	N38°05'25"	W78°52'35"	Waynesboro-Hopeman Parkway
SR6	16.9	N38°09'30"	W78°51'10"	Crimora-Department of Forestry
<u>SOUTH FORK SHENANDOAH RIVER</u>				
SF5	149.7	N38°47'15"	W78°23'20"	Fosters-boat launch
<u>NORTH RIVER</u>				
NR2	*	N38°20'40"	W78°55'00"	Burketown-USGS gage station

*Reference site, not located downriver from the historic source of mercury.

Table 2.2. Target prey items in the Shenandoah River basin, Virginia sought for analysis of total mercury and methylmercury.

South River	South Fork Shenandoah River	North River
	<u>AQUATIC INSECTS</u>	
Coleoptera	Diptera	Coleoptera
Diptera	Ephemeroptera	Diptera
Ephemeroptera	Megaloptera	Ephemeroptera
Odonata	Odonata	Odonata
Trichoptera	Plecoptera	Trichoptera
-	Trichoptera	-
	<u>TERRESTRIAL INSECTS</u>	
<i>Cotinis nitida</i>	-	-
	<u>CRUSTACEA</u>	
Crayfish	Crayfish	Crayfish
	<u>ANNELIDA</u>	
Oligochaeta	-	-
	<u>MOLLUSCA</u>	
Gastropoda	Gastropoda	Gastropoda
<i>Corbicula fluminea</i>	<i>Corbicula fluminea</i>	<i>Corbicula fluminea</i>
	<u>FORAGE FISH</u>	
<i>Etheostoma flabellare</i>	<i>Cyprinella analostana</i>	<i>Lepomis auritus</i> *
<i>Lepomis auritus</i> *	<i>Lepomis auritus</i> *	<i>Notropis amoenus</i>
<i>Luxilus cornutus</i>	<i>Noturus insignis</i>	<i>Noturus insignis</i>
<i>Noturus insignis</i>	-	-
	<u>VEGETATION</u>	
-	Filamentous green alga	-

* Juvenile fish.

Table 2.3. Precision (relative % difference) and accuracy (% recovery) of the analytical methods used by Frontier Geosciences, Inc. for analysis of total mercury and methylmercury in prey items collected in the Shenandoah River basin, Virginia.

Analytical Analysis	<i>N</i>	Mean	±SE	Control Limit
<u>TOTAL MERCURY</u>				
Replicate	26	8.2%	1.1%	<25%
Matrix spike duplicate	24	4.5%	1.3%	<25%
Standard reference material	21	98.3%	2.0%	75-125%
Matrix spike	50	98.4%	1.2%	75-125%
<u>METHYLMERCERY</u>				
Replicate	6	15.6%	4.7%	<25%
Matrix spike duplicate	5	6.1%	2.0%	<25%
Standard reference material	5	91.9%	5.0%	75-125%
Matrix spike	10	103.9%	2.5%	75-125%

Table 2.4. Concentrations of total mercury (THg) among exposure groups of hatchery reared juvenile *Salvelinus fontinalis* used for quality assurance/quality control testing during fish collections in the Shenandoah River basin, Virginia, where TL = mean total length.

Exposure Group	<i>N</i>	TL (mm)	±SE	THg (ng/g wet weight)
Electrofishing exposure group	1	106.2	2.2	7.15
Processing exposure group	1	104.0	2.8	7.08
No exposure group	1	111.4	2.0	7.53

Table 2.5. Water chemistry (mg/L) in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia during prey sampling events for total mercury and methylmercury analyses.

Site	Alkalinity	Chloride	NO ₃ -N	Total-P	Sulfate	TSS	Ca ⁺	Mg ⁺	K ⁺	Na ⁺	DOC	TOC
					<u>SPRING</u>							
SR3	82	13	1.2	0.29	9.000	0	22.70	8.51	1.75	5.13	1.36	10.60
SR4	82	26	1.5	0.61	9.665	0	23.90	9.00	1.92	10.61	1.58	11.00
SR6	88	20	1.1	0.51	10.030	7	24.60	9.29	1.91	7.36	1.69	11.80
SF5	116	16	1.3	0.76	14.074	4	36.30	11.50	2.19	6.79	1.61	10.20
NR2	48	13	1.4	0.48	10.453	0	15.50	5.19	1.77	4.42	1.82	5.41
					<u>SUMMER</u>							
SR3	120	32	1.1	0.26	9.249	0	27.20	9.83	2.00	9.60	1.18	10.80
SR4	120	20	1.4	0.41	9.815	0	26.80	9.63	2.16	6.31	1.37	10.10
SR6	120	20	1.1	0.31	9.749	0	28.70	10.50	2.19	6.34	1.48	12.40
SF5	132	22	1.1	0.31	13.630	6	44.50	13.8	2.13	7.89	1.14	8.88
					<u>FALL</u>							
SR3	108	18	1.3	0.48	8.910	0	26.10	7.96	2.07	5.25	1.36	10.70
SR4	110	32	1.8	0.67	9.698	0	28.20	8.62	2.26	10.49	1.54	9.82
SR6	118	19	1.4	0.48	10.294	0	30.00	9.29	2.53	5.78	1.84	13.90
SF5	172	22	1.9	0.77	4.933	0	20.50	5.71	1.34	3.00	1.36	14.40

Table 2.6. Concentrations of total mercury in prey items collected at site SR3 on the South River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	$\pm SE$	THg (ng/g)	$\pm SE$
<u>SPRING</u>						
Aquatic Insect		8	-	-	66.8	10.1
Anisoptera	Aeshnidae	1	-	-	135.0	-
Coleoptera	Psephenidae	2	-	-	66.2	0.7
Diptera	Chironomidae	1	-	-	60.0	-
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae	2	-	-	47.1	0.6
Trichoptera	Hydropsychidae	2	-	-	56.3	2.5
Crustacea						
Decapoda	Crayfish	2	55.0	1.8	121.0	5.0
Fish		6	66.9	4.8	180.9	33.4
Centrarchidae	<i>Lepomis auritus</i>	2	55.6	1.8	165.0	14.0
Cyprinidae	<i>Luxilus cornutus</i>	2	81.5	0.9	108.2	8.8
Percidae	<i>Etheostoma flabellare</i>	2	63.8	2.0	269.5	55.5
<u>SUMMER</u>						
Annelida						
Oligochaeta	Oligochaeta	1	-	-	647.0	-
Aquatic Insect		6	-	-	109.5	28.6
Anisoptera	Gomphidae	1	-	-	238.0	-
Coleoptera	Psephenidae	1	-	-	35.1	-
Ephemeroptera	Heptageniidae	1	-	-	67.3	-
Trichoptera	Hydropsychidae	2	-	-	97.3	11.7
Zygoptera	Coenagrionidae	1	-	-	122.0	-
Crustacea						
Decapoda	Crayfish	2	71.4	0.9	115.5	15.5
Fish		6	66.2	4.3	220.5	38.8
Centrarchidae	<i>Lepomis auritus</i>	2	58.3	0.6	297.5	0.5
Cyprinidae	<i>Luxilus cornutus</i>	2	79.8	2.5	105.5	3.5
Percidae	<i>Etheostoma flabellare</i>	2	60.5	0.7	258.5	44.5

Table 2.6. (continued) Concentrations of total mercury in prey items collected at site SR3 on the South River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	\pm SE	THg (ng/g)	\pm SE
Mollusca						
Bivalvia	<i>Corbicula fluminea</i>	2	21.0	0.0	16.8	4.7
Gastropoda	Pleuroceridae	2	-	-	30.0	6.6
	<u>FALL</u>					
Aquatic Insect		8	-	-	124.5	24.0
Anisoptera	Aeshmidae, Gomphidae, Macromiidae	3	-	-	175.0	34.2
Coleoptera	Psephenidae	2	-	-	46.8	1.1
Ephemeroptera	Isonychiidae	1	-	-	65.1	-
Trichoptera	Hydropsychidae	2	-	-	156.0	5.0
Crustacea						
Decapoda	Crayfish	2	54.7	5.6	64.6	5.8
Fish		5	74.2	5.5	279.6	72.0
Centrarchidae	<i>Lepomis auritus</i>	2	74.1	3.5	432.5	82.5
Cyprinidae	<i>Luxilus cornutus</i>	1	96.0	-	126.0	-
Percidae	<i>Etheostoma flabellare</i>	2	63.6	4.0	203.5	64.5
	<u>WINTER</u>					
Aquatic Insect						
Trichoptera	Hydropsychidae	1	-	-	53.6	-
Fish						
Cottidae	<i>Cottus bairdi</i>	2	70.2	4.4	122.6	27.4

Table 2.7. Concentrations of total mercury in prey items collected at site SR4 on the South River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	±SE	THg (ng/g)	±SE
<u>SPRING</u>						
Aquatic Insect		8	-	-	105.4	10.6
Anisoptera	Gomphidae	1	-	-	169.0	-
Diptera	Chironomidae, Tipulidae	2	-	-	94.5	21.6
Ephemeroptera	Heptageniidae	2	-	-	98.7	9.3
Trichoptera	Hydropsychidae	2	-	-	86.0	0.5
Zygotera	Coenagrionidae	1	-	-	116.0	-
Crustacea						
Decapoda	Crayfish	2	58.4	2.2	176.0	5.0
Fish		6	61.8	2.6	371.5	54.6
Centrarchidae	<i>Lepomis auritus</i>	2	56.4	0.6	487.0	14.0
Cyprinidae	<i>Luxilus cornutus</i>	2	69.9	1.1	206.5	34.5
Percidae	<i>Etheostoma flabellare</i>	1	58.1	-	403.0	-
Percidae	<i>Etheostoma olmstedti</i>	1	59.9	-	439.0	-
<u>SUMMER</u>						
Aquatic Insect		4	-	-	244.5	58.35
Anisoptera	Gomphidae	1	-	-	411.0	-
Diptera	Tipulidae	1	-	-	138.0	-
Trichoptera	Hydropsychidae	2	-	-	214.5	3.5
Annelida						
Oligochaeta	Oligochaeta	2	-	-	585.0	86.0
Crustacea						
Decapoda	Crayfish	2	69.6	0.3	225.0	26.0
Fish		9	75.7	4.5	347.7	75.7
Centrarchidae	<i>Lepomis auritus</i>	2	67.1	0.5	431.5	45.5
Cottidae	<i>Cottus caroliniae</i>	1	70.0	-	133.0	-
Cyprinidae	<i>Luxilus cornutus</i>	2	92.9	0.1	209.5	5.5
Percidae	<i>Etheostoma flabellare</i>	2	60.2	2.2	346.0	12.0
Ictaluridae	<i>Ameiurus natalis</i>	1	90.1	-	869.0	-

Table 2.7. (continued) Concentrations of total mercury in prey items collected at SR4 on the South River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	\pm SE	THg (ng/g)	\pm SE
Ictaluridae	<i>Noturus insignis</i>	1	81.0	-	153.0	-
Mollusca						
Bivalvia	<i>Corbicula fluminea</i>	2	20.3	0.4	38.7	0.0
Gastropoda	Pleuroceridae	2	-	-	65.8	10.2
Terrestrial Insect						
Coleoptera	<i>Cotinis nitida</i>	2	-	-	11,957.0	2,623.0
	<u>FALL</u>					
Aquatic Insect						
Anisoptera	Aeshnidae, Gomphidae, Macromiidae	8	-	-	223.4	54.7
Coleoptera	Psephenidae	2	-	-	216.5	10.6
Diptera	Tipulidae	1	-	-	58.4	-
Ephemeroptera	Isonychiidae, Leptohyphidae	1	-	-	577.0	-
Trichoptera	Hydropsychidae	2	-	-	144.5	37.5
Crustacea						
Decapoda	Crayfish	2	48.1	2.1	164.0	30.0
Fish						
Centrarchidae	<i>Lepomis auritus</i>	4	73.4	8.0	457.0	62.8
Cyprinidae	<i>Notropis hudsonius</i>	2	72.0	1.5	565.0	2.0
Percidae	<i>Etheostoma olmstedi</i>	1	94.3	-	331.0	-
		1	55.3	-	367.0	-

Table 2.8. Concentrations of total mercury in prey items collected at site SR6 on the South River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	\pm SE	THg (ng/g)	\pm SE
<u>SPRING</u>						
Aquatic Insect		9	-	-	249.2	40.0
Anisoptera	Gomphidae, Macromiidae	1	-	-	426.0	-
Coleoptera	Psephenidae	2	-	-	149.0	2.0
Diptera	Chironomidae	1	-	-	91.2	-
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae	2	-	-	226.5	57.5
Trichoptera	Hydropsychidae	2	-	-	278.0	21.0
Zygoptera	Coenagrionidae	1	-	-	419.0	-
Crustacea						
Decapoda	Crayfish	2	53.8	1.3	379.5	2.5
Fish		6	75.5	4.6	595.7	92.4
Centrarchidae	<i>Lepomis auritus</i>	2	63.0	2.1	848.0	19.0
Centrarchidae	<i>Micropterus dolomieu</i>	1	92.7	-	679.0	-
Cyprinidae	<i>Luxilus cornutus</i>	2	78.2	2.6	368.0	12.0
Cyprinidae	<i>Rhinichthys cataractae</i>	1	78.1	-	463.0	-
<u>SUMMER</u>						
Aquatic Insect		9	-	-	385.7	63.3
Anisoptera	Gomphidae	2	-	-	477.0	23.0
Coleoptera	Psephenidae	2	-	-	137.0	10.0
Diptera	Tipulidae	1	-	-	463.0	-
Trichoptera	Hydropsychidae	2	-	-	618.5	40.5
Zygoptera	Coenagrionidae	2	-	-	271.5	42.5
Annelida						
Oligochaeta	Oligochaeta	2	-	-	1,961.0	135.0
Crustacea						
Decapoda	Crayfish	2	63.6	1.8	266.5	16.5

Table 2.8. (continued) Concentrations of total mercury in prey items collected at site SR6 on the South River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	±SE	THg (ng/g)	±SE
Fish	<i>Lepomis auritus</i>	6	82.6	5.6	588.2	79.6
	<i>Micropterus dolomieu</i>	2	65.2	2.9	704.0	7.0
	<i>Luxilus cornutus</i>	1	95.7	-	792.0	-
	<i>Ameiurus natalis</i>	2	88.5	1.7	352.0	66.0
Mollusca		1	92.2	-	625.0	-
	Bivalvia	2	21.5	0.3	100.3	23.7
	Gastropoda	2	-	-	72.4	0.6
Terrestrial Insect		2	-	-	1,773.0	30.0
	Coleoptera					
			<u>FALL</u>			
Aquatic Insect		10	-	-	396.4	90.0
Crustacea	Anisoptera	2	-	-	400.0	49.0
	Coleoptera	2	-	-	100.0	5.0
	Diptera	1	-	-	1,080.0	-
	Ephemeroptera	2	-	-	272.0	46.0
	Trichoptera	2	-	-	527.5	20.5
	Zygoptera	1	-	-	285.0	-
Fish	Crayfish	2	56.7	1.0	346.5	11.5
		4	82.8	10.1	604.0	66.9
	<i>Lepomis auritus</i>	2	68.4	0.3	710.5	39.5
	<i>Micropterus dolomieu</i>	1	111.5	-	549.0	-
Cyprinidae	<i>Cyprinella analostana</i>	1	82.9	-	446.0	-

Table 2.9. Concentrations of total mercury in prey items collected at site SF5 on the South Fork of the Shenandoah River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	\pm SE	THg (ng/g)	\pm SE
<u>SPRING</u>						
Aquatic Insect		7	-	-	55.2	7.5
Diptera	Chironomidae	1	-	-	23.7	-
Ephemeroptera	Ephemereilidae, Heptageniidae, Isonychiidae	2	-	-	45.2	9.7
Trichoptera	Brachycentridae, Hydropsychidae	2	-	-	60.5	2.0
Zygoptera	Coenagrionidae	2	-	-	75.7	6.6
Crustacea						
Decapoda	Crayfish	2	72.3	2.4	104.0	0.0
Fish		7	96.8	11.6	214.1	19.3
Centrarchidae	<i>Lepomis auritus</i>	2	86.7	0.7	222.0	9.0
Cyprinidae	<i>Cyprinella analostana</i>	2	74.7	0.0	206.0	25.0
Ictaluridae	<i>Noturus insignis</i>	3	118.2	22.7	214.3	48.4
<u>SUMMER</u>						
Aquatic Insect		8	-	-	59.6	5.8
Ephemeroptera	Heptageniidae, Isonychiidae	2	-	-	43.0	1.5
Megaloptera	Corydalidae	2	-	-	79.7	2.0
Trichoptera	Hydropsychidae	2	-	-	52.4	0.9
Zygoptera	Coenagrionidae	2	-	-	63.5	14.4
Crustacea						
Decapoda	Crayfish	2	72.4	2.1	84.4	5.7
Fish		8	95.2	8.8	209.3	11.4
Centrarchidae	<i>Lepomis auritus</i>	2	85.2	0.4	238.5	11.5
Centrarchidae	<i>Micropterus dolomieu</i>	1	112.2	-	213.0	-
Cyprinidae	<i>Cyprinella analostana</i>	2	77.0	19.5	178.5	16.5
Ictaluridae	<i>Ameiurus natalis</i>	1	85.6	-	203.0	-
Ictaluridae	<i>Noturus insignis</i>	2	119.6	24.4	212.0	38.0

Table 2.9. (continued) Concentrations of total mercury in prey items collected at site SF5 on the South Fork of the Shenandoah River, Virginia, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	\pm SE	THg (ng/g)	\pm SE
Mollusca						
Bivalvia	<i>Corbicula fluminea</i>	2	18.4	0.3	23.2	0.9
Gastropoda	Pleuroceridae	2	-	-	23.8	0.9
Other						
Algae	Chlorophyta	2	-	-	4.4	0.8
Aquatic Insect						
Anisoptera		11	-	-	82.9	7.9
Ephemeroptera	Gomphidae, Macromiidae	1	-	-	105.0	-
Megaloptera	Heptageniidae, Isonychidae	3	-	-	52.1	1.4
Plecoptera	Corydalidae	2	-	-	112.7	15.2
Trichoptera	Perlidae	1	-	-	109.0	-
Zygoptera	Hydropsychidae	2	-	-	90.5	0.8
Crustacea	Coenagrionidae	2	-	-	67.9	3.8
Decapoda	Crayfish	1	72.0	-	90.5	-
Fish						
Centrarchidae	<i>Lepomis auritus</i>	5	89.0	12.9	157.3	16.7
Centrarchidae	<i>Micropterus dolomieu</i>	2	78.4	2.5	169.5	11.5
Cyprinidae	<i>Cyprinella analostana</i>	1	79.6	-	92.6	-
Ictaluridae	<i>Noturus insignis</i>	1	68.6	-	173.0	-
		1	139.9	-	182.0	-

Table 2.10. Concentrations of total mercury in prey items collected at site NR2 on the North River, Virginia in spring, where N = number of composite samples, TL = mean total length, and THg = mean concentration of total mercury wet weight.

Prey Type	Taxa Analyzed	N	TL (mm)	\pm SE	THg (ng/g)	\pm SE
Aquatic Insect		8	-	-	9.5	1.6
Anisoptera	Gomphidae	1	-	-	18.8	-
Diptera	Chironomidae, Tipulidae	2	-	-	4.8	0.0
Ephemeroptera	Ephemeralidae, Heptageniidae, Isonychiidae	2	-	-	7.1	0.2
Trichoptera	Hydropsychidae	2	-	-	10.7	0.6
Zygoptera	Coenagrionidae	1	-	-	11.7	-
Crustacea						
Decapoda	Crayfish	2	55.3	1.5	10.1	0.1
Forage Fish		6	67.9	2.2	29.3	2.2
Centrarchidae	<i>Lepomis auritus</i>	2	62.8	1.5	30.4	2.3
Cyprinidae	<i>Cyprinella analostana</i>	1	71.3	-	30.1	-
Cyprinidae	<i>Notropis amoenus</i>	1	67.3	-	36.9	-
Ictaluridae	<i>Noturus insignis</i>	2	71.7	5.5	24.1	3.0
Mollusca						
Bivalvia	<i>Corbicula fluminea</i>	2	-	-	1.9	0.0
Gastropoda	Pleuroceridae	2	-	-	8.5	0.6

Table 2.11. Percentages of methylmercury in prey items collected in the Shenandoah River basin, Virginia, where N = number of composite samples and MeHg = mean percentage of methylmercury.

Prey Type	Taxa Analyzed	N	MeHg	\pm SE
Aquatic Insect		14	43.4%	6.5%
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae, Leptohyphidae	11	34.5%	5.0%
Anisoptera	Gomphidae	2	79.2%	20.7%
Zygoptera	Coenagrionidae	1	68.5%	-
Crustacea				
Decapoda	Crayfish	13	78.0%	5.1%
Forage Fish		18	97.9%	1.0%
Centrarchidae	<i>Micropterus dolomieu</i>	1	100.0%	-
Cyprinidae	<i>Cyprinella analostana</i>	2	100.0%	0.0%
Cyprinidae	<i>Notropis amoenus</i>	1	100.0%	-
Cyprinidae	<i>Rhinichthys cataractae</i>	1	100.0%	-
Ictaluridae	<i>Ameiurus natalis</i>	1	100.0%	-
Ictaluridae	<i>Noturus insignis</i>	5	98.7%	1.3%
Percidae	<i>Etheostoma flabellare</i>	6	96.0%	2.8%
Percidae	<i>Etheostoma olmstedi</i>	1	92.9%	-
Mollusca				
Gastropoda	Pleuroceridae	4	55.3%	5.4%
Terrestrial Insect				
Coleoptera	<i>Cotinis nitida</i>	2	5.2%	2.3%

*Percentages of methylmercury greater than 100% were truncated.

Table 2.12. Kruskal-Wallis (KW) one-way nonparametric analysis of variance for testing whether mean concentrations of total mercury in prey items were significantly different between sites in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia. Significant differences are highlighted ($\alpha = 0.05$). For pairwise comparisons, sites with the same letter were not significantly different.

Prey Type	df	KW Statistic	P	<i>Pairwise Comparisons</i>				
				SR6	SR4	SR3	SF5	NR2
Aquatic Insects	4	68.22	<0.0001	A	AB	BC	CD	D
Ephemeroptera	4	17.04	0.0019	A	AB	AB	B	B
Odonata	4	24.06	0.0001	A	AB	AB	B	B
Trichoptera	4	20.19	0.0005	A	AB	B	B	B
Bivalvia	4	8.72	0.0683	-	-	-	-	-
Crayfish	4	21.16	0.0003	A	AB	B	B	B
Forage Fish	4	49.33	<0.0001	A	A	B	B	B
Centrarchidae	4	25.62	<0.0001	A	AB	B	B	B
Cyprinidae	4	19.68	0.0006	A	AB	B	AB	B
Gastropoda	4	7.96	0.0929	-	-	-	-	-

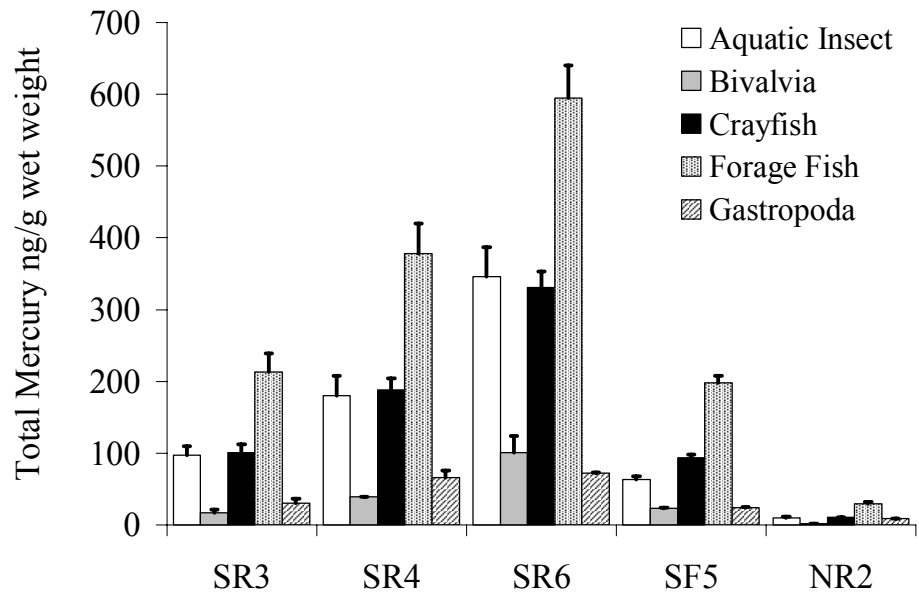


Figure 2.2. Mean concentrations of total mercury in prey items in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia.

Table 2.13. Kruskal-Wallis (KW) one-way nonparametric analysis of variance for testing whether mean concentrations of total mercury in prey items were significantly different between taxa in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia. Significant values are highlighted ($\alpha = 0.05$). For pairwise comparisons, taxa with the same letter were not significantly different.

Site	df	KW Statistic	P	<i>Pairwise Comparisons</i>					
				Aquatic Insect	Bivalvia	Crayfish	Forage Fish	Gastropoda	
SR3	4	24.35	0.0001	A	A	AB	B	A	
SR4	4	22.96	0.0001	A	A	AB	B	A	
SR6	4	23.51	0.0001	A	A	AB	B	A	
SF5	4	41.95	<0.0001	A	A	AB	B	A	
NR2	4	14.58	0.0056	A	A	AB	B	AB	

Table 2.14. Kruskal-Wallis (KW) one-way nonparametric analysis of variance for testing whether mean concentrations of total mercury in aquatic insects were significantly different between taxa in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia. Significant values are highlighted ($\alpha = 0.05$). For pairwise comparisons, taxa with the same letter were not significantly different.

Site	df	KW Statistic	P	<i>Pairwise Comparisons</i>						
				Coleoptera	Diptera	Ephemeroptera	Megaloptera	Odonata	Plecoptera	Trichoptera
SR3	3	12.81	0.0051	A	-	A	-	B	-	AB
SR4	3	3.02	0.3882	-	-	-	-	-	-	-
SR6	4	14.78	0.0052	A	AB	AB	-	B	-	B
SF5	3	12.54	0.0057	-	-	A	B	AB	-	AB
NR2	3	6.66	0.0833	-	-	-	-	-	-	-

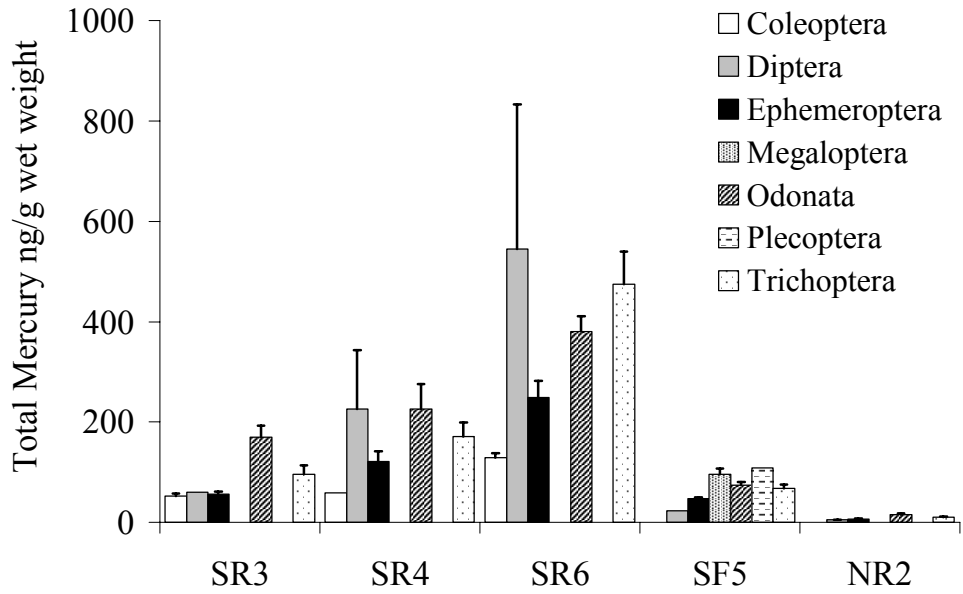


Figure 2.3. Mean concentrations of total mercury in aquatic insect larvae collected in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia.

Table 2.15. Kruskal-Wallis (KW) one-way nonparametric analysis of variance for testing whether mean concentrations of total mercury in forage fish were significantly different between taxa in the South River (SR3 and SR4), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia. Significant values are highlighted ($\alpha = 0.05$). For pairwise comparisons, taxa with the same letter were not significantly different.

Site	df	KW Statistic	P	<i>Pairwise Comparisons</i>			
				Centrarchidae	Cottidae	Cyprinidae	Percidae
SR3	4	12.24	0.0066	A	AB	B	AB
SR4	2	12.43	0.0020	A	-	B	AB
SF5	2	0.44	0.7997	-	-	-	-
NR2	2	3.71	0.1561	-	-	-	-

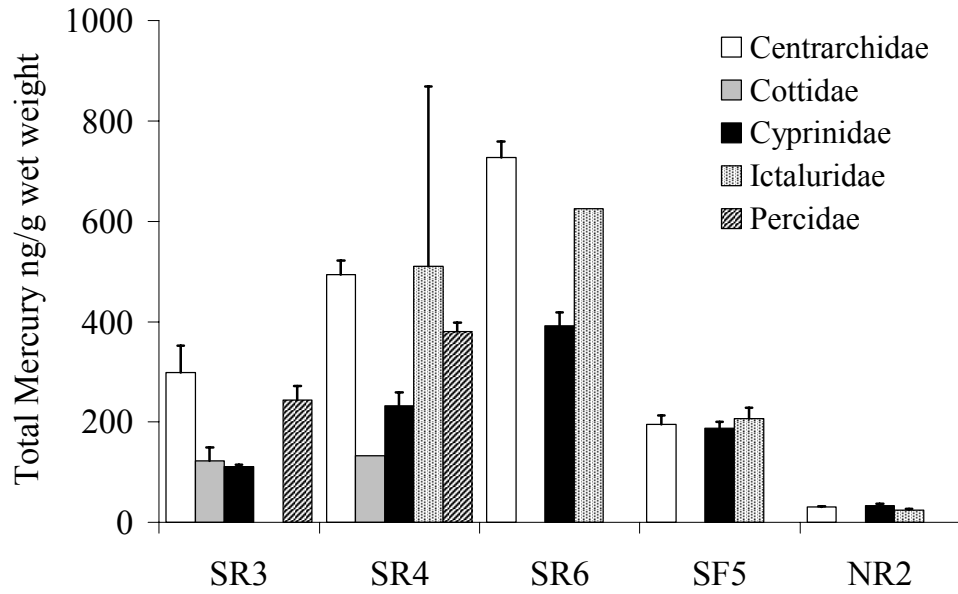


Figure 2.4. Mean concentrations of total mercury in forage fish collected in the South River (SR3, SR4, and SR6), South Fork of the Shenandoah River (SF5), and North River (NR2), Virginia.

Table 2.16. Kruskal-Wallis (KW) one-way nonparametric analysis of variance for testing whether mean concentrations of total mercury in prey items were different between seasons in the South River (SR3, SR4, and SR6) and South Fork of the Shenandoah River (SF5), Virginia. Significant values are highlighted ($\alpha = 0.05$). For pairwise comparisons, seasons with the same letter were not significantly different.

Prey Type	df	KW Statistic	P	<i>Pairwise Comparisons</i>		
				Spring	Summer	Fall
<u>SOUTH RIVER - SR3</u>						
Aquatic Insects	2	3.18	0.2038	-	-	-
Trichoptera	2	4.57	0.1017	-	-	-
Crayfish	2	3.42	0.1801	-	-	-
Forage Fish	2	1.37	0.5022	-	-	-
Centrarchidae	2	4.57	0.1017	-	-	-
Percidae	2	0.95	0.6201	-	-	-
<u>SOUTH RIVER - SR4</u>						
Aquatic Insects	2	7.72	0.0210	A	B	AB
Trichoptera	2	3.42	0.1801	-	-	-
Crayfish	2	3.42	0.1801	-	-	-
Forage Fish	2	2.11	0.3466	-	-	-
Centrarchidae	2	3.71	0.1561	-	-	-
<u>SOUTH RIVER - SR6</u>						
Aquatic Insects	2	3.09	0.2129	-	-	-
Coleoptera	2	4.19	0.1230	-	-	-
Odonata	2	0.27	0.8703	-	-	-
Trichoptera	2	4.57	0.1017	-	-	-
Crayfish	2	4.57	0.1017	-	-	-
Forage Fish	2	0.01	0.9927	-	-	-
Centrarchidae	2	2.75	0.2521	-	-	-
<u>SOUTH FORK SHENANDOAH RIVER</u>						
Aquatic Insects	2	5.96	0.0508	-	-	-
Ephemeroptera	2	1.60	0.4477	-	-	-
Odonata	2	0.60	0.7382	-	-	-
Trichoptera	2	4.57	0.1017	-	-	-
Crayfish	2	3.78	0.1504	-	-	-
Forage Fish	2	4.78	0.0913	-	-	-
Centrarchidae	2	5.09	0.0783	-	-	-

Table 2.17. Summary of total mercury concentrations in various invertebrate and forage fish taxa reported in the literature, where THg = total mercury ng/g wet weight.

Prey Type	Taxa Analyzed	Mean THg	THg Range	Study Location	Citation
			<u>ANNELIDA</u>		
Annelida	Oligochaeta	160	-	Ranger Lake, Ontario	Wong et al. 1997
Annelida	<i>Lamelligibrachia satsuma</i>	230	-	Kagoshima Bay, Japan	Ando et al. 2002
Annelida	<i>Lamelligibrachia satsuma</i>	160	-	Kagoshima Bay, Japan	Ando et al. 2002
Annelida	Oligochaeta	1,147	499-2,096	South River, VA	Murphy 2004
			<u>AQUATIC INSECTS</u>		
Anisoptera	Libellulidae	300	-	N. F. Holston River, VA	Powell 1983
Anisoptera	Aeshnidae, Gomphidae, Macromiidae	292	111-500	South River, VA	Murphy 2004
Anisoptera	Gomphidae, Macromiidae	105	-	S. F. Shenandoah River, VA	Murphy 2004
Anisoptera	Gomphidae	18	-	North River, VA	Murphy 2004
Coleoptera	Psephenidae	90	35-151	South River, VA	Murphy 2004
Diptera	Simuliidae	150	-	South River, VA	Bolgiano 1980
Diptera	Simuliidae	<120	-	S. F. Shenandoah River, VA	Bolgiano 1980
Diptera	<i>Aterix spp.</i>	700	210-1,430	N. F. Holston River, VA	Hildebrand et al. 1980
Diptera	Chironomidae, Tipulidae	324	60-1,080	South River, VA	Murphy 2004
Diptera	Chironomidae	23	-	S. F. Shenandoah River, VA	Murphy 2004
Diptera	Chironomidae, Tipulidae	4	-	North River, VA	Murphy 2004
Ephemeroptera	Heptageniidae	100	-	N. F. Holston River, VA	Powell 1983
Ephemeroptera	<i>Ephoron leukon</i> , <i>Isonychia bicolor</i>	1,160	330-1,630	South River, VA	Hendricks et al. 1989
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae, Leptohyphidae	142	46-318	South River, VA	Murphy 2004
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae	47	35-54	S. F. Shenandoah River, VA	Murphy 2004
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae	7	-	North River, VA	Murphy 2004

Table 2.17. (continued) Summary of total mercury concentrations in various invertebrate and forage fish taxa reported in the literature, where THg = total mercury ng/g wet weight.

Prey Type	Taxa Analyzed	Mean THg	THg Range	Study Location	Citation
Megaloptera	<i>Corydalis</i> spp.	350	260-450	South River, VA	Bolgiano 1980
Megaloptera	<i>Corydalis</i> spp.	240	-	S. F. Shenandoah River, VA	Bolgiano 1980
Megaloptera	<i>Corydalis</i> spp.	850	220-1,940	N. F. Holston River, VA	Hildebrand et al. 1980
Megaloptera	Corydalidae	400	-	N. F. Holston River, VA	Powell 1983
Megaloptera	<i>Corydalis</i> spp.	230	20-370	South River, VA	Hendricks et al. 1989
Megaloptera	Corydalidae	96	77-128	S. F. Shenandoah River, VA	Murphy 2004
Plecoptera	Perlidae	200	-	N. F. Holston River, VA	Powell 1983
Plecoptera	Perlidae	109	-	S. F. Shenandoah River, VA	Murphy 2004
Trichoptera	<i>Hydropsyche</i> spp.	290	200-380	South River, VA	Bolgiano 1980
Trichoptera	<i>Hydropsyche</i> spp., <i>Macronemum</i> spp.	<100	-	S. F. Shenandoah River, VA	Bolgiano 1980
Trichoptera	Hydropsychidae	1,120	210-3,750	N. F. Holston River, VA	Hildebrand et al. 1980
Trichoptera	Rhyacophilidae	800	-	N. F. Holston River, VA	Powell 1983
Trichoptera	<i>Hydropsyche morosa</i> and <i>betteni</i>	1,600	460-5,120	South River, VA	Hendricks et al. 1989
Trichoptera	<i>Hydropsyche morose</i>	-	140-1,200	South River, VA	Snyder and Hendricks 1995
Trichoptera	Hydropsychidae	239	53-659	South River, VA	Murphy 2004
Trichoptera	Brachycentridae, Hydropsychidae	67	51-91	S. F. Shenandoah River, VA	Murphy 2004
Trichoptera	Hydropsychidae	10	10-11	North River, VA	Murphy 2004
Zygoptera	Agriionidae and Coenagrionidae	200	-	N. F. Holston River, VA	Powell 1983
Zygoptera	Coenagrionidae	247	116-419	South River, VA	Murphy 2004
Zygoptera	Coenagrionidae	69	49-82	S. F. Shenandoah River, VA	Murphy 2004
Zygoptera	Coenagrionidae	11	-	North River, VA	Murphy 2004
	CRAYFISH				
Crayfish	-	-	280-550	South River, VA	Bolgiano 1980
Crayfish	-	770	270-1,310	N. F. Holston River, VA	Hildebrand et al. 1980

Table 2.17. (continued) Summary of total mercury concentrations in various invertebrate and forage fish taxa reported in the literature, where THg = total mercury ng/g wet weight.

Prey Type	Taxa Analyzed	Mean THg	THg Range	Study Location	Citation
Crayfish	<i>Cambarus bartoni</i> and <i>Orconectes obscurus, propinquus, and virilis</i>	-	20-610	13 lakes in South-Central Ontario	Allard and Stokes 1989
Crayfish	-	650	170-910	South River, VA	Hendricks et al. 1989
Crayfish	<i>Orconectes virilis</i>	165	-	Blue Chalk Lake, Ontario	Scheuhammer and Graham 1999
Crayfish	<i>Pacfasticus leniusculus</i>	100	30-540	Lake Whatcom, WA	Mueller and Serdar 2002
Crayfish	-	206	58-382	South River, VA	Murphy 2004
Crayfish	-	93	78-104	S. F. Shenandoah River, VA	Murphy 2004
Crayfish	-	10	-	North River, VA	Murphy 2004
Centrarchidae	<i>Lepomis auritus</i> ¹ , <i>Micropterus dolomieu</i> ¹	538	<u>FORAGE FISH</u> 151-867	South River, VA	Murphy 2004
Centrarchidae	<i>Lepomis auritus</i> ¹ , <i>Micropterus dolomieu</i> ¹	195	92-250	S. F. Shenandoah River, VA	Murphy 2004
Centrarchidae	<i>Lepomis auritus</i> ¹	30	28-32	North River, VA	Murphy 2004
Cottidae	<i>Cottus bairdi</i> and <i>caroliniae</i>	126	95-150	South River, VA	Murphy 2004
Cyprinidae	<i>Notropis spp.</i>	600	390-960	South River, VA	LMS 1982
Cyprinidae	<i>Notropis spp.</i>	320	210-490	S. F. Shenandoah River, VA	LMS 1982
Cyprinidae	-	740	590-970	South River, VA	Hendricks et al. 1989
Cyprinidae	<i>Luxilus chrysocephalus</i>	-	500-1,500	E. F. Popular Creek, TN	Hill et al. 1996
Cyprinidae	<i>Notropis volucellus</i>	-	82-120	Devils Lake, WA	Gorski et al. 1999
Cyprinidae	<i>Semotilus atromaculatus</i>	370	-	Blue Chalk Lake, Ontario	Scheuhammer and Graham 1999
Cyprinidae	<i>Semotilus atromaculatus</i>	450	-	Plastic Lake, Ontario	Scheuhammer and Graham 1999

Table 2.17. (continued) Summary of total mercury concentrations in various invertebrate and forage fish taxa reported in the literature, where THg = total mercury ng/g wet weight.

Prey Type	Taxa Analyzed	Mean THg	THg Range	Study Location	Citation
Cyprinidae	<i>Cyprinella analostana</i> , <i>Luxilus cornutus</i> , <i>Notropis hudsonius</i> , <i>Rhinichthys cataractae</i>	254	99-463	South River, VA	Murphy 2004
Cyprinidae	<i>Cyprinella analostana</i>	188	162-231	S. F. Shenandoah River, VA	Murphy 2004
Cyprinidae	<i>Cyprinella analostana</i> , <i>Notropis amoenus</i>	33	30-36	North River, VA	Murphy 2004
Ictaluridae	<i>Noturus insignis</i> , <i>Ameiurus natalis</i> ¹	549	153-869	South River, VA	Murphy 2004
Ictaluridae	<i>Noturus insignis</i> , <i>Ameiurus natalis</i> ¹	207	153-310	S. F. Shenandoah River, VA	Murphy 2004
Ictaluridae	<i>Noturus insignis</i>	24	21-27	North River, VA	Murphy 2004
Percidae	<i>Etheostoma flabellare</i> and <i>olmstedii</i>	305	139-439	South River, VA	Murphy 2004
			MOLLUSCA		
Bivalvia	<i>Corbicula fluminea</i>	510	160-780	South River, VA	Graber-Neufeld 2002
Bivalvia	<i>Corbicula fluminea</i>	220	-	S. F. Shenandoah River, VA	Graber-Neufeld 2002
Bivalvia	<i>Corbicula fluminea</i>	290	130-570	South River, VA	Bowles 2003
Bivalvia	<i>Corbicula fluminea</i>	180	90-280	South River, VA	Benzing 2004
Bivalvia	<i>Corbicula fluminea</i>	51	12-124	South River, VA	Murphy 2004
Bivalvia	<i>Corbicula fluminea</i>	23	22-24	S. F. Shenandoah River, VA	Murphy 2004
Bivalvia	<i>Corbicula fluminea</i>	2	-	South River, VA	Murphy 2004
Gastropoda	<i>Biithynia tentaculata</i> ²	180	90-390	St. Lawrence River, Ontario	Filion 1997
Gastropoda	<i>Biithynia tentaculata</i> ²	90	10-290	St. Lawrence River, Quebec	Désy et al. 2000
Gastropoda	<i>Pomacea scalaris</i> and <i>lineate</i> , <i>Marisa planogyra</i>	-	10-2,040	Mota Grosso, Brazil	Callil and Junk 2001

Table 2.17. (continued) Summary of total mercury concentrations in various invertebrate and forage fish taxa reported in the literature, where THg = total mercury ng/g wet weight.

Prey Type	Taxa Analyzed	Mean THg	THg Range	Study Location	Citation
Gastropoda	Pleuroceridae	56	23-76	South River, VA	Murphy 2004
Gastropoda	Pleuroceridae	23	22-24	S. F. Shenandoah River, VA	Murphy 2004
Gastropoda	Pleuroceridae	8	7-9	North River, VA	Murphy 2004
			<u>TERRESTRIAL INSECTS</u>		
Coleoptera	<i>Popillia japonica</i>	<200	-	South River, VA	Hayes 1986
Coleoptera	<i>Cotinis nitida</i>	6,865	1,743-14,580	South River, VA	Murphy 2004

¹Juvenile fish.

²Reported values were dry weight concentrations.

Table 2.18. Summary of methylmercury (MeHg) percentages in various invertebrate and forage fish taxa reported in the literature.

Taxa Analyzed	Mean MeHg	MeHg Range	Study Location	Citation
<u>AQUATIC INSECTS</u>				
Anisoptera	79%	58-100%	Shenandoah River basin, VA	Murphy 2004
Diptera	-	44-77%	N. F. Holston River, VA	Hildebrand et al. 1980
Diptera, Ephemeroptera, and Trichoptera	-	35-50%	19 boreal lakes in Canada and Sweden	Tremblay et al. 1996b
Diptera and Ephemeroptera	-	20-25%	La Grande 2 Reservoir, Quebec	Tremblay et al. 1996a
Coleoptera	37%	-	N. F. Holston River, VA	Hildebrand et al. 1980
Ephemeroptera	34%	15-64%	Shenandoah River basin, VA	Murphy 2004
Heteroptera and Coleoptera	-	60-85%	La Grande 2 Reservoir, Quebec	Tremblay et al. 1996a
Heteroptera, Coleoptera, and Odonata	-	70-95%	19 boreal lakes in Canada and Sweden	Tremblay et al. 1996b
Megaloptera	-	41-66%	N. F. Holston River, VA	Hildebrand et al. 1980
Odonata	95%	-	La Grande 2 Reservoir, Quebec	Tremblay et al. 1996a
Trichoptera	-	29-57%	N. F. Holston River, VA	Hildebrand et al. 1980
Trichoptera	-	30-40%	La Grande 2 Reservoir, Quebec	Tremblay et al. 1996a
Zygoptera	68%	-	Shenandoah River basin, VA	Murphy 2004
<u>CRAYFISH</u>				
Crayfish	-	48-80%	N. F. Holston River, VA	Hildebrand et al. 1980
Crayfish	-	60-80%	Herrington Creek and Blacklick Run, MD	Mason et al. 2000
Crayfish	78%	36-100%	Shenandoah River basin, VA	Murphy 2004
<u>FORAGE FISH</u>				
<i>Ambloplites rupestris</i> and <i>Hyppentelium nigricans</i>	92%	-	N. F. Holston River, VA	Hildebrand et al. 1980
<i>Catostomus commersoni</i> , <i>Esox lucius</i> , and <i>Perca flavescens</i>	99%	-	35 lakes in Michigan and Wisconsin	Grieb et al. 1990

Table 2.18. (continued) Summary methylmercury (MeHg) percentages in various invertebrate and forage fish taxa reported in the literature.

Taxa Analyzed	Mean MeHg	MeHg Range	Study Location	Citation
<i>Catostomus commersoni</i> , <i>Hypentelium nigricans</i> , <i>Ictalurus punctatus</i> , <i>Lepomis auritus</i> , <i>Micropterus dolomieu</i> and <i>salmoides</i> , and <i>Oncorhynchus mykiss</i>	86%	-	South River, S. F. Shenandoah River, and Shenandoah River, VA	VDEQ 2003
<i>Ameiurus natalis</i> , <i>Cyprinella analostana</i> , <i>Etheostoma flabellare</i> and <i>olmstedii</i> , <i>Micropterus dolomieu</i> , <i>Notropis amoenus</i> , <i>Noturus insignis</i> , <i>Rhinichthys cataractae</i>	97%	84-100%	Shenandoah River basin, VA	Murphy 2004
<i>Neptunea arthritica cumingii</i> , <i>Neverita didyma</i> , and <i>Rapana venosa</i>	-	20-62%	Chinese Bohai Sea	Liang et al. 2003
Pleuroceridae	55%	44-65%	Shenandoah River basin, VA	Murphy 2004
<i>Cotinis nitida</i>	5%	2-7%	South River, VA	Murphy 2004

CHAPTER 3: Bioaccumulation Dynamics of Methylmercury in Fish Communities of the Shenandoah River Basin, Virginia

ABSTRACT

Mercury is a persistent heavy metal that poses significant challenges to human health and fisheries management. Understanding the bioaccumulation dynamics of methylmercury in fish aids in the implementation of thoughtful remediation as well as forecasting the biological and human health implications to the fishery. A bioenergetics-based bioaccumulation model was used to simulate the bioaccumulation dynamics of methylmercury in fish communities in the mercury contaminated South River and South Fork Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia. Model-predicted concentrations of methylmercury in fish exhibited patterns comparable to those observed during field studies, including size dependent patterns within species and variations between species of different trophic levels. Model-predicted concentrations of methylmercury in fish increased significantly with fish size and age ($P < 0.05$) and were consistently higher in *Micropterus dolomieu*. Dietary pathways accounted for 87% of methylmercury uptake by fish in contaminated rivers, but only 57% in the reference river. Graphical analyses indicated that model-predicted and observed concentrations of methylmercury in fish were comparable. Quantitative analyses indicated that mean absolute percent error between model-predicted and observed concentrations of methylmercury in fish was 52% and ranged from 17-149%. Model-predicted bioaccumulation dynamics of methylmercury in fish were sensitive to changes in food web structure, including dietary composition, average length of prey, and specific growth rate, indicating that biomanipulation of contaminated systems, may ultimately affect concentrations of methylmercury in fish. Reducing concentrations of methylmercury in river sediment substantially reduced model-predicted concentrations of methylmercury in fish. Bioenergetics-based bioaccumulation models, such as presented here, are useful tools for evaluating field data, identifying factors critical to contaminant accumulation, and comparing outcomes of alternative management options associated with pollution control, ecosystem management, and restoration activities to provide management guidance prior to costly expenditures.

INTRODUCTION

The ability to accurately predict the bioaccumulation of contaminants in fish aids in the implementation of thoughtful remediation as well as forecasting the biological and human health implications to the fishery. Accurate bioaccumulation estimates are needed not only to predict realistic dietary exposures to humans and piscivorous wildlife but also to more accurately assess

the potential ecological risks to fish themselves (Barber 2001). Models describing methylmercury accumulation in fish first appeared in the 1970s (Fagerstrom and Asell 1973; Fagerstrom et al. 1974; Norstrom et al. 1976). Bioenergetics-based models have become particularly useful in describing methylmercury accumulation in fish because common units of energy are used to describe the uptake of methylmercury from dietary and aqueous pathways, and elimination of assimilated methylmercury (Fagerstrom and Asell 1973; Fagerstrom et al. 1974; Norstrom et al. 1976; Rodgers and Qadri 1982; Rodgers 1994; 1996; Korhonen et al. 1995; Harris and Bodaly 1998; Stafford and Haines 2001). These robust models use any available information on fish biology (i.e., diet composition, growth rate, and water temperature) and ambient concentrations of methylmercury to characterize methylmercury bioaccumulation in fish (Rodgers 1996).

Prior bioenergetics-based modeling studies describing the bioaccumulation of methylmercury in fish have failed to describe the bioaccumulation dynamics of methylmercury within a community context, which may be masking important associations. To address this concern, aid in the development of a beta test version model, and provide management guidance prior to the implementation of remediation efforts, a bioenergetics-based bioaccumulation model was used to describe the bioaccumulation dynamics of methylmercury in fish communities in the mercury contaminated South River and South Fork Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia. Tasks of this objective were to:

1. Assess model-predicted patterns of methylmercury accumulation in fish for consistency with patterns observed during field studies.
2. Determine the importance of methylmercury uptake through dietary pathways.
3. Evaluate the model's predictive ability using observed concentrations of methylmercury in fish.
4. Assess the model's sensitivity to food web structure, including dietary composition, average length of prey, and specific growth rate.
5. Demonstrate the model's utility to aid in the evaluation of alternative management options associated with mercury remediation.

MATERIALS AND METHODS

Description of Model

The model selected for this study was the Bioaccumulation and Aquatic System Simulator (BASS) version 2.1 developed by Craig Barber of the Ecosystems Research Division of the U. S. Environmental Protection Agency (U. S. EPA) in Athens, Georgia. The BASS model

version 2.1 is a beta test version that was released on a targeted basis to U. S. EPA Program and Regional Offices and to the academic community for comment and testing.

The BASS model is a FORTRAN 95 simulation program that predicts the population and bioaccumulation dynamics of age-structured fish communities exposed to hydrophobic organic pollutants and class B and borderline metals that complex with sulfhydryl groups (e.g., cadmium, copper, lead, mercury, nickel, silver, and zinc). The model's bioaccumulation algorithms, which are based on diffusion kinetics, are coupled to a process-based model for the growth of individual fish. The model's exchange algorithms consider both biological attributes of fishes and physico-chemical properties of the chemicals of concern that determine diffusive exchange across gill membranes and intestinal mucosa. Biological characteristics used by the model include the fish's gill morphometry, feeding and growth rate, and proximate composition (i.e., its fractional aqueous, lipid, and structural organic content). Relevant physico-chemical properties are the chemical's aqueous diffusivity, n-octanol/water partition coefficient (K_{ow}), and, for metals, binding coefficients to proteins and other organic matter. The model simulates the growth of individual fish using a standard mass balance, bioenergetics model (i.e., growth = ingestion - egestion - respiration - specific dynamic action - excretion). A fish's realized ingestion is calculated from its maximum consumption rate adjusted for the availability of prey of the appropriate size and taxonomy. The community's food web is specified by defining one or more foraging classes for each fish species based on its length, weight, or age. The dietary composition of each of these foraging classes is specified as a combination of benthos, incidental terrestrial insects, periphyton/attached algae, phytoplankton, zooplankton, and one or more fish species. Population dynamics are generated by predatory mortalities defined by community's food web and standing stocks, size dependent physiological mortality rates, maximum longevity of species, and toxicological responses to chemical exposures. The model's temporal and spatial scales of resolution are a day and a hectare. Currently, the model ignores the migration of fish into and out of the simulated hectare (Barber 2001).

The BASS model operates in two modes, including community mode, which models growth, bioaccumulation, and population dynamics of age-structured fish communities, and Food and Gill Exchange of Toxic Substances (FGETS) mode, which only models growth and bioaccumulation dynamics of age-structured fish communities (Figure 3.1). Because population data for the rivers of interest was insufficient and/or nonexistent, the model was operated in FGETS mode during this study.

Description of Study Sites

The BASS model was used to simulate the bioaccumulation dynamics of methylmercury in fish communities in the mercury contaminated South River (at sites SR3, SR4, and SR6) and South Fork of the Shenandoah River and uncontaminated North River, located in the Shenandoah River basin, Virginia (Figure 3.2; Table 3.1). The South River is a fourth-order stream that originates on the western slope of the Blue Ridge Mountains, drains an area of 373 km², and has an average annual discharge of 7.1 m³/s. The North River is a fifth-order stream that originates in the Allegheny foothills, drains an area of 1140 km², and has an average annual discharge of 10.2 m³/s. The South River and North River converge at Port Republic, forming the South Fork of the Shenandoah River. The South Fork of the Shenandoah River is a sixth-order stream that flows for 160 rkm and drains an area of 4,144 km² before joining the North Fork of the Shenandoah River at Front Royal to form the main stem of the Shenandoah River, approximately 290 rkm from the Chesapeake Bay.

Simulated Fish Communities

Fish communities simulated in this study were selected based on trophic relationships identified during diet analyses (Chapter 1) and discussion with fishery biologists of the Virginia Department of Game and Inland Fisheries (pers. comm. P. Bugas and S. Reeser, VDGIF). In the South River, the simulated fish community consisted of *Catostomus commersoni*, *Etheostoma flabellare*, *Lepomis auritus*, *Luxilus cornutus*, *Micropterus dolomieu*, and *Noturus insignis*. In the South Fork of the Shenandoah River, the simulated fish community consisted of *C. commersoni*, *Cyprinella analostana*, *Ictalurus punctatus*, *L. auritus*, *M. dolomieu*, and *N. insignis*. In the North River, the simulated fish community consisted of *C. commersoni*, *L. auritus*, *M. dolomieu*, *Notropis amoenus*, and *N. insignis*.

Model Parameterization

Input parameters required for the BASS model are broadly classified into three categories, including simulation control, chemical, and fish parameters. These parameters are presented in brief in Table 3.2 and described in the following sections.

Simulation Control Parameters

Project titles were selected based on river and site. Lengths of simulations were selected as 11, 12, and 10 years for the South River (at sites SR3, SR4, and SR6), South Fork of the Shenandoah River, and North River to correspond with the maximum fish age within each

system, assuring that all cohorts were exposed to methylmercury (pers. comm. C. Barber, USEPA). January was designated as the initial month of simulation for each project to correspond with fish age and growth methodologies. Water temperature was collected using Onset® Optic StowAway temperature loggers (measurable range -4°C to +37°C, accuracy $\pm 0.2^\circ$ at 70°C) which were secured with airline cable at site SR6 on the South River, SF3 on the South Fork of the Shenandoah River, and NR1 on the North River from February 6, 2002 to December 3, 2003. Temperature loggers were anchored in shaded locations of flowing water and were downloaded seasonally to minimize data loss. Only temperature data from February 6, 2002 to February 5, 2003 was used for simulations (Figure 3.3). Temperature data was repeated for each year of simulation. Mean water temperatures (\pm SE) were 14.7 (± 0.4), 15.3 (± 0.4), and 14.3 (± 0.4) °C in the South River, South Fork of the Shenandoah River, and North River, respectively. Because the BASS model required an input value for water depth and water depth had no effect on simulations in this study, a constant water depth of 1 m was selected for all projects.

Chemical Parameters

The BASS model was distributed with a file that included input values for methylmercury's physico-chemical properties, which were not changed during this study (Table 3.3). Aqueous concentrations of dissolved methylmercury in the South River (at sites SR3, SR4, and SR6), South Fork of the Shenandoah River, and North River were estimated using monitoring data collected by the Virginia Department of Environmental Quality. Data from 1997-1999 was used to estimate the percentage of dissolved methylmercury to total mercury (11%) in the Shenandoah River basin because of insufficient river specific data (VDEQ unpublished). Aqueous concentrations of dissolved total mercury from 2002-2003 were multiplied by this percentage to estimate mean aqueous concentrations of dissolved methylmercury. Estimated aqueous concentrations of dissolved methylmercury were held constant among seasons due to insufficient seasonal data. Estimated mean aqueous concentrations of dissolved methylmercury were 0.312, 0.371, and 0.522 ng/L in the South River at sites SR3, SR4, and SR6, 0.212 ng/L in the South Fork of the Shenandoah River, and 0.176 ng/L in the North River (Figure 3.4). Aqueous concentrations of dissolved methylmercury were specified as a chemical equilibrium with benthic sediments.

Recent data on concentrations of total mercury and methylmercury in river sediment were not available for the Shenandoah River basin (VDEQ is scheduled for river sediment sampling in 2007). Therefore, concentrations of methylmercury in river sediment were estimated using data collected in 1997, which only provided concentrations of total mercury (AMRL 1998). Based on

studies conducted by Kannan et al. (1998) and Gray et al. (2000), the percentage of methylmercury in river sediment was assumed to be 0.89%. Estimated mean concentrations of methylmercury in river sediment were 0.029, 0.034, and 0.140 $\mu\text{g/g}$ dry weight at sites SR3, SR4, and SR6 on the South River, 0.004 $\mu\text{g/g}$ in the South Fork of the Shenandoah River, and 0.001 $\mu\text{g/g}$ in the North River (Figure 3.4).

Methylmercury exposures via benthos were calculated using data collected during this study (Chapter 2). Mean concentrations of total mercury in benthos were estimated for the South River (at sites SR3, SR4, and SR6), South Fork of the Shenandoah River, and North River (Table 3.4). The percentages of methylmercury in various taxa of benthos were measured in this study (Chapter 2) and obtained from literature. The percentages of methylmercury used to estimate dietary exposures via benthos were 43, 12 (Ando et al. 2002), 55, 38 (Benzing 2004), and 78% in aquatic insects, Annelida, Gastropoda, Bivalvia, and crayfish, respectively. Moisture contents of benthic organisms were determined by drying for 24 hr at 60 °C (Table 3.5). Dry weight concentrations of methylmercury in benthos were estimated by multiplying mean concentrations of total mercury by the percentage of methylmercury and dividing by the dry weight percentage. Estimated mean concentrations of methylmercury in benthos were 245.6, 365.7, and 868.3 ng/g dry weight in the South River at sites SR3, SR4, and SR6, 142.5 ng/g dry weight in the South Fork of the Shenandoah River, and 18.8 ng/g dry weight in the North River (Figure 3.4). Concentrations of methylmercury in benthos were specified as a chemical equilibrium with aqueous concentrations of dissolved methylmercury.

Methylmercury exposure via terrestrial insects consumed by fish in the South River was estimated using data collected in this study (Chapter 2). The mean concentration of total mercury in terrestrial insects (Coleoptera: *Cotinis nitida*) was 6,865 ng/g wet weight. The percentage of methylmercury was 5% and the dry weight percentage was 68%. The estimated concentration of methylmercury in terrestrial insects in the South River was 1,072.6 ng/g dry weight, which was utilized for all sites. Due to sampling constraints, concentrations of total mercury were not measured in terrestrial insects along the South Fork of the Shenandoah River or North River. Therefore, concentrations of methylmercury in terrestrial insects consumed by fish in the South Fork of the Shenandoah River and North River were assumed to be 2.8x the concentration of methylmercury estimated in benthos, which was consistent with the pattern observed in the South River. Estimated concentrations of methylmercury in terrestrial insects along the South Fork of the Shenandoah River and North River were 399.0 and 52.8 ng/g dry weight, respectively.

Periphyton was used as a general diet category to account for detritus consumed by *C. commersoni*. Dietary exposure to methylmercury via periphyton was estimated based on an

established bioconcentration factor between water and periphyton (500,000x aqueous concentration) (pers. comm. C. Barber, USEPA).

Phytoplankton was used as a general diet category for vegetation (mainly filamentous green algae) consumed by fish in the South Fork of the Shenandoah River. Dietary exposure to methylmercury via phytoplankton was calculated from data collected in this study (Chapter 2). The mean concentration of total mercury in filamentous green algae in the South Fork of the Shenandoah River was 4.4 ng/g wet weight. Based on the study by Watras and Bloom (1992), the percentage of methylmercury was assumed to be 20% and the dry weight percentage was assumed to be 80%. The estimated concentration of methylmercury in vegetation was 4.4 ng/g dry weight. Due to sampling constraints and infrequency in the diet, concentrations of total mercury in vegetation were not measured in the South River or North River and were not specified in this study.

Fish Parameters

Common and scientific names of fish were specified using Jenkins and Burkhead (1994) and age class duration was designated as year for all fish species. Spawning periods were estimated from the literature (Carlander 1969, 1977, 1997; Jenkins and Burkhead 1994). Reproductive biomass investment ratio (i.e., grams gametes per gram spawning fish) was specified as 15% for all species, which is the model default. Age-0 weight specified the live weight of fish recruited into the population and represented the initial fish size used for growth calculations. For standardization, initial age-0 total length was assumed 15 mm for all species. Age-0 weights were estimated using species-specific length versus weight power regressions described in the following section. The maximum life span of each species was determined using age data collected in this study and from the literature (Table 3.6) (Carlander 1969, 1977, 1997; Jenkins and Burkhead 1994).

Length and weight relationships were estimated using river- and species-specific length versus weight power regressions (Table 3.7). Length versus weight data for *N. insignis* was only available for the South Fork of the Shenandoah River (VDGIF unpublished). Therefore, the length and weight relationship of *N. insignis* in the South Fork of the Shenandoah River was assumed for *N. insignis* in the South River and North River. Length and weight relationships were not available for *C. analostana* and *N. amoenus*. Therefore, the length and weight relationship of *L. cornutus* in the South River was assumed for *C. analostana* and *N. amoenus*. Input values for morphometric (Table 3.8) (Price 1931; Saunders 1962; Barber 2001, 2003; Brockway et al. unpublished), compositional (Table 3.9) (Lowe et al. 1985; Schmitt et al. 1990;

Schmitt and Brumbaugh 1990; Barber 1991, Brockway et al. unpublished), and physiological parameters (Table 3.10) (Barber 2001, 2004) were obtained from the literature.

Feeding variable was assigned as year for all species. Average lengths of prey (piscivores only) were estimated using data collected during this study (Chapter 1). Average lengths of prey were 25, 12, and 25% for *I. punctatus*, *L. auritus*, and *M. dolomieu* in the Shenandoah River basin, respectively. Because assimilation, egestion, specific dynamic action, and excretion can be calculated as linear functions of feeding and growth, it is then a straightforward matter to calculate a fish's expected ingestion given its projected growth and respiration (Barber 2001). Specific growth rates were estimated using length versus weight power regressions and age and growth data. Length versus weight power regressions used to estimate specific growth rates were discussed in the previous section. Ages of *C. commersoni*, *L. auritus*, and *M. dolomieu* were determined from otoliths and *I. punctatus* ages were determined from pectoral spines. Otoliths and spines were viewed using an Olympus SZ-ST scope with magnification range 1x-6.3x equipped with an Olympus SZ-CTV scope adapter, Samsung CCD SAC-410NA color camera, and Image-Pro Plus® software. Otoliths and spines were viewed submerged in water with black background and fiber optic lighting. Ages were estimated by two independent readers. Reader agreement (± 1 yr) was 83, 89, 96, and 84% for *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu*, respectively. In addition to aging otoliths and spines, growth was determined using the direct proportion back-calculation method (Table 3.11) (Devries and Frie 1996). Specific growth rates were calculated as:

$$SG = ((W_2 - W_1) / W_1) / D$$

where SG is specific growth (g/g/day), W_1 is the initial weight of the fish, W_2 is the final weight of the fish, and D is the number of days between the initial and final weight. Specific growth rates were calculated by age class for each species. Older age classes with less than five individuals were not used for specific growth rate calculations because of variance. Specific growth rates were plotted against initial body weights of each age class to calculate power regressions that described specific growth rates for each species (Table 3.12). Age and growth data was not available for forage fish in the Shenandoah River basin (i.e., *C. analostana*, *E. flabellare*, *L. cornutus*, and *N. insignis*). Therefore, specific growth rates were estimated using age and growth data obtained from the literature (Carlander 1969, 1997). Age and growth data for *C. analostana* was insufficient and did not exist for *N. amoenus*. Therefore, age and growth

data for *L. cornutus* was assumed for *C. analostana* and *N. amoenus*, which yielded reasonable estimates.

For any given foraging class, constant dietary percentages were specified (must equal 100% and cannot be $\leq 1\%$ for any given diet category) (pers. comm. C. Barber, USEPA). Diet categories were specified as one of the fish species within the given fish community or one of the following generalized categories, including benthos, incidental terrestrial insects, periphyton, and phytoplankton. Diets of *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* in the South River, South Fork of the Shenandoah River, and North River were determined during this study (Chapter 1). Diets of *C. analostana*, *E. flabellare*, *L. cornutus*, *N. amoenus*, and *N. insignis* in the Shenandoah River basin were not available. Therefore, diets of these species were assumed 100% benthos (Carlander 1969, 1997; Jenkins and Burkhead 1994). Periphyton was utilized as a general diet category to account for detritus consumed by *C. commersoni*. Phytoplankton was utilized as a general diet category for vegetation (mainly filamentous green algae) consumed by fish in the South Fork of the Shenandoah River (Table 3.13).

Initial ages by age class were specified by year depending on the maximum life span of the species. Initial live body weights by age class were estimated using mean back-calculated total lengths at age and length versus weight power regressions (Table 3.14). Initial whole body chemical concentrations by age class were assumed zero (also model default value).

Model Predictive Ability

Although the BASS model predicts whole body concentrations of methylmercury in fish, concentrations of methylmercury in fish muscle tissue are normally higher than whole body concentrations (Goldstein et al. 1996; Harris and Bodaly 1998). Therefore, model-predicted concentrations of methylmercury in fish muscle tissue were estimated by multiplying model-predicted whole body concentrations of methylmercury by 1.5 (Harris and Bodaly 1998). The BASS model's predictive ability was graphically assessed through the evaluation of model-predicted and observed concentrations of methylmercury in fish muscle tissue. Observed data were measured during this study (Chapter 2) and obtained from the mercury monitoring program in the Shenandoah River basin (VDEQ 2003). Because these data were concentrations of total mercury, concentrations of methylmercury were estimated using the reported methylmercury percentages of 97.9% (Chapter 2) and 85.5% (VDEQ 2003).

The BASS model's predictive ability was also assessed using mean absolute percent error (deviance measure) between model-predicted and observed concentrations of methylmercury in fish, which is calculated using the following equation:

$$MA\%E=100[\Sigma(|y_i-\hat{y}_i|/|y_i|)]/n$$

where MA%E is the mean absolute percent error between model-predicted and observed concentrations of methylmercury in fish muscle tissue, y_i is the observed concentration of methylmercury in fish muscle tissue, and \hat{y}_i is the model-predicted concentration of methylmercury in fish muscle tissue (Mayer and Butler 1993).

Model Sensitivity to Food Web Structure

Sensitivity of the BASS model to food web structure was assessed by adjusting dietary composition, average length of prey, and specific growth rate. These parameters were selected based on discussion with BASS developers, who indicated that these parameters were important to the bioaccumulation dynamics of methylmercury in fish communities, had not been evaluated previously, and may be altered through biomanipulation (pers. comm. C. Barber, USEPA). Although fish are normally the principal diet item of larger *I. punctatus* (Starostka and Nelson 1974), filamentous green algae was documented as the principal diet item (63%) of larger *I. punctatus* in the South Fork of the Shenandoah River during this study (Chapter 1). Because observed concentrations of methylmercury in *I. punctatus* in the South Fork of the Shenandoah River were suggestive of a piscivorous diet and uncertainty in the data used to parameterize dietary composition, the BASS model's sensitivity to dietary composition was assessed for *I. punctatus* in the South Fork of the Shenandoah River by adjusting the percentage of piscivory. Model simulations were performed for diets composed of 19.5, 50.0, and 75.0% fish. Because the average length of prey parameter is only applicable to piscivores, the BASS model's sensitivity to average length of prey was only assessed for *M. dolomieu* at site SR3 on the South River. The average length of prey measured in this study was 25% and ranged from 9.5 to 42.6% (Chapter 1). Therefore, model simulations were performed using these values. The model's sensitivity to specific growth rate was assessed for *C. commersoni*, *L. auritus*, and *M. dolomieu* at site SR6 on the South River. Measured specific growth rates were conservatively increased and decreased by 25% for each species.

Example Management Application - Sediment Remediation

Sediment remediation was assessed as a potential management option for pollution control and restoration of the South River at site SR6. This site was selected because concentrations of mercury are exceptionally high in the physical environment and aquatic biota at

this site (AMRL 1998; VDEQ 2003; VDEQ unpublished; Chapter 2), making it of particular interest to resource managers overseeing remediation efforts. Model simulations were performed for 25, 50, and 75% reduced concentrations of methylmercury in river sediment.

RESULTS

Bioaccumulation Dynamics of Methylmercury in Fish

Model-predicted concentrations of methylmercury in fish muscle tissue increased significantly ($P < 0.05$) with fish size and age for all species in the South River (Table 3.15; Appendix A. Tables 3.1-3.3), South Fork of the Shenandoah River (Table 3.16; Appendix A. Table 3.4), and North River (Table 3.17; Appendix A. Table 3.5), with only two exceptions. For instance, model-predicted concentrations of methylmercury in the muscle tissue of *M. dolomieu* at site SR3 on the South River increased from 0.37 to 1.80 $\mu\text{g/g}$ wet weight (386%) as *M. dolomieu* increased in size from 14.1 to 595.0 g and age from age-1 to age-10.

Model-predicted concentrations of methylmercury in fish muscle tissue in the South River (Figure 3.5) and South Fork of the Shenandoah River (Figure 3.6) were consistently higher in *M. dolomieu*. Despite this pattern, model-predicted concentrations of methylmercury in fish muscle tissue in the North River were highest in *C. commersoni* (Figure 3.7). Model-predicted accumulation rates of methylmercury in fish muscle tissue appeared faster in *E. flabellare* and *M. dolomieu* in the South River (Table 3.15), *C. analostana* and *M. dolomieu* in the South Fork of the Shenandoah River (Table 3.16), and *C. commersoni* and *N. amoenus* in the North River (Table 3.17) when analyzed by fish age. Model-predicted accumulation rates of methylmercury in fish muscle tissue were consistently faster in forage fish, including *E. flabellare* and *L. cornutus* in the South River, *C. analostana* and *N. insignis* in the South Fork of the Shenandoah River, and *N. amoenus* and *N. insignis* in the North River, when analyzed by fish weight.

Dietary pathways accounted for 88% of methylmercury uptake by fish in the South River, which ranged from 83% in *C. commersoni* to 94% in *M. dolomieu* (Figure 3.8; Appendix A. Tables 3.1-3.3). Dietary pathways accounted for 84% of methylmercury uptake by fish in the South Fork of the Shenandoah River, which ranged from 78% in *C. commersoni* to 90% in *M. dolomieu* (Figure 3.9; Appendix A. Table 3.4). Despite these patterns, dietary pathways only accounted for 57% of methylmercury uptake by fish in the North River, which ranged from 42% in *L. cornutus* to 73% in *C. commersoni* (Figure 3.10; Appendix A. Table 3.5).

Model Predictive Ability

Graphical analysis of model-predicted and observed concentrations of methylmercury in fish muscle tissue indicated that model-predicted concentrations of methylmercury were comparable to observed conditions in the South River at sites SR3 (Figure 3.11), SR4 (Figure 3.12), and SR6 (Figure 3.13), South Fork of the Shenandoah River (Figure 3.14), and North River (Figure 3.15). Although model-predicted concentrations of methylmercury in *E. flabellare* at sites SR3 and SR4 and *L. auritus* and *M. dolomieu* at site SR6 on the South River were higher than observed concentrations, they were within reasonable limits. Observed concentrations of methylmercury in *N. insignis* at sites SR3 and SR6 and *E. flabellare* at site SR6 on the South River were not available, which prevented the comparison of model-predicted and observed concentrations of methylmercury.

Mean absolute percent error between model-predicted and observed concentrations of methylmercury in the muscle tissue of fish was 52% and ranged from 17 to 127%. Mean absolute percent error was lowest for the South Fork of the Shenandoah River (44%) and highest for site SR3 on the South River (75%) (Table 3.18). Mean absolute percent error was normally lower for forage fish (i.e., *Cyprinella analostana*, *Notropis amoenus*, and *Noturus insignis*).

Model Sensitivity to Food Web Structure

Concentrations of methylmercury in the muscle tissue of *I. punctatus* in the South Fork of the Shenandoah River increased substantially with increased piscivory (Figure 3.16). Concentrations of methylmercury in the muscle tissue of *I. punctatus* age-1 to age-12 ranged from 0.08-0.64, 0.12-1.22, and 0.14-1.61 $\mu\text{g/g}$ wet weight for diets composed of 19.5, 50.0, and 75.0% fish, respectively (Appendix A. Table 3.6). Methylmercury uptake through dietary pathways increased from 88 to 95% as the percentage of piscivory increased from 19.5 to 75.0%. The quantity of methylmercury uptake through aqueous pathways was not affected by changes in dietary composition.

Concentrations of methylmercury in the muscle tissue of *M. dolomieu* at site SR3 on the South River increased substantially with increased average length of prey (Figure 3.17). Concentrations of methylmercury in the muscle tissue of *M. dolomieu* age-1 to age-10 ranged from 0.24-1.74, 0.37-1.89, and 0.44-2.46 $\mu\text{g/g}$ wet weight for average lengths of prey of 9.5, 25.0, and 42.6%, respectively (Appendix A. Table 3.7). Methylmercury uptake through dietary pathways increased from 91 to 94% as the average length of prey increased from 9.5 to 42.6%. The quantity of methylmercury accumulated through aqueous pathways was not affected by changes in the average length of prey.

Concentrations of methylmercury in the muscle tissue of *C. commersoni* and *L. auritus* were slightly affected by changes in specific growth rates. Increasing specific growth rates of *C. commersoni* (Figure 3.18) and *L. auritus* (Figure 3.19) slightly decreased concentrations of methylmercury, while decreasing specific growth rates increased concentrations of methylmercury. *Micropterus dolomieu* only exhibited this pattern from age-2 to age-5 (Figure 3.20). Although the quantity of methylmercury uptake through aqueous and dietary pathways increased or decreased with changes in specific growth rate, the percentage of methylmercury uptake through each pathway remained relatively consistent (Appendix A. Tables 3.8-3.10).

Example Management Application - Sediment Remediation

Reducing concentrations of methylmercury in river sediment caused a substantial decrease in concentrations of methylmercury in fish muscle tissue at site SR6 on the South River (Figure 3.21). For instance, concentrations of methylmercury in the muscle tissue of *L. auritus* age-1 to age-9 ranged from 0.64-2.66, 0.43-1.95, and 0.22-1.22 $\mu\text{g/g}$ wet weight for 25, 50, and 75% reductions of methylmercury in river sediment, respectively (Appendix A. Tables 3.11-3.13). This pattern was analogous for all species. Although the quantity of methylmercury uptake through aqueous and dietary pathways decreased as concentrations of methylmercury in river sediment were reduced, the percentage of methylmercury uptake through each pathway remained relatively consistent

DISCUSSION

Bioaccumulation Dynamics of Methylmercury in Fish

Model-predicted patterns of methylmercury accumulation in fish in this study, including size dependent patterns within species and variations between species of different trophic levels, were consistent with the results of field studies conducted in other mercury contaminated systems (Kelso and Frank 1974; Scott 1974; Phillips et al. 1980; Grieb et al. 1990; Brouard et al. 1994; Olivero et al. 1998; Neumann and Ward 1999; Ward and Neumann 1999; Mueller and Serdar 2002). Neumann and Ward (1999) found that concentrations of total mercury in *E. niger*, *L. macrochirus*, *M. dolomieu* and *salmoides*, *Perca flavescens*, and *Pomoxis nigromaculatus* increased significantly with fish size and age ($P < 0.05$) in Pickerel Lake and Lake Lillinonah, Connecticut. Mueller and Serdar (2002) found that concentrations of total mercury in Lake Whatcom, Washington were highest in predaceous *M. dolomieu*, followed by omnivorous *P. flavescens* and *Ameiurus nebulosus*, zooplanktivorous *Oncorhynchus nerka*, and benthivorous *Lepomis gibbosus*, respectively.

Dietary pathways accounted for the majority of methylmercury uptake by fish in the South River and South Fork of the Shenandoah River during this study, which is consistent with the results of field (Hall et al. 1997), laboratory (Jernelöv and Lann 1971; Phillips and Buhler 1978; Rodgers and Beamish 1981), and bioenergetics studies (Harris and Snodgrass 1993; Rodgers 1994). Hall et al. (1997) found that dietary pathways accounted for 85% or more of methylmercury uptake by *Phoxinus neogaeus* in an oligotrophic lake in northwestern Ontario. Harris and Snodgrass (1993) demonstrated that dietary pathways accounted for 90% or more of methylmercury uptake in *P. flavescens* and *Stizostedion vitreum*. Although dietary pathways accounted for the majority of methylmercury uptake by fish in the South River and South Fork of the Shenandoah River, dietary pathways accounted for a lower percentage of methylmercury uptake by fish in the North River. Differences in the percentage of methylmercury accumulated through dietary pathways in this study were presumably due to differences between aqueous and dietary exposure levels. Concentrations of methylmercury in water and benthos in the North River were more similar than concentrations of methylmercury in water and benthos in the South River and South Fork of the Shenandoah River.

Model Predictive Ability

The comparison of a model's predictions with observed data is necessary to determine whether the model is suitable for its intended purpose. This process is a mandatory step in the complex task of simulation (Mayer and Butler 1993). Graphical and quantitative analyses indicated that model-predicted and observed concentrations of methylmercury in fish muscle tissue were comparable. Based on mean absolute percent error calculations, model predictive ability was better for the South Fork of the Shenandoah River than South River and North River, most likely caused by the amount of observed data available for comparison. Fewer observed data points were available for the South River and North River, which may have inflated mean absolute percent error estimates higher than would have been observed if more observed data was available. Mean absolute percent error indicated that model-predicted concentrations of methylmercury were more accurate for forage fish, including *C. analostana*, *Notropis amoenus*, and *Noturus insignis*. However, very few observed data points were available for comparison and they only represented a small size range of fish. Although mean absolute percent error estimates appear high, these values are relative to the type of modeling application. There is a large amount of error involved with predicting concentrations of methylmercury in fish because concentrations of methylmercury within fish populations are extremely variable.

Due to the complexities of models and data types, there is no set combination of validation techniques applicable across all modeling situations (Mayer and Butler 1993). For instance, mean absolute percent error was 140% for *C. commersoni* in the North River. Yet, model-predicted concentrations of methylmercury in *C. commersoni* fit through the middle of the observed data points, appearing to be the best possible fit. Based on this example and other similar situations, it became apparent that mean absolute percent error was heavily influenced by variability of observed data, not just poor model predictions. Results of this study indicate that multiple validation techniques should be used to assess concentrations of methylmercury in fish predicted by the BASS model. Suitable validation techniques include subjective assessment, graphical displays, deviance measures, and statistical tests.

Model Sensitivity to Food Web Structure

Bioaccumulation dynamics of methylmercury in fish muscle tissue predicted by the BASS model appeared sensitive to changes in food web structure, including dietary composition, average length of prey, and specific growth rate. Increasing the percentage of piscivory for *I. punctatus* in the South Fork of the Shenandoah River substantially increased concentrations of methylmercury, which is not surprising considering that forage fish typically exhibit the highest concentrations of methylmercury among prey (Chapter 2) and dietary pathways account for the majority of methylmercury uptake by fish (Jernelöv and Lann 1971; Phillips and Buhler 1978; Rodgers and Beamish 1981; Harris and Snodgrass 1993; Hall et al. 1997). Because the BASS model appears sensitive to dietary composition, collecting accurate data on dietary composition of fish is critical for accurate simulations and ultimately remediation efforts.

Piscivores, such as *M. dolomieu*, are gape-limited predators, consuming only prey they can swallow whole (Hambright 1991; Carothers et al., in press). Carothers et al. found that *M. dolomieu* had maximum lengths of prey of 60 and 40% of their body length for *Semotilus atromaculatus* and *Lepomis gibbosus* consumed during laboratory feeding trials. Results of this study indicate that concentrations of methylmercury in fish muscle tissue increase as the average length of prey increases. Therefore, natural variability associated with changes in the abundance, composition, and distribution of fish in natural systems may ultimately affect concentrations of methylmercury in piscivores. Size relationships identified between piscivores and their prey also indicate that attempts made to maintain desirable species through regulation of trophic interactions, may also affect concentrations of methylmercury in the fish.

Growth rate has the potential to influence concentrations of persistent contaminants in fish via biodilution (Hammar et al. 1993; Madenjian et al. 1994). Field studies (Rask et al. 1996;

Doyon et al. 1998) and bioenergetics simulations (Borgmann and Whittle 1992; Harris and Bodaly 1998) indicate that methylmercury accumulation in fish is inversely related to growth rate. Rask et al. (1996) reported that a 10-fold increase in growth rate of *P. flavescens* after a fish kill was associated with a 50% decrease in concentrations of mercury. Doyon et al. (1998) reported that dwarf *Coregonus clupeaformis* accumulated mercury more rapidly than normal individuals in the same reservoir, despite similar concentrations of methylmercury in prey items. In this study, model-predicted concentrations of methylmercury in *C. commersoni*, *L. auritus*, and *M. dolomieu* at site SR6-Crimora on the South River increased slightly as specific growth rate decreased, and decreased slightly as specific growth rate increased. This observation was consistent for nearly all ages/sizes of *C. commersoni* and *L. auritus*, but was variable for *M. dolomieu*. Although growth rate did not appear to influence concentrations of methylmercury as much as reported in other studies, it is important to note that growth rates were conservatively adjusted in this study. Conservative adjustments of 25% were utilized because they seemed realistic for a riverine system, such as the South River.

Example Management Application - Sediment Remediation

Resource managers overseeing remediation efforts in the South River and South Fork of the Shenandoah River have hypothesized that mercury remaining in the system is bound to sediment particles. Messing and Winfield (1998) reported that concentrations of total mercury in river sediment in the South River ranged from 0.72-147.00 µg/g dry weight and were substantially higher than background concentrations (<0.10 µg/g). Based on sediment chemistry and tissue residue data, they suggested that high concentrations of mercury in fish in the South River were directly related to high concentrations of mercury in river sediment (Messing and Winfield 1998). Therefore, sediment remediation appears to be a logical management option for pollution control and restoration of the South River. Model-predicted concentrations of methylmercury in fish muscle tissue indicate that concentrations of methylmercury in river sediment need to be reduced by greater than 75% to effectively lower concentrations of methylmercury in fish below the U. S. FDA's action level for methylmercury in the edible portion of fish (1.0 µg/g wet weight). Although the BASS model was not developed to predict the period needed for the predicted reductions to occur, it can be coupled to several fate and transport models, such as the Water Quality Analysis Simulation Program (WASP) or Exposure Analysis Modeling Systems (EXAMS). Coupling the BASS model with a fate and transport model, such as WASP or EXAMS, would enable the user to predict the period necessary for the predicted reductions to occur. Although sediment remediation is a viable management option for

restoration of the South River and South Fork of the Shenandoah River, the environmental impacts of such actions need thorough evaluation prior to implementation.

Conclusions

Bioaccumulation models, such as presented here, are valuable tools for evaluating field data, identifying critical processes and pathways affecting contaminant accumulation, and comparing outcomes of alternative management options associated with pollution control, ecosystem management, and/or restoration activities for management guidance prior to costly expenditures. This study has developed a working model for the mercury contaminated South River (at sites SR3, SR4, and SR6) and South Fork of the Shenandoah River and uncontaminated North River that accurately predicts the bioaccumulation dynamics of methylmercury in fish communities. Model simulations confirmed that dietary pathways are the most important pathway of mercury uptake by fish. Model-predicted concentrations of methylmercury in fish were responsive to changes in food web structure, including dietary composition, average length of prey, and specific growth rate, indicating that biomanipulation of contaminated systems may ultimately affect concentrations of methylmercury in fish. Finally, model simulations indicate that sediment remediation appears to be a viable option for restoration of the South River, but a thorough environmental impact assessment should be conducted before such activities commence.

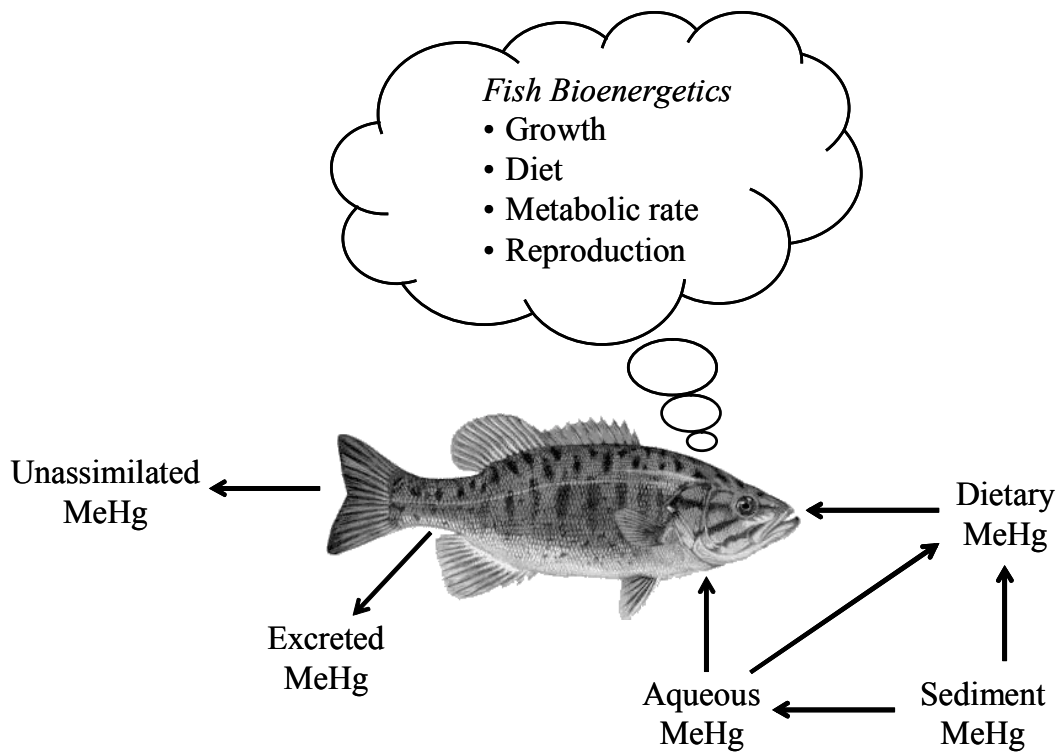


Figure 3.1. Schematic of the bioenergetics involved in the bioaccumulation of methylmercury (MeHg) in fish using the Bioaccumulation and Aquatic System Simulator.

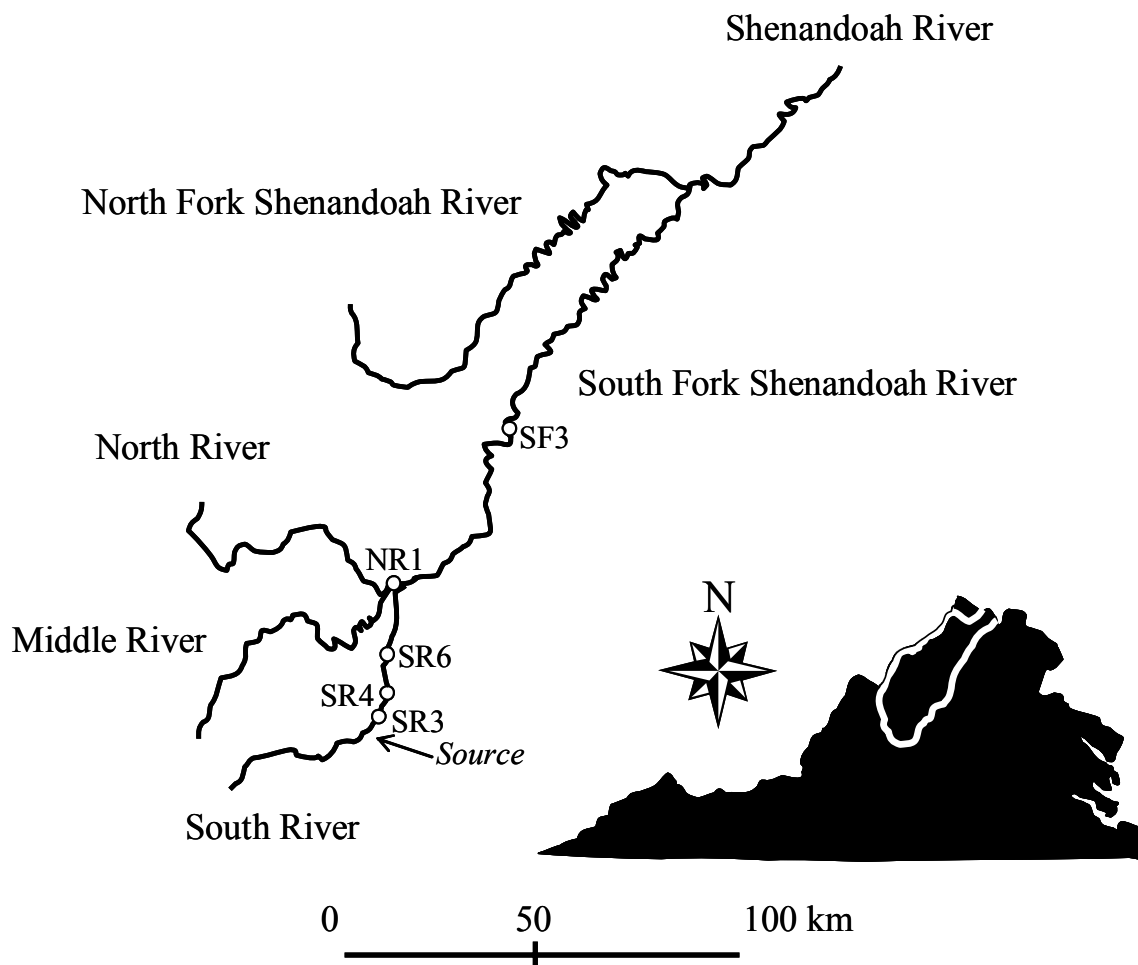


Figure 3.2. Study area and sites in the Shenandoah River basin, Virginia used to collect data for parameterization of the Bioaccumulation and Aquatic System Simulator.

Table 3.1. Description of study sites in the Shenandoah River basin, Virginia used to collect data for parameterization of the Bioaccumulation and Aquatic System Simulator, including approximate distance downriver from the historic source of mercury.

Site	Distance (rkm)	Latitude	Longitude	Site Description
<u>SOUTH RIVER</u>				
SR3	2.1	N38°04'40"	W78°52'45"	Waynesboro-North Park
SR4	3.7	N38°05'25"	W78°52'35"	Waynesboro-Hopeman Parkway
SR6	16.9	N38°09'30"	W78°51'10"	Crimora-Department of Forestry
<u>SOUTH FORK SHENANDOAH RIVER</u>				
SF3	104.6	N38°35'00"	W78°35'40"	Newport-Rt. 340 boat launch
<u>NORTH RIVER</u>				
NR1	*	N38°17'07"	W78°51'02"	Grottoes-Rt. 668 bridge

*Reference site, not located downriver from the historic source of mercury.

Table 3.2. Parameters required by the Bioaccumulation and Aquatic System Simulator in community and Food and Gill Exchange of Toxic Substances (FGETS) modes, and in modeling rivers in the Shenandoah River basin, Virginia.

Model Parameter	Community	FGETS	Virginia
Simulation Control Parameters			
Project title	X	X	X
Length of simulation	X	X	X
Initial month of simulation	X	X	X
Water temperature	X	X	X
Water depth	X	X	X
Benthos standing stocks	X		
Terrestrial insect standing stocks	X		
Periphyton standing stocks	X		
Phytoplankton standing stocks	X		
Zooplankton standing stocks	X		
Chemical Parameters			
Chemical name	X	X	X
Log of chemical's aqueous activity coefficient	X	X	X
Log of metal's binding constant (non-lipid org. matter)	X	X	X
Log of metal's binding constant (refract. org. matter)	X	X	X
Log of chemical's n-octanol/water partition coefficient	X	X	X
Chemical's molar weight (g/mol.)	X	X	X
Chemical's molecular volume (cm ³ /mol.)	X	X	X
Chemical's melting point (°C)	X	X	X
Exposure via benthic organisms	X	X	X
Exposure via incidental terrestrial insects	X	X	X
Exposure via periphyton	X	X	X
Exposure via phytoplankton	X	X	X
Exposure via sediment concentrations	X	X	X
Exposure via aqueous concentrations	X	X	X
Exposure via zooplankton	X	X	
Lethality (LC ₅₀)	optional	optional	
Metabolism (biotransformation rate)	optional	optional	
Fish Parameters			
Common name	X	X	X
Species	X	X	X
Age class duration	X	X	X
Spawning period	X	X	X
Length at maturity	X		
Age-0 weight	X	X	X
Maximum life span	X	X	X
Reproductive biomass investment ratio	X	X	X
Non predatory mortality rate	X		
Weight and length relationship	X	X	X
Gill area	X	X	X
Lamellar length	X	X	X
Lamellar density	X	X	X
Interlamellar distance	X	X	X
Aqueous-lipid relationship	X	X	X

Table 3.2. (continued) Parameters required by the Bioaccumulation and Aquatic System Simulator in community and Food and Gill Exchange of Toxic Substances (FGETS) modes, and in modeling rivers in the Shenandoah River basin, Virginia.

Parameters	Community	FGETS	Virginia
Lipid fraction	X	X	X
Assimilation efficiency for fish	X	X	X
Assimilation efficiency for invertebrates	X	X	X
Assimilation efficiency for vegetation	X	X	X
Routine/standard oxygen consumption	X	X	X
Respiratory quotient	X	X	X
Specific dynamic action/ingestion ratio	X	X	X
Standard oxygen consumption	X	X	X
Feeding variable	X	X	X
Average length of prey (piscivores)	X	X	X
Maximum ingestion (allometric)	X	X	
Specific growth rate (linear)	X	X	X
Maximum filtering (clearance)	X	X	
Satiation meal (holling)	X	X	
Time to satiation (holling)	X	X	
Gastric evacuation (holling)	X	X	
Dietary composition by age/size range	X	X	X
Initial age by age class	X	X	X
Initial weight by age class	X	X	X
Initial population by age class	X		
Initial chemical concentration by age class	optional	optional	

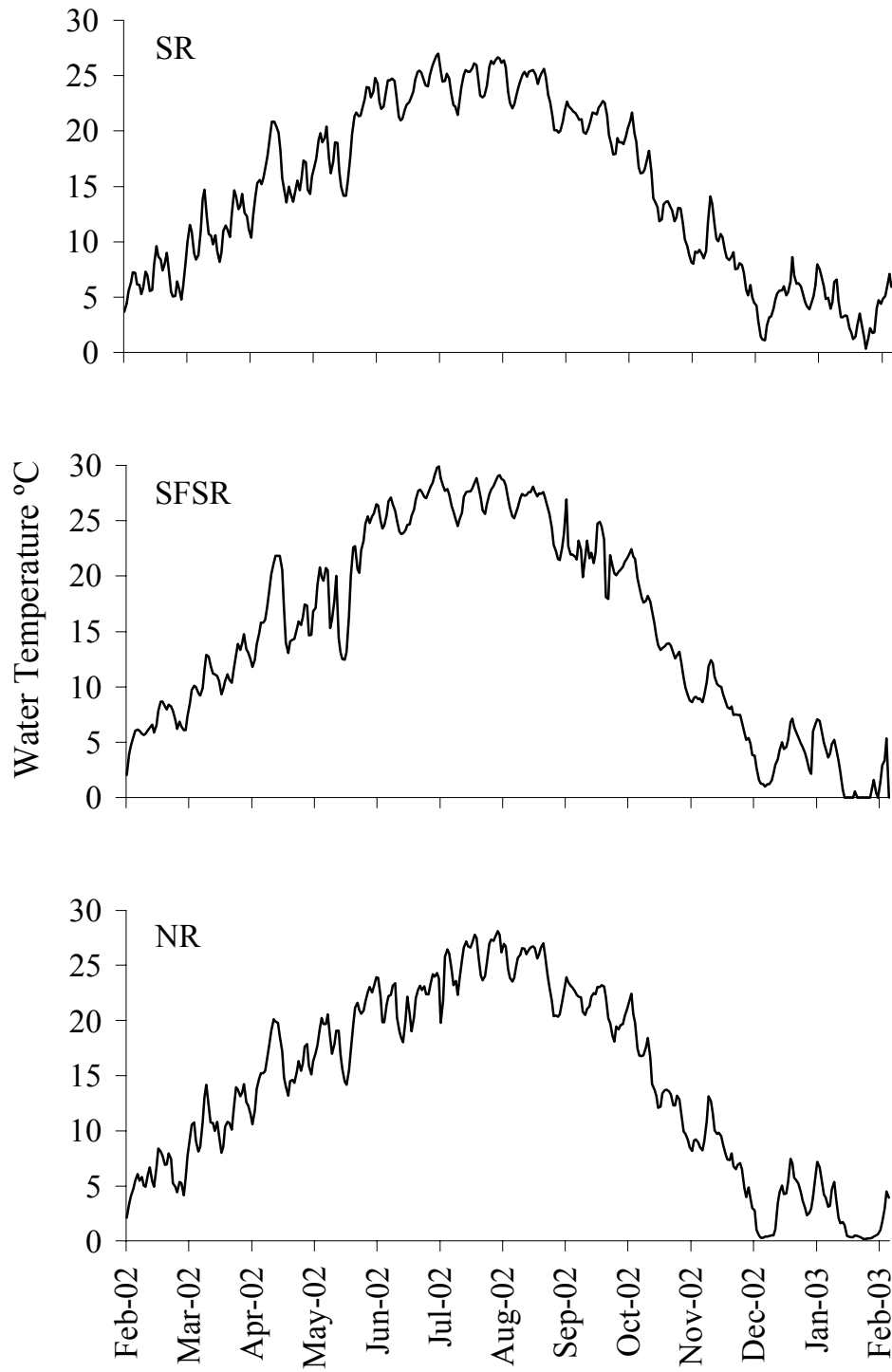


Figure 3.3. Mean daily water temperature in the South River (SR), South Fork of the Shenandoah River (SFSR), and North River (NR), Virginia used for parameterization of the Bioaccumulation and Aquatic System Simulator.

Table 3.3. Chemical properties of methylmercury used for parameterization of the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia.

Chemical Property	Input Values
Log of chemical's aqueous activity coefficient	Model estimates
Log of metal's binding constant (non-lipid organic matter)	7.0
Log of metal's binding constant (refractory organic matter)	5.7
Log of chemical's n-octanol/water partition coefficient	-0.4
Chemical's molar weight (g/mol.)	215.6
Chemical's molecular volume (cm ³ /mol.)	51.0
Chemical's melting point (°C)	25.0

Barber 2001.

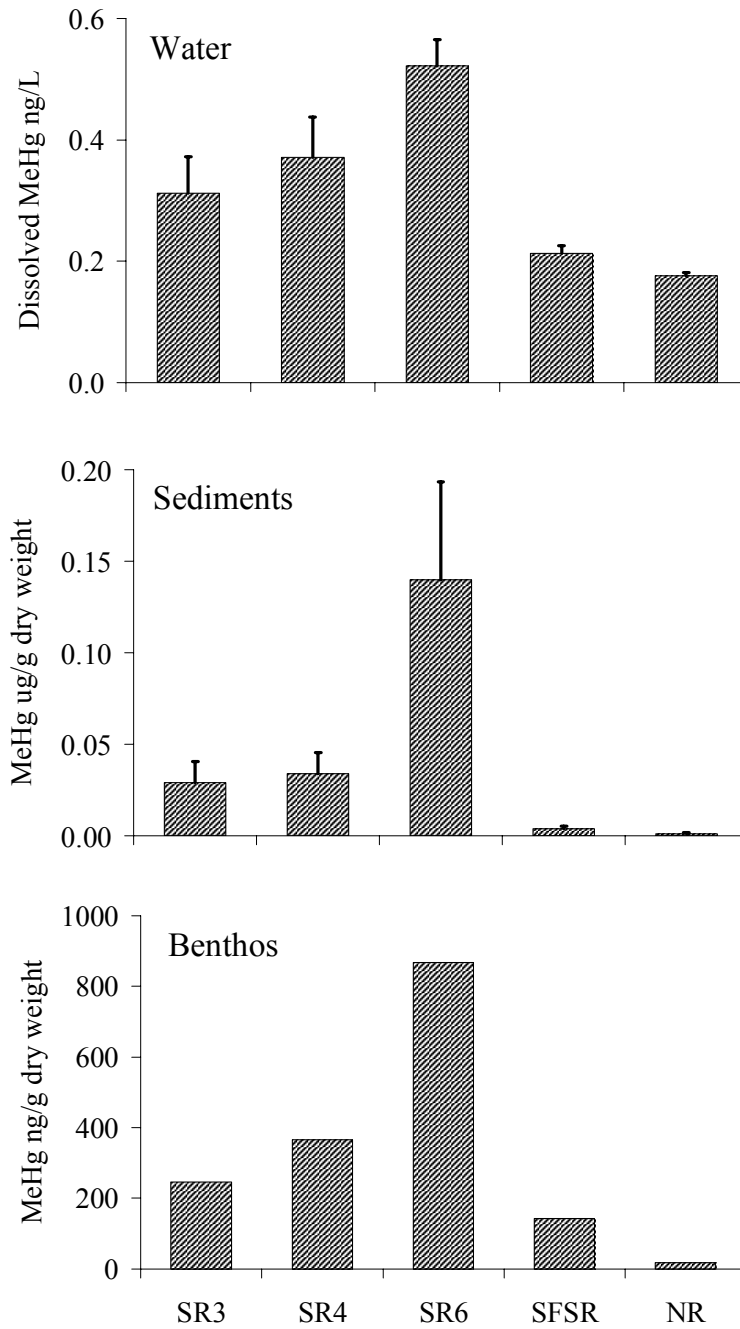


Figure 3.4. Estimated concentrations of methylmercury in water¹, sediments², and benthos³ in the South River (at sites SR3, SR4, and SR6), South Fork of the Shenandoah River (SFSR), and North River (NR), Virginia used to parameterize the Bioaccumulation and Aquatic System Simulator.

¹VDEQ unpublished.

²AMRL 1997.

³Chapter 2.

Table 3.4. Mean concentrations of total mercury (THg) in various taxa of benthos in the South River (at sites SR3, SR4, and SR6), South Fork of the Shenandoah River (SFSR), and North River (NR), Virginia used to parameterize the Bioaccumulation and Aquatic System Simulator.

Prey Type	Taxa Analyzed	THg ng/g wet weight					
		SR3	SR4	SR6	SFSR	NR	
Aquatic Insects							
Anisoptera	Aeshnidae, Gomphidae, Macromiidae	179.6	253.3	436.0	105.0	18.8	
Coleoptera	Psephenidae	52.2	58.4	128.7	-	-	
Diptera	Chironomidae, Tipulidae	60.0	226.0	544.7	23.7	4.8	
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae, Leptohyphidae	56.6	121.6	249.3	47.5	7.1	
Megaloptera	Corydalidae	-	-	-	96.2	-	
Plecoptera	Perlidae	-	-	-	109.0	-	
Trichoptera	Brachycentridae, Hydropsychidae	96.1	171.8	474.7	67.8	10.7	
Zygoptera	Coenagrionidae	122.0	116.0	311.8	69.0	11.7	
Annelida							
Oligochaeta	Oligochaeta	647.0	585.0	1,961.0	-	-	
Mollusca							
Bivalvia	<i>Corbicula fluminea</i>	16.8	38.7	100.3	23.2	1.9	
Gastropoda	Pleuroceridae	30.0	65.8	72.4	23.8	8.5	
Crustacea							
Decapoda	Crayfish	100.4	188.3	330.8	93.4	10.1	

Chapter 2.

Table 3.5. Mean moisture contents (%) of whole invertebrates collected in the Shenandoah River basin, Virginia.

Prey Type	Taxa Analyzed	<i>N</i>	Moisture	±SE
Aquatic Insect				
Anisoptera	Aeshnidae, Gomphidae, Macromiidae	27	82	1.1
Coleoptera	Psephenidae	29	69	0.9
Ephemeroptera	Ephemerellidae, Heptageniidae, Isonychiidae	29	82	1.3
Megaloptera	Corydalidae	12	80	0.5
Trichoptera	Hydropsychidae	30	82	1.0
Zygoptera	Coenagrionidae	28	84	0.7
Terrestrial Insect				
Coleoptera	<i>Cotinis nitida</i>	10	68	1.2
Annelida				
Oligochaeta	Oligochaeta	30	91	0.5
Mollusca				
Bivalvia	<i>Corbicula fluminea</i> (+shell)	24	32	0.8
Gastropoda	Pleuroceridae (+shell)	29	43	0.7
Crustacea				
Decapoda	Crayfish	30	75	0.9

Table 3.6. Recruitment and mortality parameters of *Catostomus commersoni* (WHS), *Cyprinella analostana* (SAT), *Etheostoma flabellare* (FAN), *Ictalurus punctatus* (CCF), *Lepomis auritus* (RDB), *Luxilus cornutus* (COS), *Micropterus dolomieu* (SMB), *Notropis amoenus* (COM), and *Noturus insignis* (MAM) used to parameterize the Bioaccumulation and Aquatic System Simulator for mercury bioaccumulation modeling in the Shenandoah River basin, Virginia.

Parameter	SOUTH RIVER					
	WHS	FAN	RDB	COS	SMB	MAM
Spawning Period ^a	March-April	April-June	May-July	May-June	April-May	May-June
YOY Weight (g) ^b	0.057	0.033	0.068	0.024	0.031	0.030
Maximum Life Span (yr)	11 ^d	5 ^a	9 ^d	5 ^a	10 ^d	4 ^a
Parameter	SOUTH FORK SHENANDOAH RIVER					
	WHS	SAT	CCF	RDB	SMB	MAM
Spawning Period ^a	March-April	April-August	May-July	May-July	April-May	May-June
YOY Weight (g) ^b	0.022	0.024	0.014	0.067	0.035	0.030
Maximum Life Span (yr)	11 ^d	3 ^a	12 ^d	8 ^d	11 ^d	4 ^a
Parameter	NORTH RIVER					
	WHS	RDB	SMB	COM	MAM	-
Spawning Period ^a	March-April	May-July	April-May	April-August	May-June	-
YOY Weight (g) ^b	0.057	0.069	0.032	0.024	0.030	-
Maximum Life Span (yr)	10 ^d	7 ^d	9 ^d	3 ^a	4 ^a	-

^aCarlander 1969, 1977, 1997; Jenkins and Burkhead 1994.

^bEstimated using species and river specific length versus weight power regression assuming initial total length of 15 mm.

^cMaximum age found in this study.

Table 3.7. Summary of allometric coefficients and exponents for length and weight relationships of fish used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation in fish communities in the Shenandoah River basin, Virginia.

Species	α	β	r^2
<u>SOUTH RIVER</u>			
<i>Catostomus commersoni</i>	0.000020	2.9435	0.98
<i>Etheostoma flabellare</i>	0.000010	2.9957	0.90
<i>Lepomis auritus</i>	0.000020	3.0043	0.99
<i>Luxilus cornutus</i>	0.000005	3.1383	0.96
<i>Micropterus dolomieu</i>	0.000010	2.9693	0.99
<u>SOUTH FORK SHENANDOAH RIVER</u>			
<i>Catostomus commersoni</i>	0.000004	3.1879	0.84
<i>Ictalurus punctatus</i>	0.000002	3.2710	0.98
<i>Lepomis auritus</i>	0.000020	3.0006	0.98
<i>Micropterus dolomieu</i>	0.000010	3.0207	0.99
<i>Noturus insignis</i> ¹	0.000008	3.0418	0.80
<u>NORTH RIVER</u>			
<i>Catostomus commersoni</i>	0.000020	2.9423	0.96
<i>Lepomis auritus</i>	0.000020	3.0129	0.99
<i>Micropterus dolomieu</i>	0.000010	2.9820	0.99

¹VDGIF unpublished.

Table 3.8. Summary of allometric coefficients and exponents for gill surface area (cm²), lamellar length (cm), lamellar density (lamellae/mm), and interlamellar distance (cm) used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia. Parameters were specified as allometric power functions of the fish's body weight.

Species	Gill Area		Lamellar Length		Lamellar Density		Interlamellar Distance	
	α	β	α	β	α	β	α	β
<i>Catostomus commersoni</i>	11.2 ^b	0.587 ^e	0.01880 ^b	0.294 ^b	25.2 ^b	-0.1090 ^e		c
<i>Cyprinella analostana</i>	4.33 ^a	0.815 ^a	0.01880 ^b	0.294 ^b	28.9 ^a	-0.0780 ^a		c
<i>Etheostoma flabellare</i>	4.33 ^a	0.815 ^a	0.01880 ^b	0.294 ^b	28.9 ^a	-0.0780 ^a		c
<i>Ictalurus punctatus</i>	4.33 ^a	0.815 ^a	0.00465 ^d	0.265 ^d	10.2 ^d	-0.0560 ^d	0.000607 ^d	0.188 ^d
<i>Lepomis auritus</i>	4.33 ^a	0.815 ^a	0.00364 ^e	0.234 ^e	20.1 ^c	-0.0980 ^e	0.001160 ^e	0.047 ^e
<i>Luxilus cornutus</i>	4.33 ^a	0.815 ^a	0.01880 ^b	0.294 ^b	28.9 ^a	-0.0780 ^a		c
<i>Micropterus dolomieu</i>	7.36 ^f	0.819 ^f	0.01880 ^b	0.294 ^b	30.0 ^f	-0.0615 ^f		c
<i>Notropis amoenus</i>	4.33 ^a	0.815 ^a	0.01880 ^b	0.294 ^b	28.9 ^a	-0.0780 ^a		c
<i>Noturus insignis</i>	4.98 ^h	0.728 ^h	0.01880 ^b	0.294 ^b	15.9 ^h	-0.0917 ^h		c

^aBASS default, geometric mean power function of Tables 5 and 6 in Barber 2003.

^bBASS default, interspecific functional regression in Barber 2001, 2003.

^cBASS estimates interlamellar distance from lamellar density.

^dBarber 2001.

^eAssumed value of *Lepomis macrochirus*, Brockway et al. unpublished.

^fPrice 1931.

^gSaunders 1962.

^hAssumed value of *Ameiurus nebulosus*; Saunders 1962.

Table 3.9. Summary of coefficients for aqueous lipid relationships and lipid fractions used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in the Shenandoah River basin, Virginia. Aqueous fraction was specified as a linear function of the fish's lipid fraction and lipid fraction was specified as an allometric function of the fish's body weight.

Species	Aqueous Fraction		Lipid Fraction	
	α	β	α	β
<i>Catostomus commersoni</i>	0.795 ^c	-0.818 ^c	0.04824 ^c	-
<i>Cyprinella analostana</i>	0.820 ^a	-1.250 ^a	0.04000 ^b	-
<i>Etheostoma flabellare</i>	0.820 ^a	-1.250 ^a	0.04000 ^b	-
<i>Ictalurus punctatus</i>	0.781 ^c	-0.665 ^c	0.05470 ^c	0.054 ^c
<i>Lepomis auritus</i>	0.763 ^d	-0.721 ^d	0.00219 ^d	0.881 ^d
<i>Luxilus cornutus</i>	0.820 ^a	-1.250 ^a	0.04000 ^b	-
<i>Micropterus dolomieu</i>	0.800 ^c	-1.568 ^c	0.00408 ^c	0.369 ^c
<i>Notropis amoenus</i>	0.820 ^a	-1.250 ^a	0.04000 ^b	-
<i>Noturus insignis</i>	0.760 ^{ce}	-1.226 ^{ce}	0.00836 ^{ce}	0.277 ^{ce}

^aBASS default, geometric mean of data in Table 3 in Barber et al. 1991.

^bBASS default, pers. comm. C. Barber, USEPA (corresponds to moisture content of 77%).

^cLowe et al. 1985; Schmitt et al. 1990; Schmitt and Brumbaugh 1990.

^dAssumed value for *Lepomis macrochirus*, Brockway et al. unpublished.

^eAssumed value for *Ameiurus nebulosus*.

Table 3.10. Physiological parameters used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia, where RT/SO = routine/standard oxygen consumption, RQ = respiratory quotient, and SDA/ingestion = specific dynamic action/ingestion ratio.

Species	Assimilation Efficiency			RT/SO ²	RQ ¹²	SDA/Ingestion ²	Standard Oxygen Consumption ³
	Fish ³	Invert ³	Veg ²				
<i>Catostomus commersoni</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.047*W[g] ^{0.659} e ^{-0.121T[Celsius]}
<i>Cyprinella analostana</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.013*W[g] ^{-0.935} e ^{0.095T[Celsius]}
<i>Etheostoma flabellare</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.015*W[g] ^{-0.833} e ^{0.113T[Celsius]}
<i>Ictalurus punctatus</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.030*W[g] ^{-0.883} e ^{0.037T[Celsius]}
<i>Lepomis auritus</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.226*W[g] ^{-0.606} e ^{0.006T[Celsius]}
<i>Luxilus cornutus</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.013*W[g] ^{-0.935} e ^{0.095T[Celsius]}
<i>Micropterus dolomieu</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.226*W[g] ^{-0.606} e ^{0.006T[Celsius]}
<i>Notropis amoenus</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.013*W[g] ^{-0.935} e ^{0.095T[Celsius]}
<i>Noturus insignis</i>	0.85	0.82	0.44	2	1	0.17	sol[mg(O ₂)/hr]=0.030*W[g] ^{-0.883} e ^{0.037T[Celsius]}

¹Barber 1991.

²Barber 2001.

³Barber 2004.

Table 3.1.1. Back-calculated total lengths at age of fish used to parameterize the Bioaccumulation and Aquatic System Simulator to model bioaccumulation dynamics of methylmercury in fish communities in the Shenandoah River basin, Virginia. Older age classes with few individuals were truncated due to variance.

Species	Age-1	Age-2	Age-3	Age-4	Age-5	Age-6	Age-7	Age-8	Age-9	Age-10
	<u>SOUTH RIVER</u>									
<i>Catostomus commersoni</i>	145.4	241.1	308.2	349.6	382.3	395.0	403.6	428.2	453.2	
<i>Etheostoma flabellare</i>	42.0	49.0	57.0	68.0						
<i>Lepomis auritus</i>	60.4	97.3	127.3	145.9	159.5	163.9	169.4			
<i>Luxilus cornutus</i>	58.5	83.3	107.3	132.0	140.1					
<i>Micropterus dolomieu</i>	104.2	167.0	217.4	251.2	285.0	317.5	349.4	383.7	401.2	
<i>Noturus insignis</i>	54.0	91.0	118.0	134.0						
	<u>SOUTH FORK SHENANDOAH RIVER</u>									
<i>Catostomus commersoni</i>	166.9	281.6	344.0	387.7	415.5	417.6	429.9	457.3	479.7	
<i>Cyprinella analostana</i>	58.5	83.3	107.3							
<i>Ictalurus punctatus</i>	164.4	285.3	387.0	467.3	528.9	555.2	584.7	634.9	659.9	
<i>Lepomis auritus</i>	66.9	114.1	151.7	175.1	187.6	193.0				
<i>Micropterus dolomieu</i>	118.1	182.1	232.0	275.1	315.8	354.2	375.6	394.8	398.4	
<i>Noturus insignis</i>	54.0	91.0	118.0	134.0						
	<u>NORTH RIVER</u>									
<i>Catostomus commersoni</i>	151.9	256.7	325.3	372.3	403.6	412.4	420.0	436.7	472.2	503.9
<i>Lepomis auritus</i>	69.0	110.8	144.6	168.7	178.7	201.0	210.0			
<i>Micropterus dolomieu</i>	107.2	170.4	212.0	243.6	282.7	321.1	335.6	353.0		
<i>Notropis amoenus</i>	58.5	83.3	107.3							
<i>Noturus insignis</i>	54.0	91.0	118.0	134.0						

Table 3.12. Summary of allometric coefficients and exponents for specific growth rates of fish used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia.

Species	α	β	r^2
<u>SOUTH RIVER</u>			
<i>Catostomus commersoni</i>	0.2481	-0.9250	0.97
<i>Etheostoma flabellare</i> ¹	0.0021	-1.0707	0.94
<i>Lepomis auritus</i>	0.0320	-0.9500	0.87
<i>Luxilus cornutus</i> ¹	0.0126	-0.8718	0.97
<i>Micropterus dolomieu</i>	0.0679	-0.7762	0.97
<i>Noturus insignis</i> ¹	0.0141	-0.8056	0.99
<u>SOUTH FORK SHENANDOAH RIVER</u>			
<i>Catostomus commersoni</i>	0.2707	-0.9568	0.92
<i>Cyprinella analostana</i> ¹	0.0119	-0.8841	0.99
<i>Ictalurus punctatus</i>	0.3536	-0.8346	0.99
<i>Lepomis auritus</i>	0.0473	-0.9117	0.96
<i>Micropterus dolomieu</i>	0.1175	-0.8997	0.94
<i>Noturus insignis</i> ¹	0.0141	-0.8056	0.99
<u>NORTH RIVER</u>			
<i>Catostomus commersoni</i>	0.2801	-0.9282	0.95
<i>Lepomis auritus</i>	0.0506	-0.8806	0.98
<i>Micropterus dolomieu</i>	0.0733	-0.8560	0.98
<i>Notropis amoenus</i> ¹	0.0141	-0.8056	0.99
<i>Noturus insignis</i> ¹	0.0119	-0.8841	0.99

¹Age data obtained from Carlander 1969, 1997.

Table 3.13. Dietary composition (%) of *Catostomus commersoni* (WHS), *Cyprinella analostana* (SAT), *Etheostoma flabellare* (FAN), *Ictalurus punctatus* (CCF), *Lepomis auritus* (RDB), *Luxilus cornutus* (COS), *Micropterus dolomieu* (SMB), *Notropis amoenus* (COM), and *Noturus insignis* (MAM) used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia.

SOUTH RIVER											
Diet Category	WHS	FAN	COS	<100	RDB			SMB			MAM
					100-150	>150	<100	100-199	200-299	>299	
Benthos	28.0	100.0	100.0	100.0	99.0	80.0	89.0	63.0	82.0	50.0	100.0
Terrestrial Insect	-	-	-	-	1.0	20.0	3.0	3.0	3.0	2.0	-
FAN	-	-	-	-	-	-	2.0	26.8	10.0	-	-
COS	-	-	-	-	-	-	2.0	2.0	1.1	29.0	-
RDB	-	-	-	-	-	-	2.0	1.1	1.9	19.0	-
MAM	-	-	-	-	-	-	2.0	5.0	2.0	-	-
Periphyton	72.0	-	-	-	-	-	-	-	-	-	-

SOUTH FORK SHENANDOAH RIVER											
Diet Category	WHS	SAT	CCF	<100	RDB			SMB			MAM
					100-150	>150	<100	100-199	200-299	>299	
Benthos	29.6	100.0	12.2	96.6	97.1	89.9	100.0	82.9	66.9	47.6	100.0
Terrestrial Insect	-	-	3.0	-	-	3.6	-	-	-	-	-
SAT	-	-	-	-	-	-	-	4.6	6.2	3.5	-
RDB	-	-	7.9	-	-	1.8	-	10.5	16.4	23.2	-
SMB	-	-	11.6	-	-	-	-	-	2.3	6.1	-
MAM	-	-	-	-	-	-	-	-	8.2	17.4	-
Phytoplankton	4.1	-	65.3	3.4	2.9	4.7	-	2.0	-	2.2	-
Periphyton	66.3	-	-	-	-	-	-	-	-	-	-

Table 3.13. (continued) Dietary composition (%) of *Catostomus commersoni* (WHS), *Cyprinella analostana* (SAT), *Etheostoma flabellare* (FAN), *Ictalurus punctatus* (CCF), *Lepomis auritus* (RDB), *Luxilus cornutus* (COS), *Micropterus dolomieu* (SMB), *Notropis amoenus* (COM), and *Noturus insignis* (MAM) used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia.

Diet Category	NORTH RIVER									
	WHS	COM	<100	100-150	>150	<100	100-199	200-299	>299	MAM
Benthos	29.9	100.0	100.0	98.0	87.0	100.0	77.4	72.3	65.2	100.0
Terrestrial Insect	-	-	-	2.0	11.9	-	3.2	5.7	16.7	-
RDB	-	-	-	-	1.1	-	14.0	6.9	1.1	-
SMB	-	-	-	-	-	-	5.4	8.4	2.0	-
COM	-	-	-	-	-	-	-	4.6	4.8	-
MAM	-	-	-	-	-	-	-	2.1	10.2	-
Periphyton	70.1	-	-	-	-	-	-	-	-	-

Table 3.14. Initial body weights (g) of fish by cohort used to parameterize the Bioaccumulation and Aquatic System Simulator to model methylmercury bioaccumulation dynamics in fish communities in the Shenandoah River basin, Virginia. Older age classes with <5 individuals were truncated due to variance.

Species	Age-1	Age-2	Age-3	Age-4	Age-5	Age-6	Age-7	Age-8	Age-9	Age-10
<u>SOUTH RIVER</u>										
<i>Catostomus commersoni</i>	46.0	205.4	422.7	615.9	796.8	879.3	939.5	1,113.5	1,316.0	-
<i>Etheostoma flabellare</i>	0.7	1.2	1.8	3.1	-	-	-	-	-	-
<i>Lepomis auritus</i>	4.5	18.8	42.2	63.4	82.9	90.0	99.4	-	-	-
<i>Luxilus cornutus</i>	1.8	5.3	11.8	22.6	27.3	-	-	-	-	-
<i>Micropterus dolomieu</i>	9.8	39.8	86.6	133.5	194.6	266.9	355.1	471.7	536.4	-
<i>Noturus insignis</i>	1.5	7.4	16.0	23.6	-	-	-	-	-	-
<u>SOUTH FORK SHENANDOAH RIVER</u>										
<i>Catostomus commersoni</i>	48.6	258.9	487.9	716.1	894.3	908.0	993.8	1,206.7	1,411.2	-
<i>Cyprinella analostana</i>	1.8	5.3	11.8	-	-	-	-	-	-	-
<i>Ictalurus punctatus</i>	35.1	214.2	582.7	1,077.4	1,619.8	1,895.0	2,251.1	2,943.8	3,340.1	-
<i>Lepomis auritus</i>	6.0	29.7	70.4	107.5	133.3	144.2	-	-	-	-
<i>Micropterus dolomieu</i>	18.1	67.1	139.8	233.6	355.5	500.9	601.0	697.5	713.6	-
<i>Noturus insignis</i>	1.5	7.4	16.0	23.6	-	-	-	-	-	-
<u>NORTH RIVER</u>										
<i>Catostomus commersoni</i>	52.6	246.5	491.8	731.7	932.8	988.2	1,045.7	1,175.2	1,474.2	1,788.1
<i>Lepomis auritus</i>	6.9	29.1	65.0	103.1	122.6	173.9	198.4	-	-	-
<i>Micropterus dolomieu</i>	11.3	44.8	86.5	131.6	204.8	298.1	341.6	395.8	-	-
<i>Notropis amoenus</i>	1.8	5.3	11.8	-	-	-	-	-	-	-
<i>Noturus insignis</i>	1.5	7.4	16.0	23.6	-	-	-	-	-	-

Table 3.15 Linear relationships between model-predicted concentrations of methylmercury in fish muscle tissue and fish weight and age at sites SR3, SR4, and SR6 on the South River, Virginia. Significant relationships are highlighted ($\alpha = 0.05$).

Species	<i>m</i>	B	<i>r</i> ²	<i>P</i>	Variable
<u>SR3</u>					
<i>Catostomus commersoni</i>	0.0540	0.354	0.94	<0.0001	Age
<i>Etheostoma flabellare</i>	0.1920	0.158	0.99	0.0003	Age
<i>Lepomis auritus</i>	0.1240	0.148	0.99	<0.0001	Age
<i>Luxilus cornutus</i>	0.0880	0.124	0.99	<0.0001	Age
<i>Micropterus dolomieu</i>	0.1420	0.385	0.96	<0.0001	Age
<i>Noturus insignis</i>	0.0930	0.100	0.99	0.0003	Age
<i>Catostomus commersoni</i>	0.0003	0.408	0.92	<0.0001	Weight
<i>Etheostoma flabellare</i>	0.2245	0.261	0.98	0.0006	Weight
<i>Lepomis auritus</i>	0.0087	0.233	0.99	<0.0001	Weight
<i>Luxilus cornutus</i>	0.0184	0.198	0.98	0.0007	Weight
<i>Micropterus dolomieu</i>	0.0021	0.582	0.94	<0.0001	Weight
<i>Noturus insignis</i>	0.0116	0.182	0.97	0.0110	Weight
<u>SR4</u>					
<i>Catostomus commersoni</i>	0.0690	0.453	0.94	<0.0001	Age
<i>Etheostoma flabellare</i>	0.2700	0.238	0.99	0.0002	Age
<i>Lepomis auritus</i>	0.1790	0.265	0.99	<0.0001	Age
<i>Luxilus cornutus</i>	0.1750	0.133	0.99	<0.0001	Age
<i>Micropterus dolomieu</i>	0.2010	0.538	0.96	<0.0001	Age
<i>Noturus insignis</i>	0.1300	0.155	0.99	0.0006	Age
<i>Catostomus commersoni</i>	0.0004	0.522	0.91	<0.0001	Weight
<i>Etheostoma flabellare</i>	0.3157	0.383	0.98	0.0005	Weight
<i>Lepomis auritus</i>	0.0105	0.396	0.99	<0.0001	Weight
<i>Luxilus cornutus</i>	0.0260	0.288	0.98	0.0005	Weight
<i>Micropterus dolomieu</i>	0.0030	0.816	0.94	<0.0001	Weight
<i>Noturus insignis</i>	0.0163	0.270	0.97	0.0122	Weight
<u>SR6</u>					
<i>Catostomus commersoni</i>	0.1200	0.801	0.94	<0.0001	Age
<i>Etheostoma flabellare</i>	0.5850	0.561	0.99	0.0003	Age
<i>Lepomis auritus</i>	0.3000	0.831	0.96	<0.0001	Age
<i>Luxilus cornutus</i>	0.3800	0.326	0.99	<0.0001	Age
<i>Micropterus dolomieu</i>	0.4330	1.187	0.96	<0.0001	Age
<i>Noturus insignis</i>	0.2910	0.365	0.99	0.0003	Age
<i>Catostomus commersoni</i>	0.0007	0.922	0.92	<0.0001	Weight
<i>Etheostoma flabellare</i>	0.6839	0.876	0.98	0.0007	Weight
<i>Lepomis auritus</i>	0.0176	1.054	0.96	<0.0001	Weight
<i>Luxilus cornutus</i>	0.0564	0.662	0.98	0.0005	Weight
<i>Micropterus dolomieu</i>	0.0064	1.786	0.94	<0.0001	Weight
<i>Noturus insignis</i>	0.0366	0.622	0.97	0.0103	Weight

Table 3.16. Linear relationships between model-predicted concentrations of methylmercury in fish muscle tissue and fish weight and age in the South Fork of the Shenandoah River, Virginia. Significant relationships are highlighted ($\alpha = 0.05$).

Species	<i>m</i>	<i>b</i>	<i>r</i> ²	<i>P</i>	Variable
<i>Catostomus commersoni</i>	0.0370	0.250	0.92	<0.0001	Age
<i>Cyprinella analostana</i>	0.0850	0.040	0.98	0.0646	Age
<i>Ictalurus punctatus</i>	0.0520	0.079	0.93	<0.0001	Age
<i>Lepomis auritus</i>	0.0470	0.129	0.97	<0.0001	Age
<i>Micropterus dolomieu</i>	0.0759	0.085	0.99	<0.0001	Age
<i>Noturus insignis</i>	0.0560	0.065	0.99	0.0006	Age
<i>Catostomus commersoni</i>	0.0002	0.286	0.90	<0.0001	Weight
<i>Cyprinella analostana</i>	0.0168	0.102	0.99	0.0241	Weight
<i>Ictalurus punctatus</i>	0.0001	0.159	0.89	<0.0001	Weight
<i>Lepomis auritus</i>	0.0015	0.175	0.94	<0.0001	Weight
<i>Micropterus dolomieu</i>	0.0007	0.158	0.98	<0.0001	Weight
<i>Noturus insignis</i>	0.0074	0.113	0.98	0.0092	Weight

Table 3.17. Linear relationships between model-predicted concentrations of methylmercury in fish muscle tissue and fish weight and age in the South Fork of the Shenandoah River, Virginia. Significant relationships are highlighted ($\alpha = 0.05$).

Species	<i>m</i>	<i>b</i>	<i>r</i> ²	<i>P</i>	Variable
<i>Catostomus commersoni</i>	0.0260	0.120	0.95	<0.0001	Age
<i>Lepomis auritus</i>	0.0160	0.024	0.96	0.0001	Age
<i>Micropterus dolomieu</i>	0.0160	0.024	0.98	<0.0001	Age
<i>Notropis amoenus</i>	0.0250	0.003	0.98	0.0732	Age
<i>Noturus insignis</i>	0.0170	0.005	0.97	0.0102	Age
<i>Catostomus commersoni</i>	0.0001	0.144	0.93	<0.0001	Weight
<i>Lepomis auritus</i>	0.0005	0.038	0.94	0.0002	Weight
<i>Micropterus dolomieu</i>	0.0002	0.042	0.96	<0.0001	Weight
<i>Notropis amoenus</i>	0.0049	0.020	0.99	0.0076	Weight
<i>Noturus insignis</i>	0.0021	0.020	0.93	0.0313	Weight

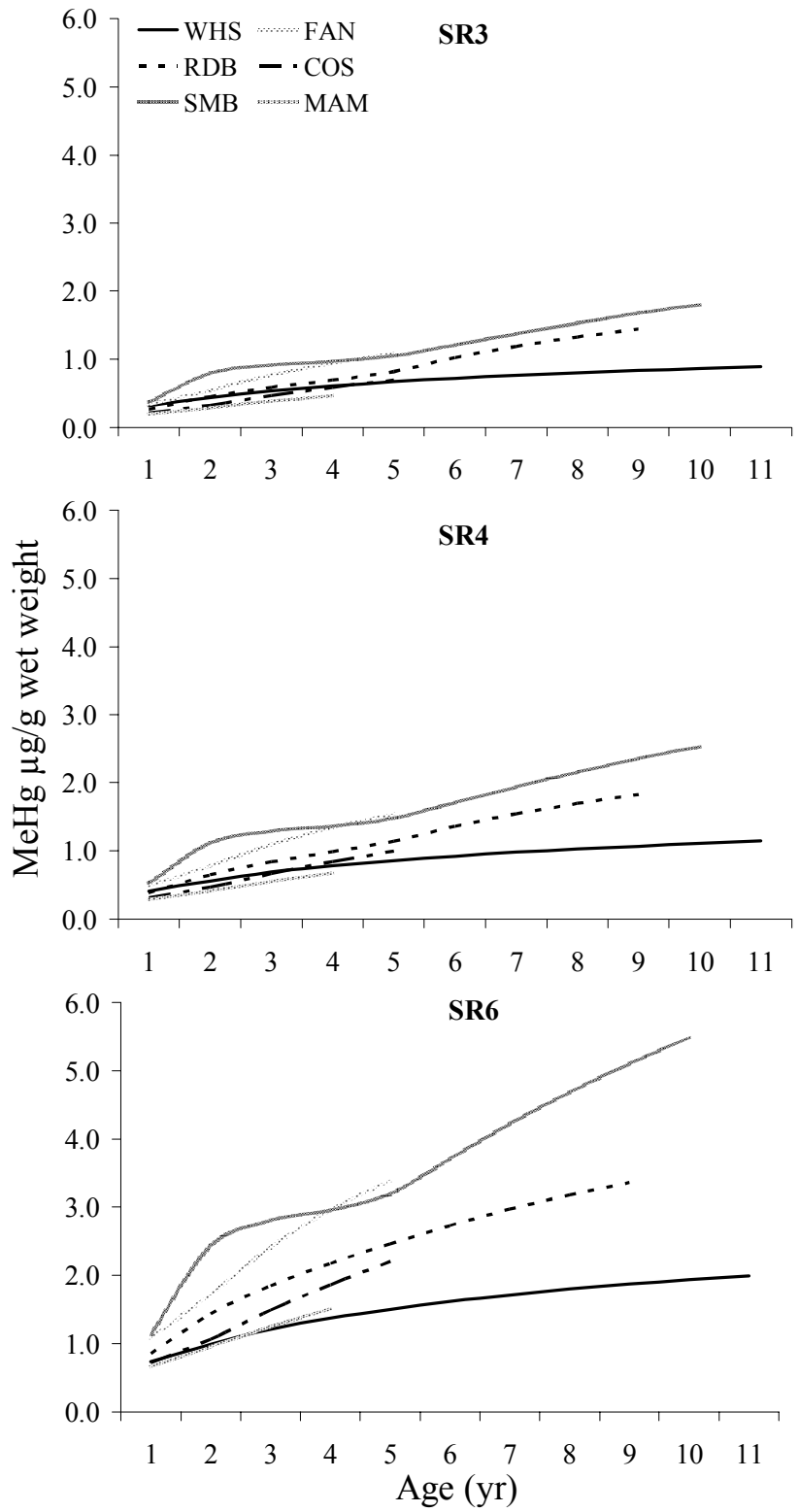


Figure 3.5. Model-predicted concentrations of methylmercury (MeHg) in *Catostomus commersoni* (WHS), *Etheostoma flabellare* (FAN), *Lepomis auritus* (RDB), *Luxilus cornutus* (COS), *Micropterus dolomieu* (SMB), and *Noturus insignis* (MAM) at sites SR3, SR4, and SR6 on the South River, Virginia.

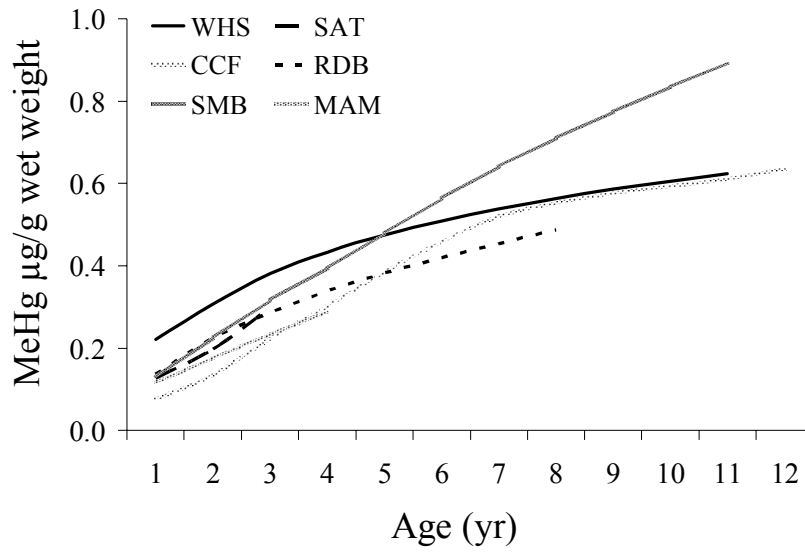


Figure 3.6. Model-predicted concentrations of methylmercury (MeHg) in *Catostomus commersoni* (WHS), *Cyprinella analostana* (SAT), *Ictalurus punctatus* (CCF), *Lepomis auritus* (RDB), *Micropterus dolomieu* (SMB), and *Noturus insignis* (MAM) in the South Fork of the Shenandoah River, Virginia.

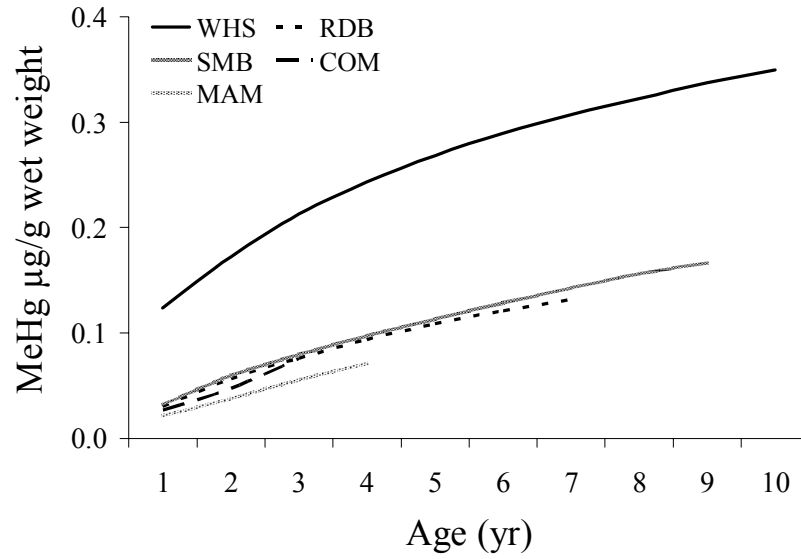


Figure 3.7. Model-predicted concentrations of methylmercury (MeHg) in *Catostomus commersoni* (WHS), *Lepomis auritus* (RDB), *Micropterus dolomieu* (SMB), *Notropis amoenus* (COM), and *Noturus insignis* (MAM) in the North River, Virginia.

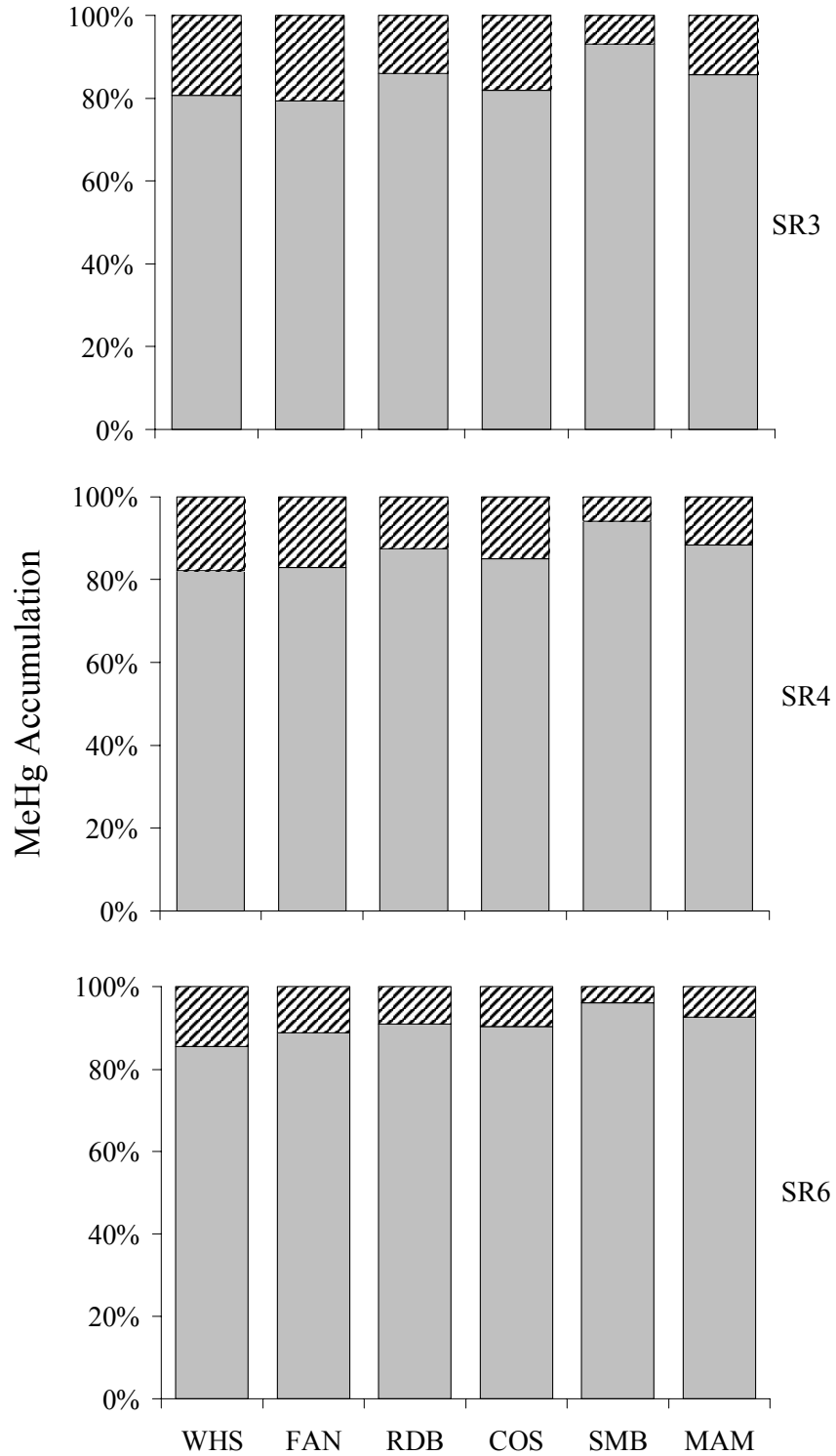


Figure 3.8. Model-predicted uptake of methylmercury (MeHg) through dietary (solid) and aqueous (bars) pathways by *Catostomus commersoni* (WHS), *Etheostoma flabellare* (FAN), *Lepomis auritus* (RDB), *Luxilus cornutus* (COS), *Micropterus dolomieu* (SMB), and *Noturus insignis* (MAM) at sites SR3, SR4, and SR6 on the South River, Virginia.

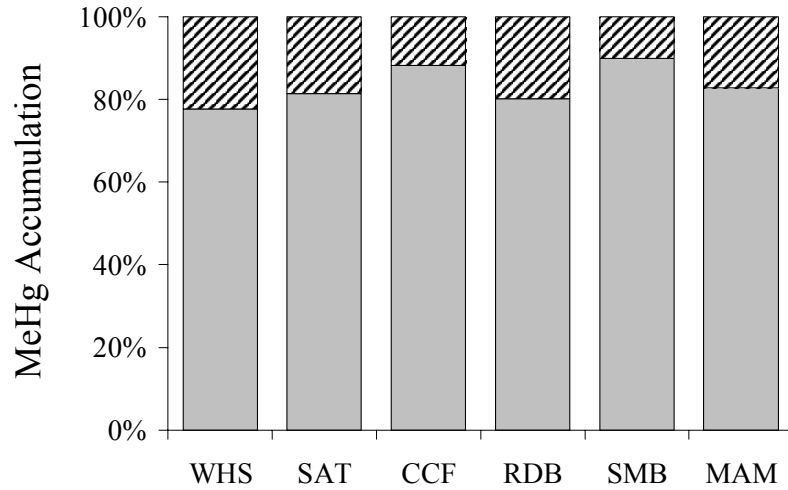


Figure 3.9. Model-predicted uptake of methylmercury (MeHg) through dietary (solid) and aqueous (bars) pathways by *Catostomus commersoni* (WHS), *Cyprinella analostana* (SAT), *Ictalurus punctatus* (CCF), *Lepomis auritus* (RDB), *Micropterus dolomieu* (SMB), and *Noturus insignis* (MAM) in the South Fork of the Shenandoah River, Virginia.

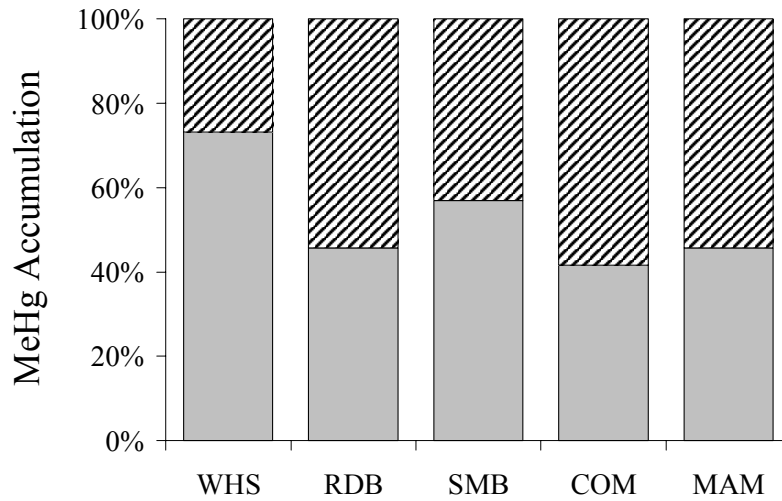


Figure 3.10. Model-predicted uptake of methylmercury (MeHg) through dietary (solid) and aqueous (bars) pathways by *Catostomus commersoni* (WHS), *Lepomis auritus* (RDB), *Micropterus dolomieu* (SMB), *Notropis amoenus* (COM), and *Noturus insignis* (MAM) in the North River, Virginia.

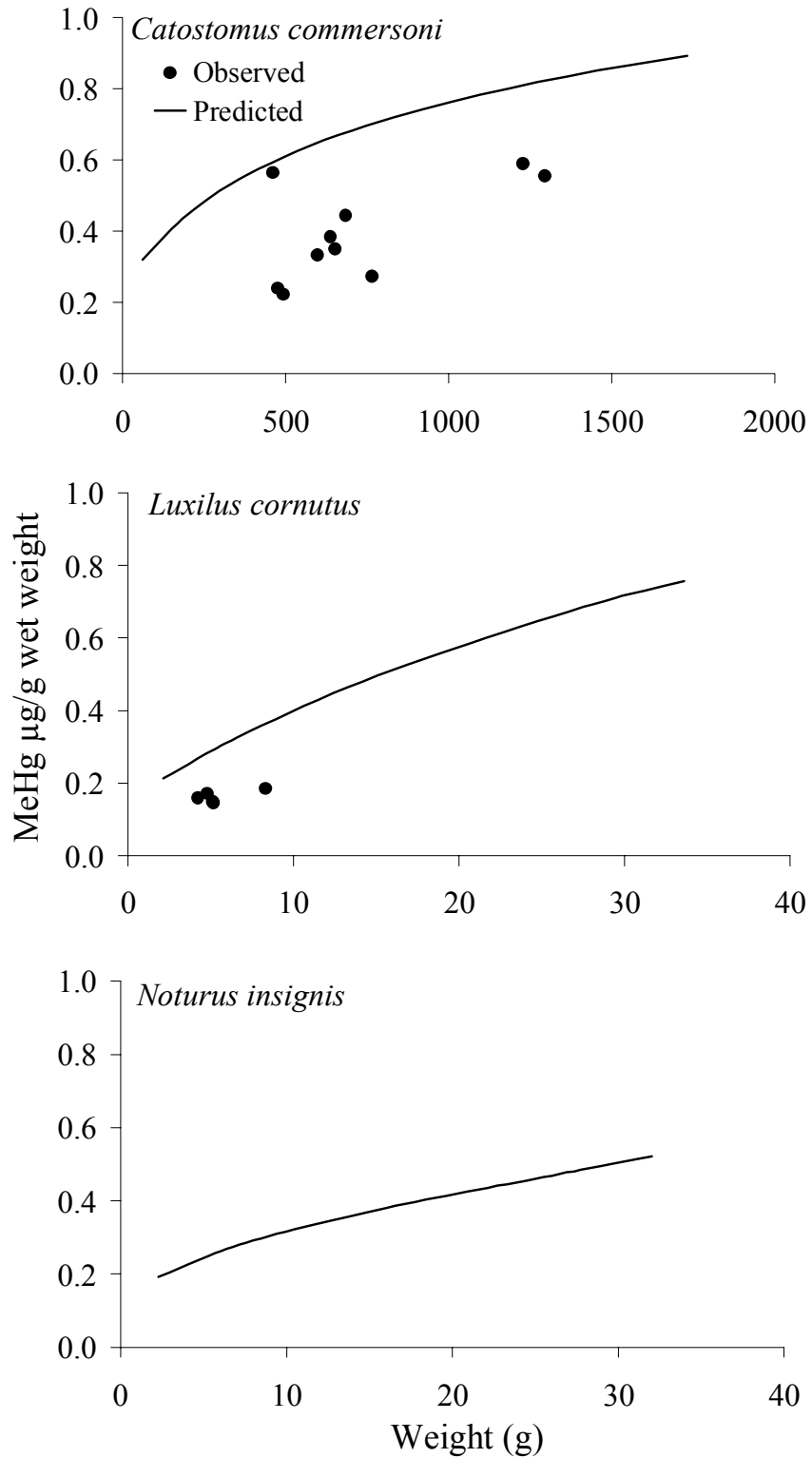


Figure 3.11. Model-predicted and observed concentrations of methylmercury (MeHg) in fish muscle tissue at site SR3 on the South River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

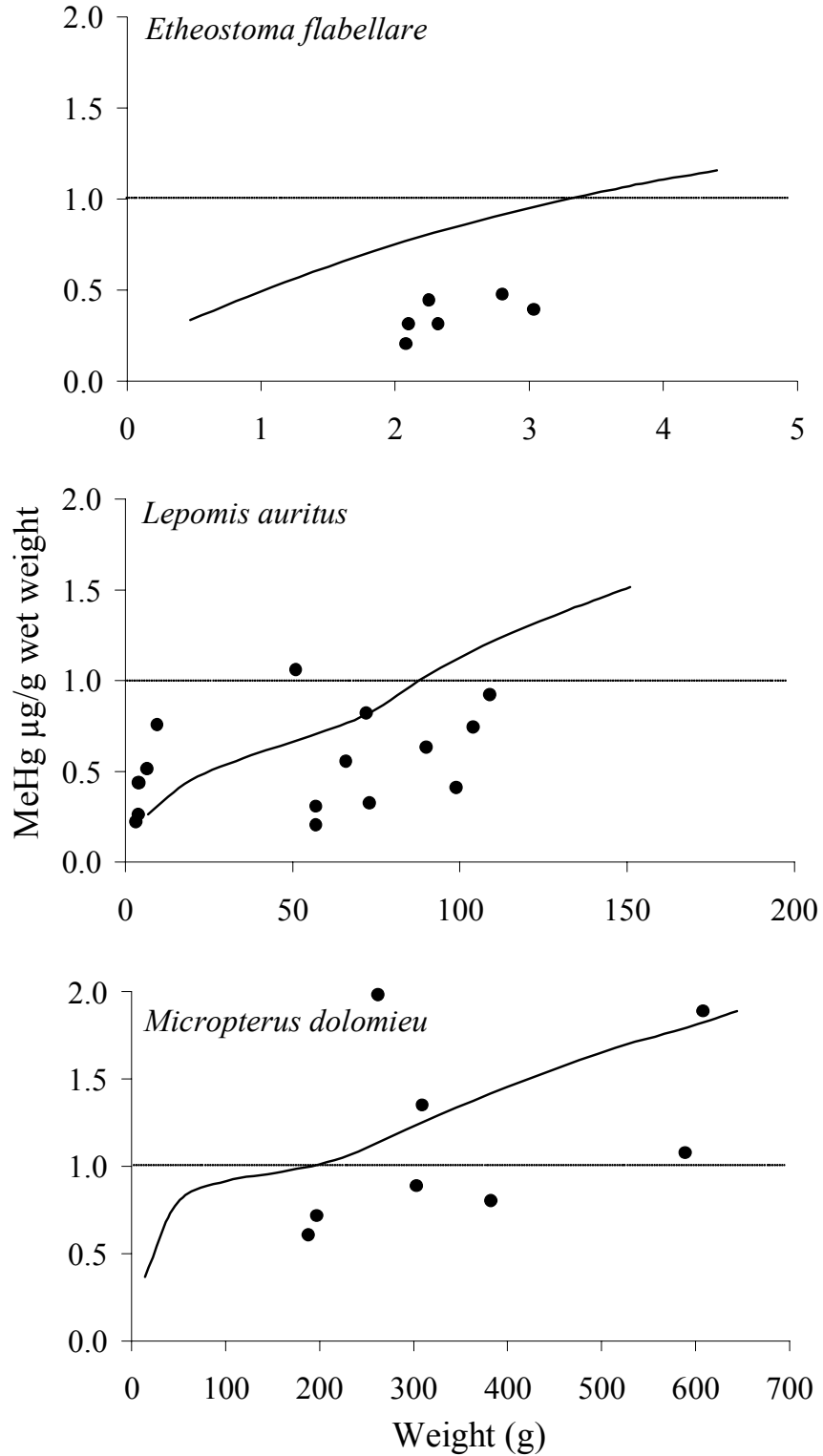


Figure 3.11. (continued) Model-predicted and observed concentrations of methylmercury (MeHg) in fish at site SR3 on the South River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

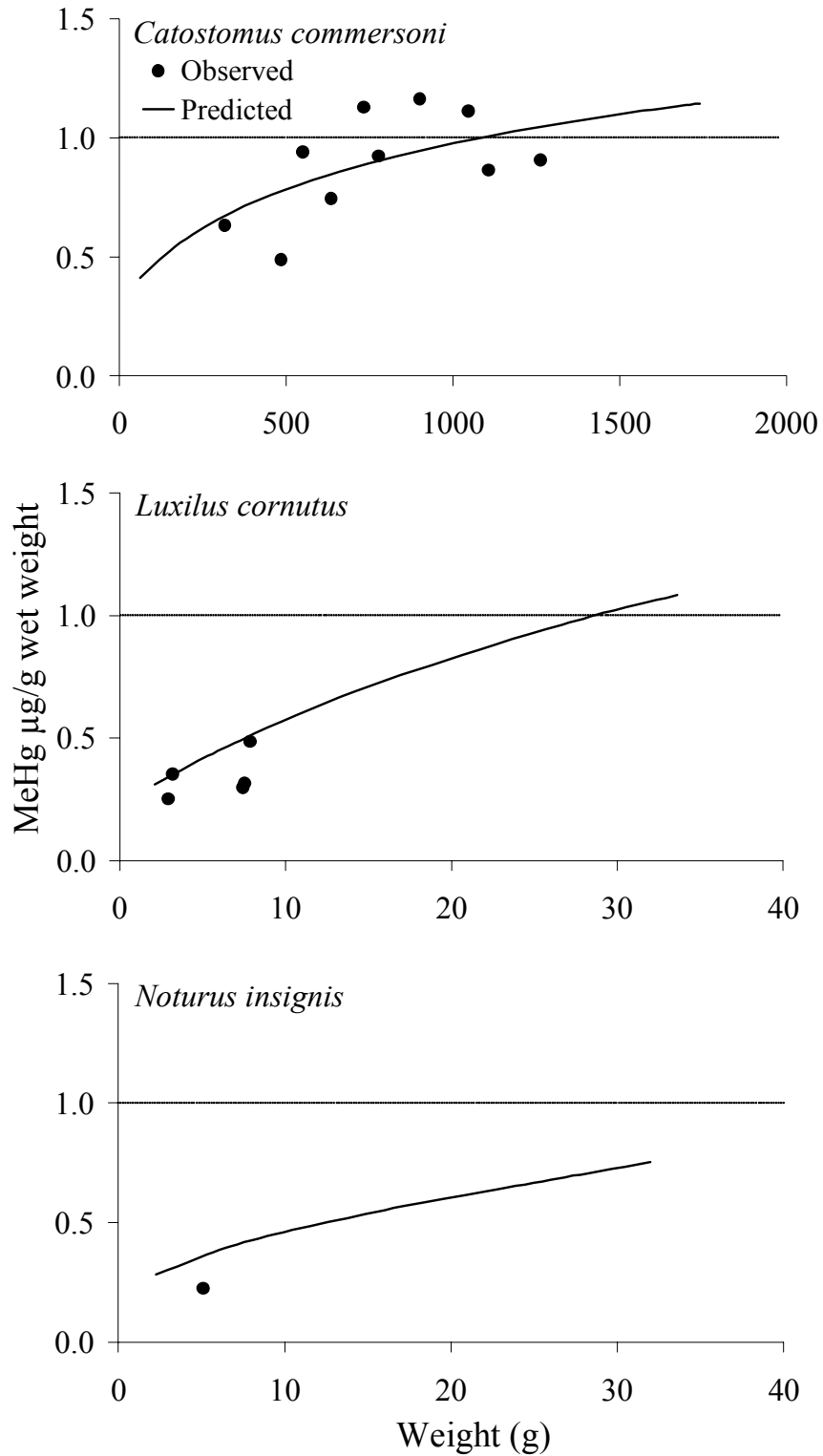


Figure 3.12. Model-predicted and observed concentrations of methylmercury (MeHg) in fish at site SR4 on the South River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

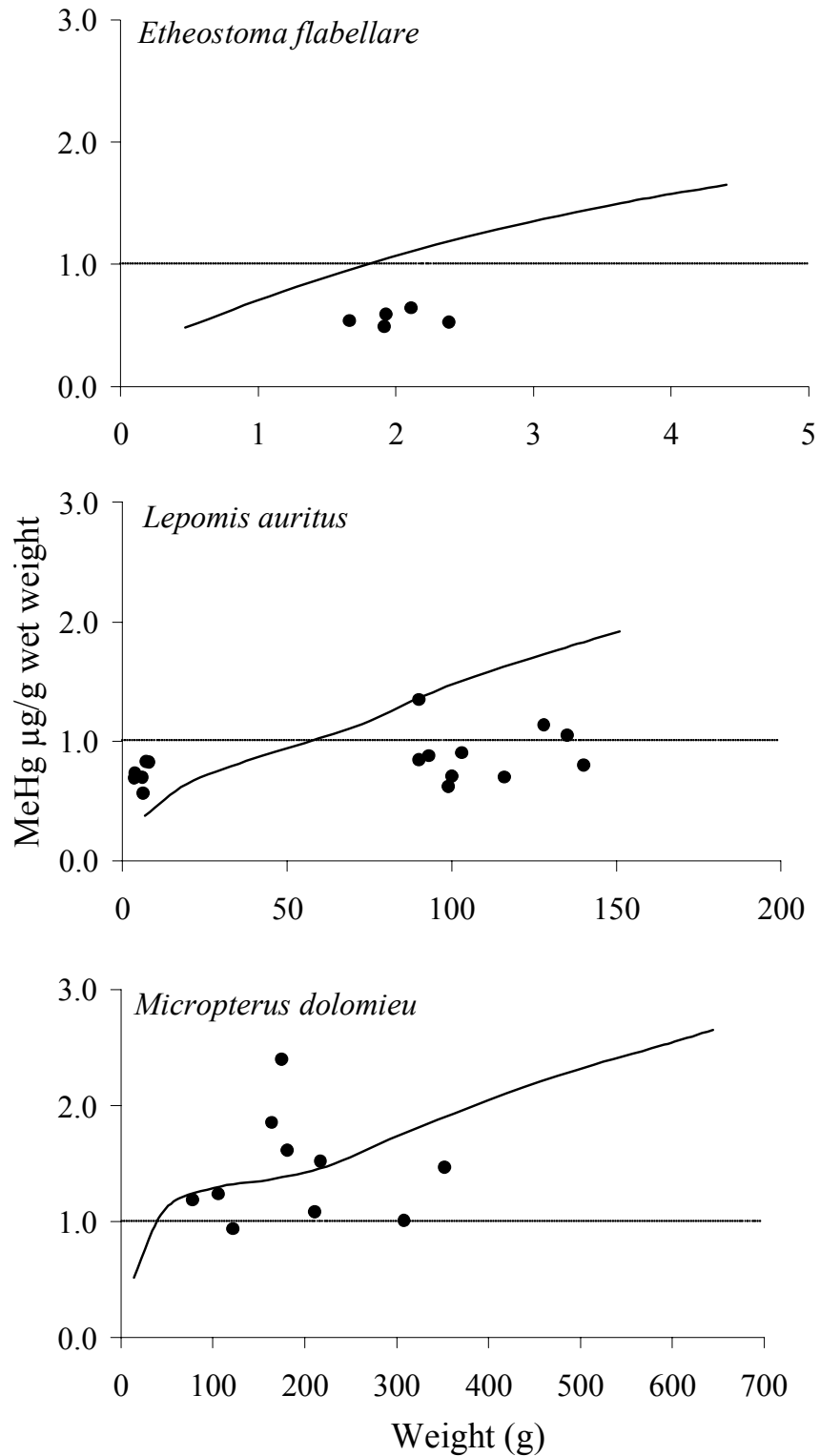


Figure 3.12. (continued) Model-predicted and observed concentrations of methylmercury (MeHg) in fish at site SR4 on the South River, Virginia. Reference line indicates the U.S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

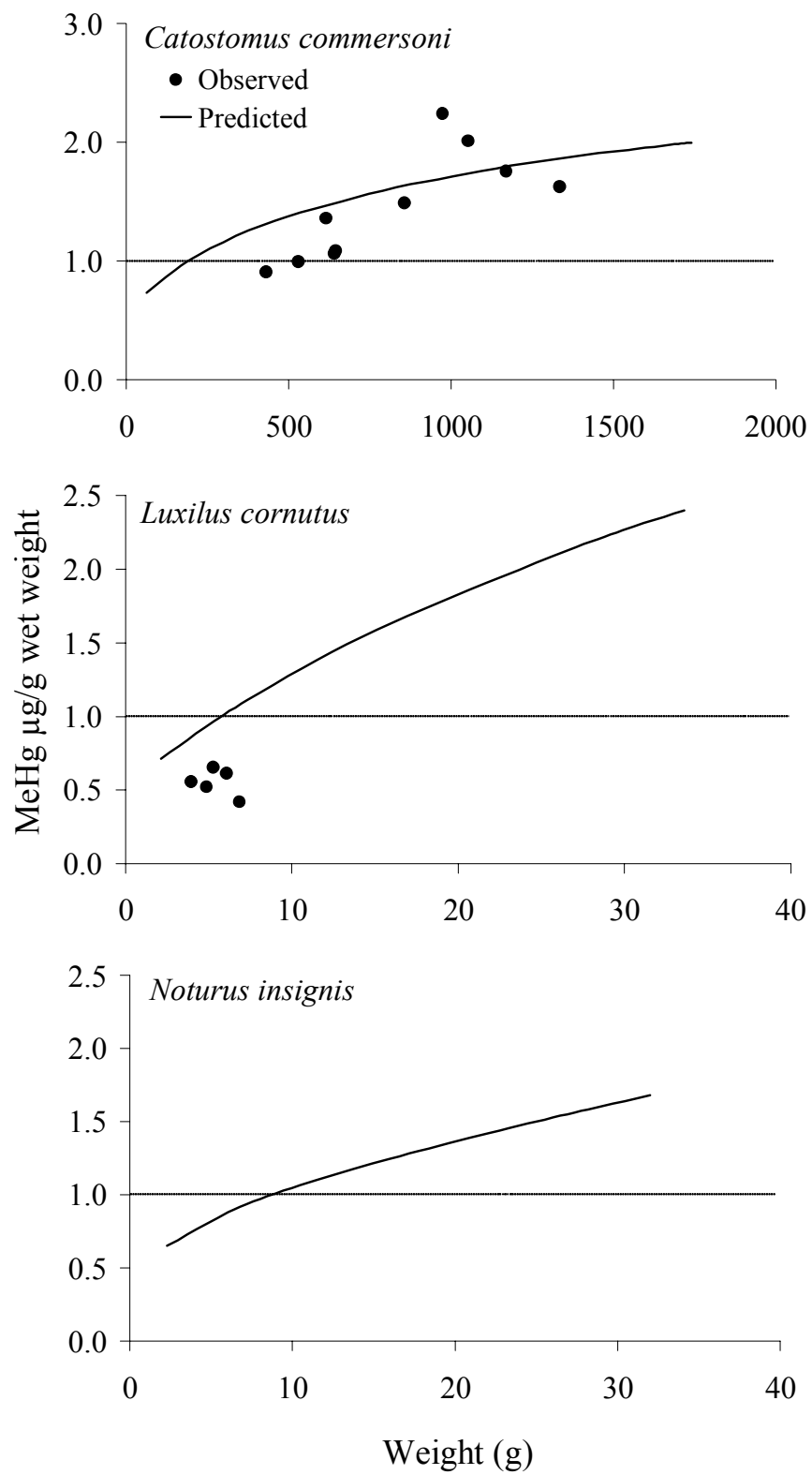


Figure 3.13. Model-predicted and observed concentrations of methylmercury (MeHg) in fish at site SR6 on the South River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

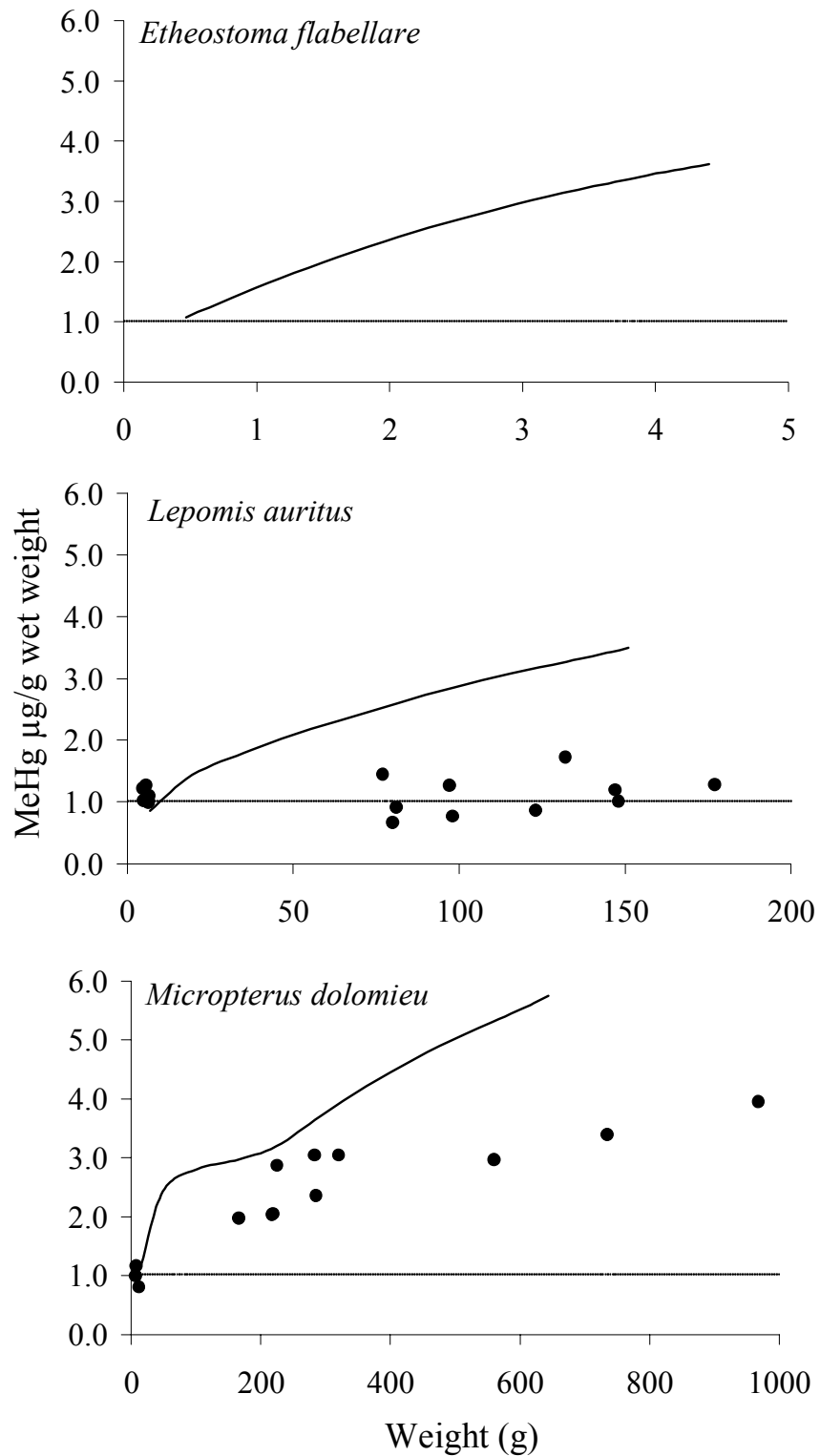


Figure 3.13. (continued) Model-predicted and observed concentrations of methylmercury (MeHg) in fish at site SR6 on the South River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

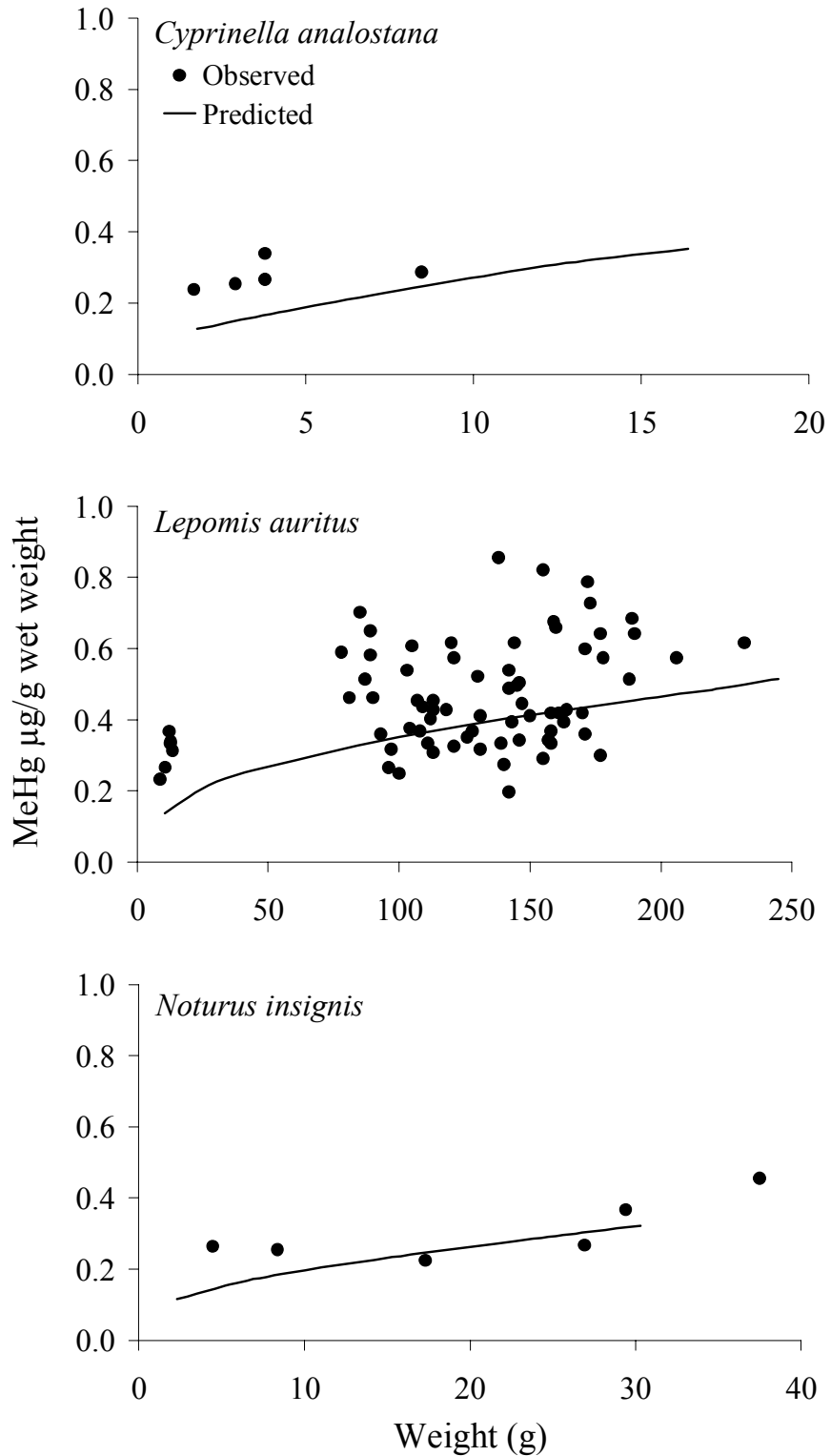


Figure 3.14. Model-predicted and observed concentrations of methylmercury (MeHg) in fish in the South Fork of the Shenandoah River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

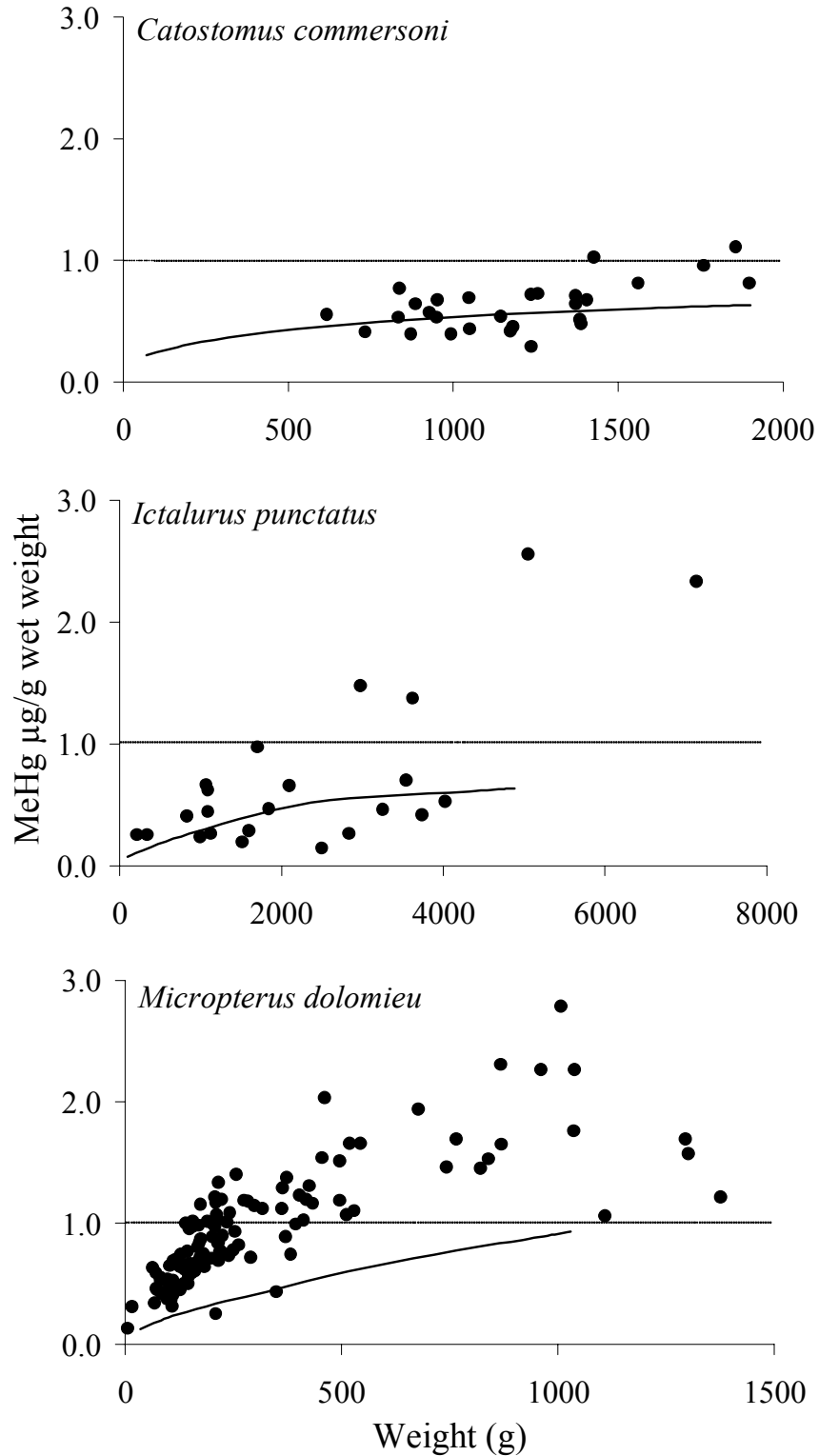


Figure 3.14. (continued) Model-predicted and observed concentrations of methylmercury (MeHg) in fish in the South Fork of the Shenandoah River, Virginia. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

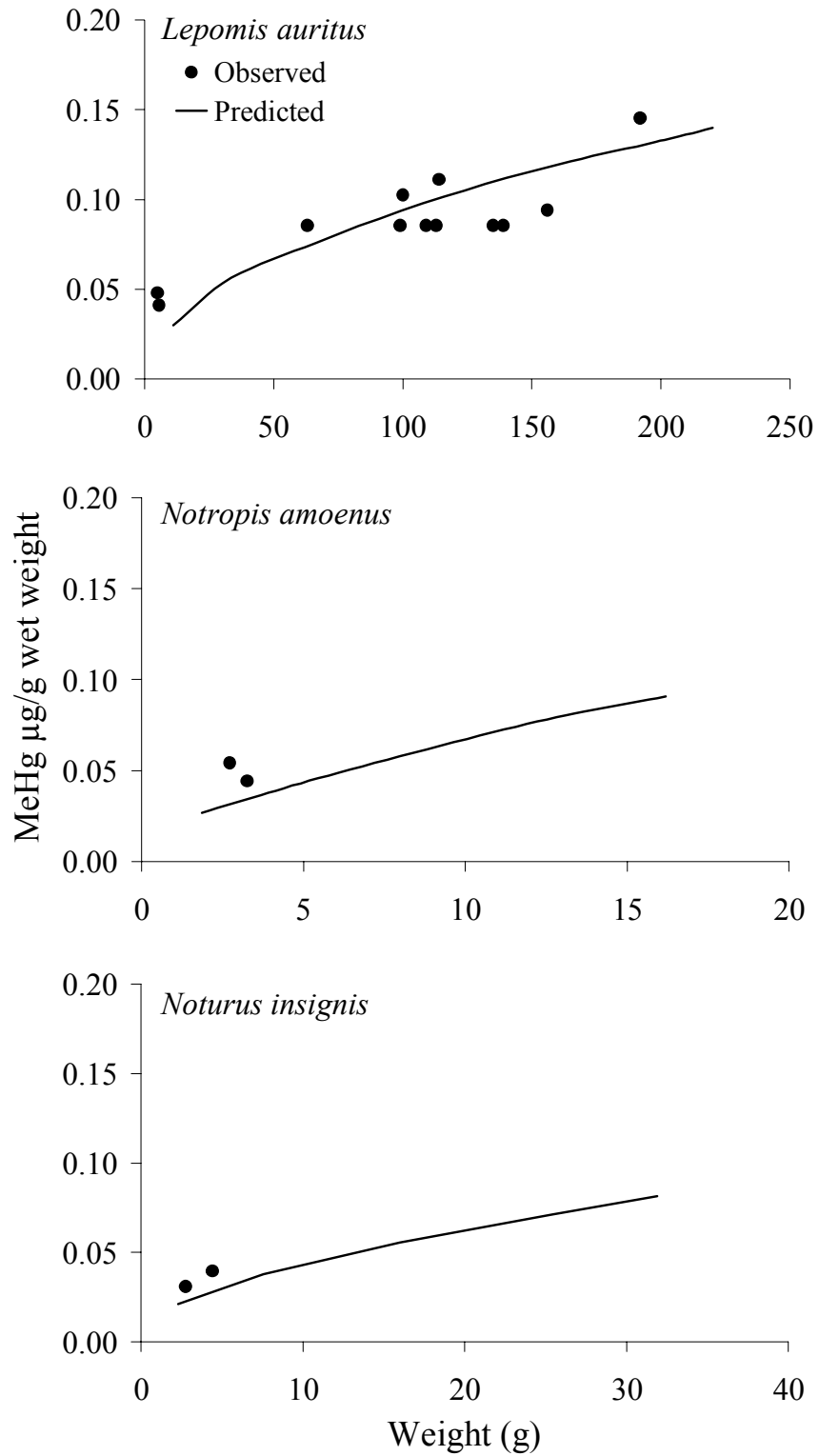


Figure 3.15. Model-predicted and observed concentrations of methylmercury (MeHg) in fish in the North River, Virginia.

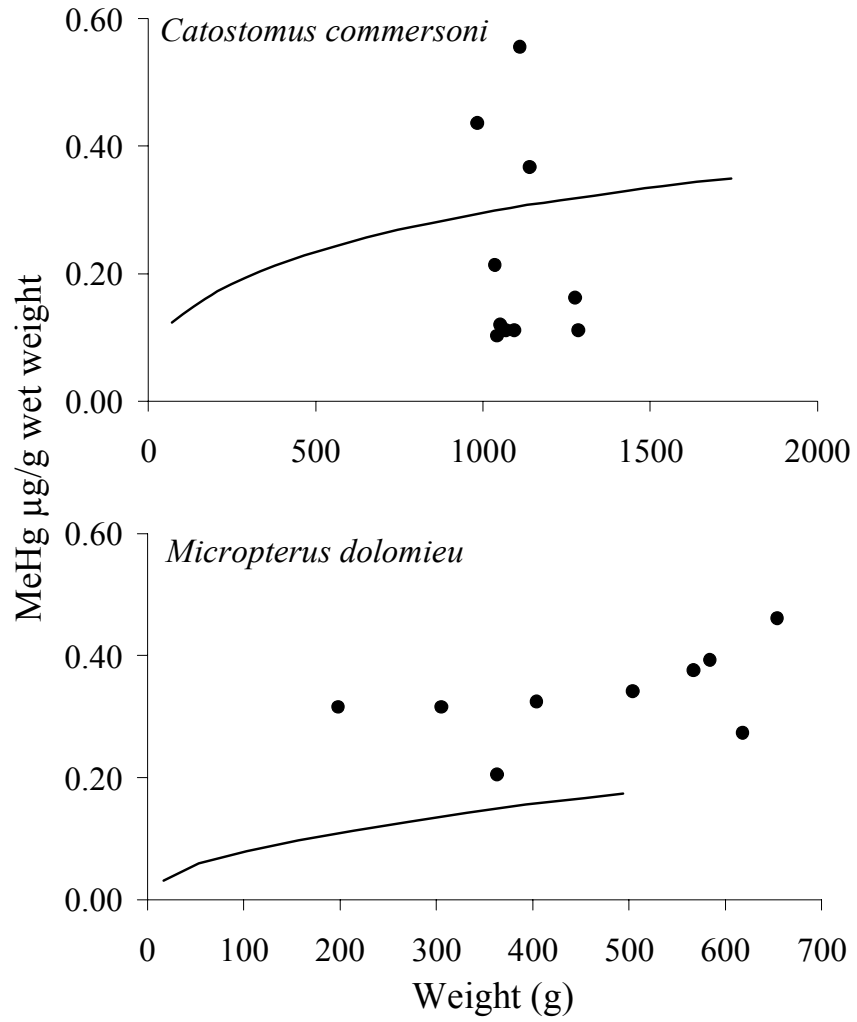


Figure 3.15. (continued) Model-predicted and observed concentrations of methylmercury (MeHg) in fish in the North River, Virginia.

Table 3.18. Mean absolute percent error (MA%E) between model-predicted and observed concentrations of methylmercury in fish muscle tissue in the South River (at sites SR3, SR4, and SR6), South Fork of the Shenandoah River (SFSR), and North River (NR), Virginia.

Species	SR3	SR4	SR6	SFSR	NR	Total
<i>Catostomus commersoni</i>	75%	17%	22%	25%	140%	48%
<i>Cyprinella analostana</i>	-	-	-	38%	-	38%
<i>Etheostoma flabellare</i>	149%	92%	-	-	-	123%
<i>Ictalurus punctatus</i>	-	-	-	64%	-	64%
<i>Lepomis auritus</i>	68%	70%	127%	27%	21%	48%
<i>Luxilus cornutus</i>	83%	33%	79%	-	-	65%
<i>Micropterus dolomieu</i>	32%	22%	35%	57%	48%	51%
<i>Notropis amoenus</i>	-	-	-	-	32%	32%
<i>Noturus insignis</i>	-	59%	-	23%	27%	28%
Total	75%	47%	73%	44%	63%	52%

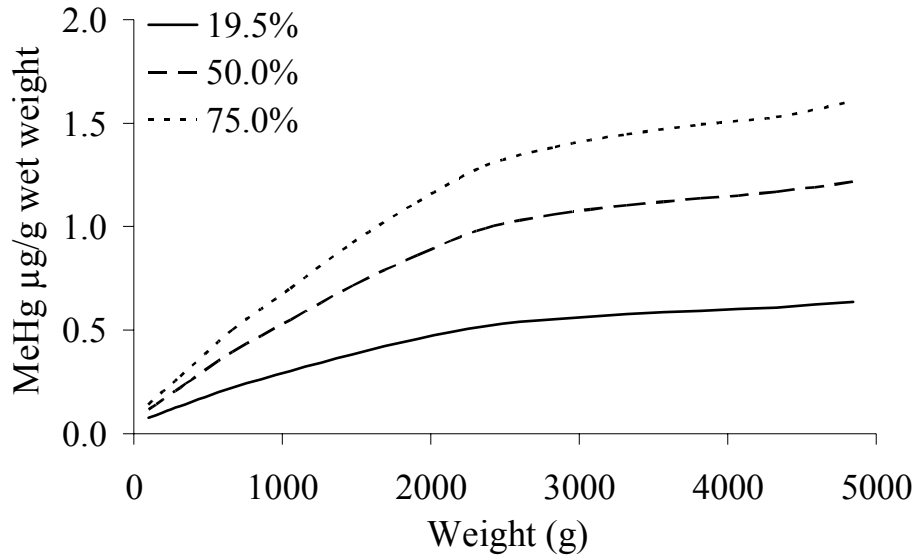


Figure 3.16. Model-predicted concentrations of methylmercury (MeHg) in the muscle tissue of *Ictalurus punctatus* in the South Fork of the Shenandoah River, Virginia for diets composed of 19.5, 50.0, and 75.0% fish.

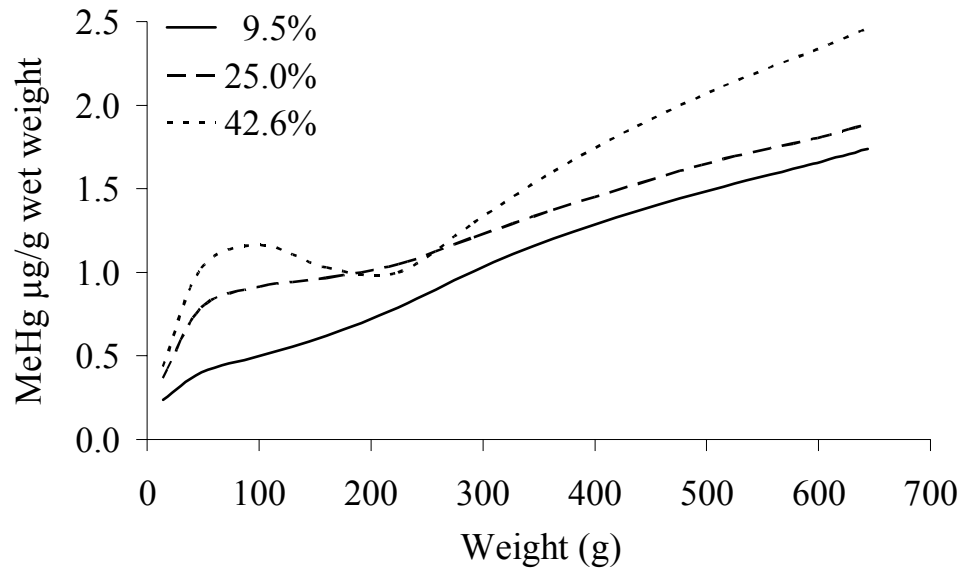


Figure 3.17. Model-predicted concentrations of methylmercury (MeHg) in the muscle tissue of *Micropterus dolomieu* at site SR3 on the South River, Virginia for average lengths of prey of 9.5, 25.0, and 42.6%.

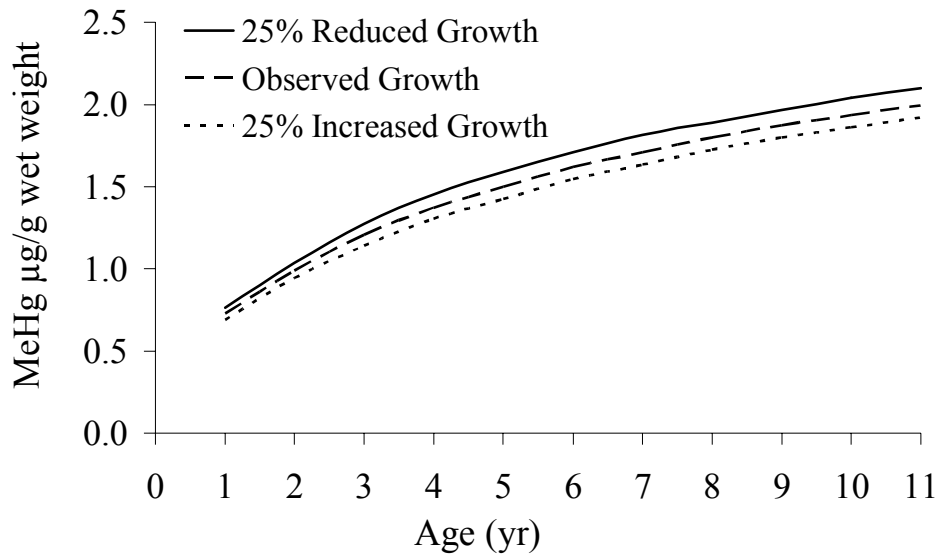


Figure 3.18. Model-predicted concentrations of methylmercury (MeHg) in *Catostomus commersoni* at site SR6 on the South River, Virginia for the observed specific growth rate and for specific growth rates increased and decreased by 25%.

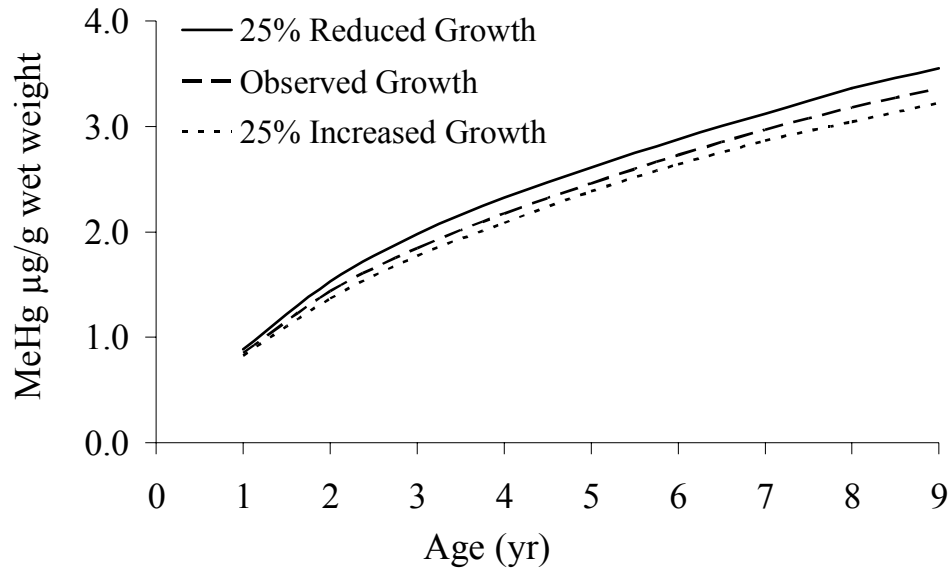


Figure 3.19. Model-predicted concentrations of methylmercury (MeHg) in *Lepomis auritus* at site SR6 on the South River, Virginia for the observed specific growth rate and for specific growth rates increased and decreased by 25%.

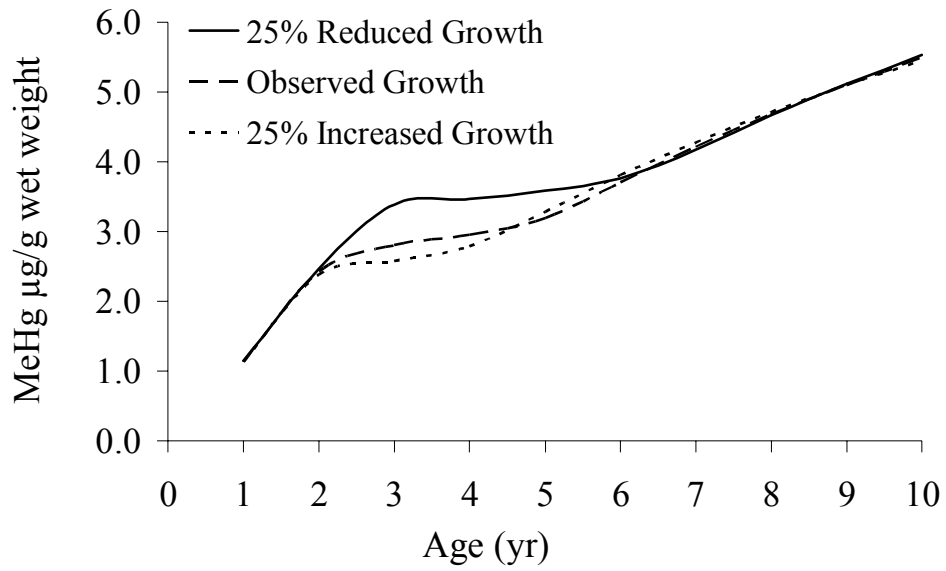


Figure 3.20. Model-predicted concentrations of methylmercury (MeHg) in *Micropterus dolomieu* at site SR6 on the South River, Virginia for the observed specific growth rate and for specific growth rates increased and decreased by 25%.

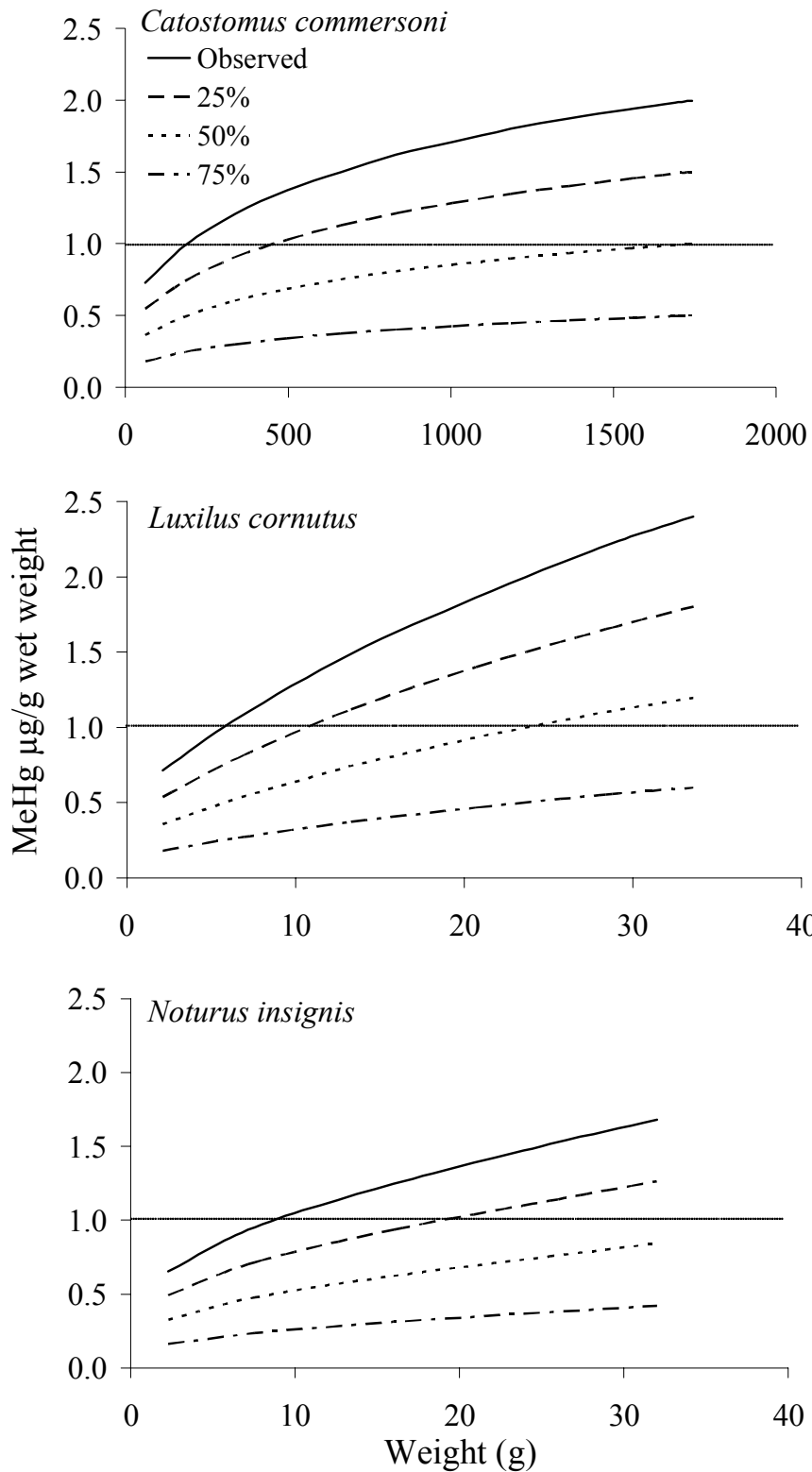


Figure 3.21. Model-predicted concentrations of methylmercury (MeHg) in the muscle tissue of fish at site SR6 on the South River, Virginia for 25, 50, and 75% reduced concentrations of methylmercury in river sediment and observed conditions. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

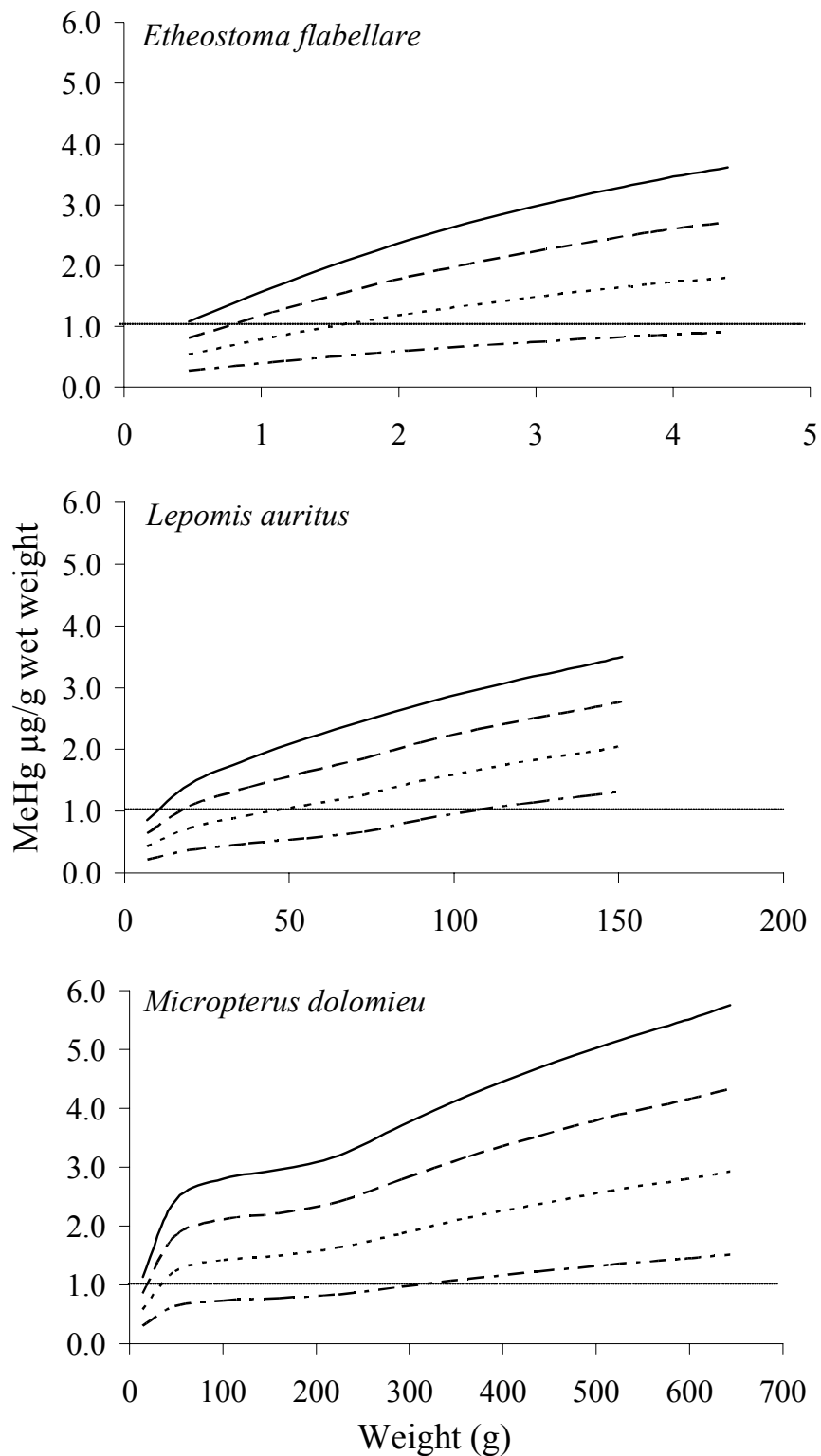


Figure 3.21. (continued) Model-predicted concentrations of methylmercury (MeHg) in the muscle tissue of fish at site SR6 on the South River, Virginia for 25, 50, and 75% reduced concentrations of methylmercury in river sediment and observed conditions. Reference line indicates the U. S. Food and Drug Administration action level for methylmercury in the edible portion of fish.

CHAPTER 4: Sexual and Seasonal Variations of Total Mercury in *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia

ABSTRACT

To further assess the consistency and magnitude of sexual and seasonal variations of total mercury among fish species, concentrations of total mercury in the muscle tissue of *Micropterus dolomieu* were assessed during spring, summer, and fall 2002 in the mercury contaminated South Fork of the Shenandoah River, Virginia. The mean concentration of total mercury in muscle tissue was 0.79 µg/g wet weight and ranged from 0.30-1.38 µg/g. There was a significant positive relationship between the concentrations of total mercury and fish length, weight, and age ($P < 0.05$). Mean concentrations of total mercury were significantly different between sexes after adjustment for fish length and weight ($P < 0.05$) and were 19-20% higher in females than males. Mean concentrations of total mercury adjusted for fish length were nearly significant between seasons ($P = 0.051$) and were 14-21% higher during spring than summer and fall after adjustment for fish length and weight. Results of this study indicate that resource managers should account for sexual and seasonal variations of total mercury in fish by recording fish sex and standardizing sampling periods to assure more accurate and precise comparisons during mercury monitoring and assessment programs.

INTRODUCTION

Due to the human health risks associated with the consumption of mercury contaminated fish, extensive research efforts have been directed towards advancing the understanding of the biological processes affecting mercury accumulation in fish (Nicoletto and Hendricks 1988; Grieb et al. 1990; Lange et al. 1994; Rodgers 1994, 1996; Hanten et al. 1998; Neumann and Ward 1999; Ward and Neumann 1999). Yet, factors controlling the accumulation of mercury in fish remain poorly understood. This is largely because concentrations of persistent contaminants, such as mercury, are extremely variable within fish populations (Verta 1990; Hammar et al. 1993; Madenjian et al. 1994). Understanding intrapopulation variability in concentrations of mercury in fish is critical to mercury monitoring and assessment programs that rely upon accurate and precise data that can be compared among water bodies and tracked over time (Ward and Neumann 1999). Therefore, assessing sexual and seasonal variations of total mercury in the muscle tissue of *Micropterus dolomieu* is well-justified and critical to mercury monitoring and assessment programs. The objective of this study was to:

- 1.) Assess sexual and seasonal variations of total mercury in the muscle tissue of *Micropterus dolomieu*.

MATERIALS AND METHODS

Description of Study Site

The study site was located near Lynwood, Virginia (latitude 38°18'40"N, longitude 78°46'20"W) on the South Fork of the Shenandoah River, which is a sixth-order stream that meanders for approximately 160 rkm and drains 4,144 km² of a five county region in northern Virginia before joining the North Fork of the Shenandoah River at Front Royal to form the main stem of the Shenandoah River, approximately 290 rkm from the Chesapeake (Figure 4.1).

Data Collection

Adult *M. dolomieu* were collected during spring (April 11), summer (July 17), and fall (October 1) 2002 using boat mounted pulsed direct-current electrofishers. Fish were measured for total length (mm) and weighed (g). Sagittal otoliths were removed using clean utensils. Sex was determined by visual examination of the gonads. Fish were double-sealed in clean polyethylene bags, stored on ice, and frozen within eight hours.

Otoliths were viewed using an Olympus SZ-ST scope with magnification range 1x-6.3x equipped with an Olympus SZ-CTV scope adapter, Samsung CCD SAC-410NA color camera, and Image-Pro Plus® software. Otoliths were viewed submerged in water with black background and fiber optic lighting. Ages were estimated by two independent readers.

Total Mercury Analysis

Total mercury analysis was conducted by the Virginia Division of Consolidated Laboratory Services. Individual muscle tissue fillets were analyzed to represent the portion of fish normally consumed by humans. Total mercury analysis was conducted using a modification of U. S. Environmental Protection Agency method 245.6 (USEPA 1991), which incorporated a microwave assisted nitric acid digestion procedure (SW-846 method 3051), followed by further oxidation with KMnO₄ and K₂S₂O₈. Following digestion, mercury analysis was conducted using cold vapor atomic absorption (VDEQ 2002).

Data Analysis

Because of the known relationship between mercury concentration and fish size and age, sexual and seasonal variations in concentrations of total mercury in *M. dolomieu* were tested using the analysis of covariance (ANCOVA), with concentration of total mercury as the dependent variable, sex and season as independent variables, and total length, weight, and age as

covariates. Main assumptions of ANCOVA include normality and homogeneity of regression slopes. Therefore, normality of total mercury concentration residuals and homogeneity of mercury concentration-length, mercury concentration-weight, and mercury concentration-age regression slopes between sexes and among seasons were tested prior to ANCOVA.

RESULTS

A total of 45 adult *M. dolomieu* were collected, including 24 males and 21 females. Total length, weight, and age ranged from 197-290 mm, 82-284 g, and 2-5 yr, respectively. The mean concentration of total mercury in the muscle tissue of *M. dolomieu* was 0.79 µg/g wet weight and ranged from 0.30-1.38 µg/g (Table 4.1).

Total mercury concentration residuals were normally distributed ($P > 0.05$). No significant results were found for total mercury concentration-length, total mercury concentration-weight, or total mercury concentration-age regression slopes between sexes or among seasons ($P > 0.05$).

There was a significant positive relationship between the concentration of total mercury and length ($P < 0.0001$), weight ($P < 0.0001$), and age ($P = 0.0010$). Mean concentrations of total mercury were significantly different between sexes after adjustment for fish length ($P = 0.0158$) and weight ($P = 0.0157$), and were 19-20% higher in females than males (Table 4.2). After adjustment for fish age, mean concentrations of total mercury were not significantly different between sexes ($P = 0.2820$), but were 10% higher in females than males.

Mean concentrations of total mercury in the muscle tissue of *M. dolomieu* were not significantly different between seasons after adjustment for fish length ($P = 0.0510$), weight ($P = 0.1651$), or age ($P = 0.3433$). However, mean concentrations of total mercury adjusted for fish length and weight were 14-21% higher during spring than summer or fall, which warrants discussion.

DISCUSSION

Sexual Variations of Total Mercury

Sexual variations in concentrations of total mercury in *M. dolomieu* observed in this study were consistent with the results of previous studies in other mercury contaminated systems (Nicoletto and Hendricks 1988; Ward and Neumann 1999). Nicoletto and Hendricks (1988) found that in the South River, South Fork of the Shenandoah River, and Shenandoah River, mean concentrations of total mercury in *Ambloplites rupestris* and *Lepomis spp.* were significantly higher in females than males of the same age. Although Ward and Neumann (1999) reported that

sexual differences in concentrations of total mercury in the axial muscle tissue of *Micropterus salmoides* were not consistent, mean concentrations of total mercury were significantly higher in females than males during fall in Pickerel Lake, Connecticut.

Sexual variations in concentrations of total mercury in fish have been attributed to biodilution (Lange et al. 1994) and differences in reproductive demands (Nicoletto and Hendricks 1988). Lange et al. (1994) found that concentrations of total mercury in the muscle tissue of *M. salmoides* collected in Lake Tohopekaliga, Florida were substantially higher in males than females, which they attributed to growth dilution of faster growing females. Due to sexual dimorphic growth of *M. salmoides* in Lake Tohopekaliga, faster growing females exhibit lower concentrations of mercury than males of the same length or weight, while males and females of the same age have similar concentrations of mercury (Lange et al. 1994). Back-calculated growth estimates of *M. dolomieu* in the South Fork of the Shenandoah River indicate that growth is slightly faster for males than females, which may partly explain sexual variations in concentrations of mercury observed in this study (Figure 4.2). However, mean concentrations of total mercury adjusted for age remained 10% higher in females than males. Therefore, other factors must be partially responsible for the sexual variations observed in this study.

Nicoletto and Hendricks (1988) attributed sexual variations in concentrations of total mercury to differences in reproductive demands. They found no differences in concentrations of total mercury between sexes of fish prior to sexual maturity, but found significant differences after the onset of reproduction. Nicoletto and Hendricks (1988) hypothesized that females increased consumption rates, relative to males, to meet the increased energy demands of reproduction and therefore, exhibited higher concentrations of mercury. In addition to this hypothesis, male *M. dolomieu* have substantial parental responsibilities during the spawning period, which normally consists of 24 hour fanning and guarding of the nest for as long as one month. During the parental care period, male home ranges are considerably reduced, which may ultimately reduce feeding opportunities (Gillooly and Baylis 1999; Mackereth et al. 1999; Cooke et al. 2002). Therefore, sexual variations observed in this study may be partially explained by differences in reproductive demands, including increased consumption by females and reduced consumption by nest guarding males.

Seasonal Variations of Total Mercury

Seasonal variations in concentrations of total mercury in *M. dolomieu* observed in this study were also consistent with the results of previous studies in other mercury contaminated systems (Kelso and Frank 1974; Meili 1991; Ward and Neumann 1999). Ward and

Neumann (1999) found that in Lake Lillionah and Pickerel Lake mean concentrations of total mercury in *M. salmoides* adjusted for length and age were significantly different between seasons and were 14-43% higher during spring than summer and fall. Meili (1991) found that in Swedish lakes, concentrations of total mercury in *Esox lucius*, *Perca fluviatilis*, and *Rutilus rutilus* were highest during spring at the start of the ice-free period and declined throughout summer. Although Kelso and Frank (1974) reported that mean concentrations of total mercury in *M. dolomieu* collected in Long Point Bay, Lake Erie were not significantly different between seasons, the reported mean concentration of total mercury during spring was more than twice as high than during summer.

Seasonal variations in concentrations of total mercury in fish may be influenced by several factors, including mercury methylation rates, dietary composition, consumption rates, concentrations of mercury in prey, and proximate composition of muscle tissue. Methylmercury production is strongly associated with several environmental factors, including warmer sediment temperatures (Ramlal et al. 1993), anoxic conditions and particulate recycling (Hurley et al. 1991; Gilmour et al. 1992), and flooding of soils and wetlands (St. Louis et al. 1994; Kelley et al. 1997). Most of these conditions occur seasonally and normally result in increased methylmercury concentrations during summer (Foster et al. 2000). Bodaly et al. (1993) found that in remote Canadian shield lakes, mercury methylation to demethylation rates were higher during July and August when water temperatures exceeded 16.0°C, resulting in higher concentrations of mercury in fish from lakes with higher summer temperatures. In this study, mean concentrations of total mercury in *M. dolomieu* were substantially higher during spring than summer, even though mean water temperatures were measured at 15.8 and 25.1°C during the spring and summer sampling events, respectively. Therefore, it seems doubtful that water temperature was the main factor influencing seasonal variations in concentrations of total mercury in *M. dolomieu* in the South Fork of the Shenandoah River. A more likely association exists between higher river flow and more rainfall events during spring, which may inundate floodplain soils and increase particulate recycling, possibly stimulating mercury methylation.

Seasonal variations in concentrations of total mercury in fish may also be influenced by changes in diet composition and/or consumption rates. Concentrations of mercury in fish are significantly affected by the length of the food chain (Cabana et al. 1994) and are highly responsive to dietary shifts (MacCrimmon et al. 1983; Mathers and Johansen 1985; Driscoll et al. 1994). MacCrimmon et al. (1983) found that in Tadenac Lake, Canada, *Salvelinus namaycush* exhibited an abrupt increase in concentration of mercury when they switched from a diet mainly composed of benthic invertebrates to one primarily composed of smelt. Driscoll et al. (1994)

found that concentrations of mercury in *Perca flavescens* increased sharply after age-5 in Adirondack lakes, which corresponded to the size at which they became predominately piscivorous (200 mm). Results of this study indicate that *M. dolomieu* 200-299 mm in the South Fork of the Shenandoah River shift from a diet primarily composed of aquatic insects and fish during spring to one primarily composed of crayfish and fish during fall (Figure 4.3) (Chapter 1). In addition to dietary shifts, seasonal changes in consumption rates may also influence concentrations of total mercury in fish. Based on the percentage of empty stomachs reported for *M. dolomieu* in the South Fork of the Shenandoah River, it appears that consumption is highest during spring and then declines with the advancement of seasons (Figure 4.4) (Chapter 1).

Seasonal variations in concentrations of total mercury in prey items may also influence concentrations of total mercury in fish. Snyder and Hendricks (1995) found that in the South River, Virginia, concentrations of total mercury in *Hydropsyche morose* were significantly higher during summer than other seasons, which they attributed to a seasonal shift in diet from algae to seston. Seasonal variations in concentrations of total mercury in prey may be a contributing factor to seasonal variations observed in this study. However, concentrations of total mercury in prey in the vicinity of site SF1 on the South Fork of the Shenandoah River remain unknown.

In addition to the aforementioned factors, higher levels of total mercury in *M. dolomieu* during spring may also be associated with a seasonal change in proximate composition of fish muscle tissue. Methylmercury has a high affinity for binding to protein in fish muscle tissue and is depurated very slowly compared to its rate of uptake. Therefore, changes in proximate composition of muscle tissue during reproductive and winter periods (depletion of lipid stores), particularly protein percentage, may result in a corresponding change in concentration of total mercury (Ward and Neumann 1999).

Conclusions

Results of this study clearly indicate that *M. dolomieu* in the South Fork of the Shenandoah River had substantial differences in concentrations of total mercury between sexes and among seasons. Sexual variations in concentrations of total mercury may have been influenced by growth dilution and/or differences in reproductive demands between sexes, such as increased consumption by females and reduced consumption by nest guarding males. Seasonal variations in concentrations of total mercury in *M. dolomieu* may have been influenced by the interaction of several environmental factors, including mercury methylation rates, dietary shifts, consumption rates, concentrations of total mercury in prey, and proximate composition of muscle tissue. Regardless of the mechanisms causing these differences, resource managers should

account for sexual and seasonal variations of total mercury in fish by recording fish sex and standardizing sampling periods to assure more accurate and precise comparisons during mercury monitoring and assessment programs.

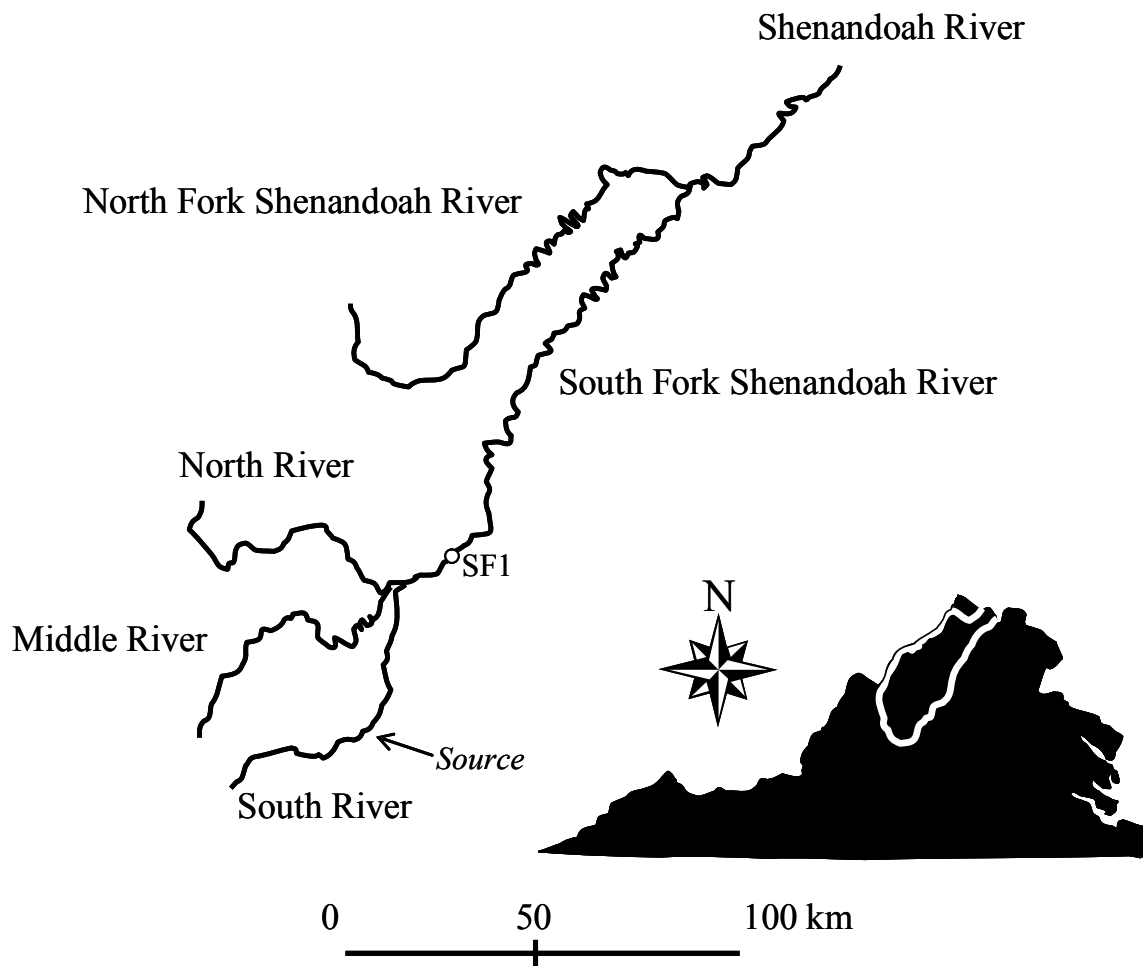


Figure 4.1. Location of study site SF1 on the South Fork of the Shenandoah River, Virginia, located approximately 44.9 rkm downriver from the historic source of mercury.

Table 4.1. Total length (TL), weight (WT), age, and concentrations of total mercury wet weight in the muscle tissue of *Micropterus dolomieu* collected at site SF1 on the South Fork of the Shenandoah River, Virginia.

<i>N</i>	TL range (mm)	WT range (g)	Age range (yr)	Mean THg (µg/g)	THg range (µg/g)
<u>SPRING</u>					
8 females	206-270	105-253	4-5	0.94	0.37-1.37
9 males	200-263	88-239	4-5	0.78	0.47-1.14
<u>SUMMER</u>					
7 females	197-263	82-221	2-5	0.79	0.62-1.05
10 males	200-255	100-183	3-4	0.65	0.48-0.82
<u>FALL</u>					
6 Females	209-243	103-171	2-5	0.86	0.66-1.12
5 Males	225-290	127-284	2-5	0.82	0.30-1.38

Table 4.2. Analysis of covariance for testing whether concentrations of total mercury in the muscle tissue of *Micropterus dolomieu* vary between sexes and seasons in the South Fork of the Shenandoah River, Virginia. Fish age, total length, and weight were used as covariates. Significant effects are highlighted ($\alpha = 0.05$).

Source	Type III sum of squares	Mean square	F	P
Age	0.594	0.594	12.62	0.0010
Sex	0.056	0.056	1.19	0.2820
Season	0.025	0.012	0.27	0.7667
Sex*Season	0.012	0.006	0.13	0.8742
Total Length	1.078	1.078	31.39	<0.0001
Sex	0.219	0.219	6.38	0.0158
Season	0.220	0.110	3.21	0.0516
Sex*Season	0.068	0.034	1.00	0.3775
Weight	1.192	1.192	38.08	<0.0001
Sex	0.200	0.200	6.39	0.0157
Season	0.118	0.059	1.89	0.1651
Sex*Season	0.091	0.045	1.45	0.2466

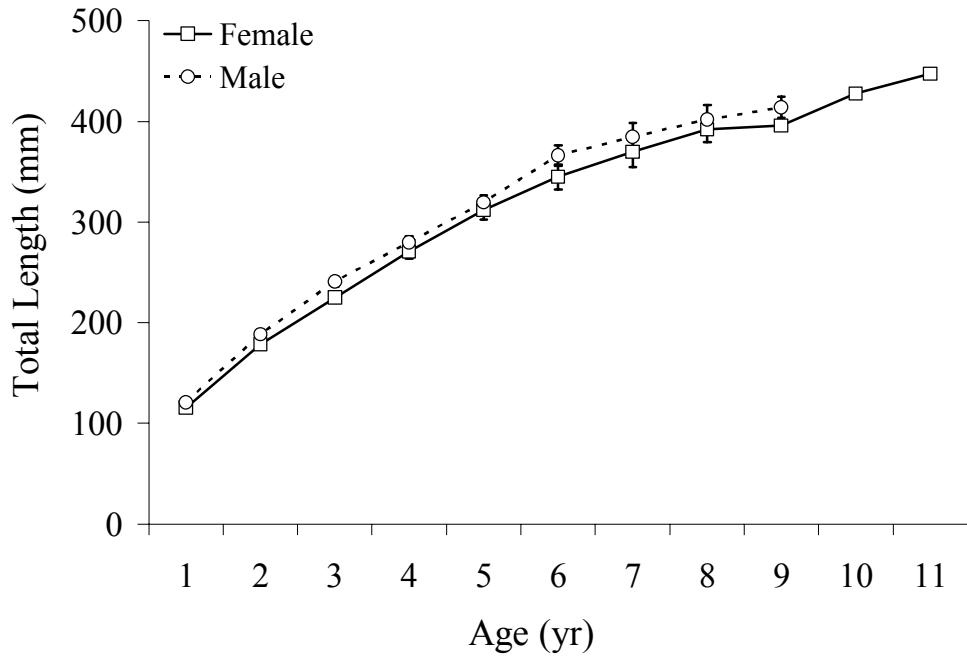


Figure 4.2. Mean back-calculated total lengths at age of male and female *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia.

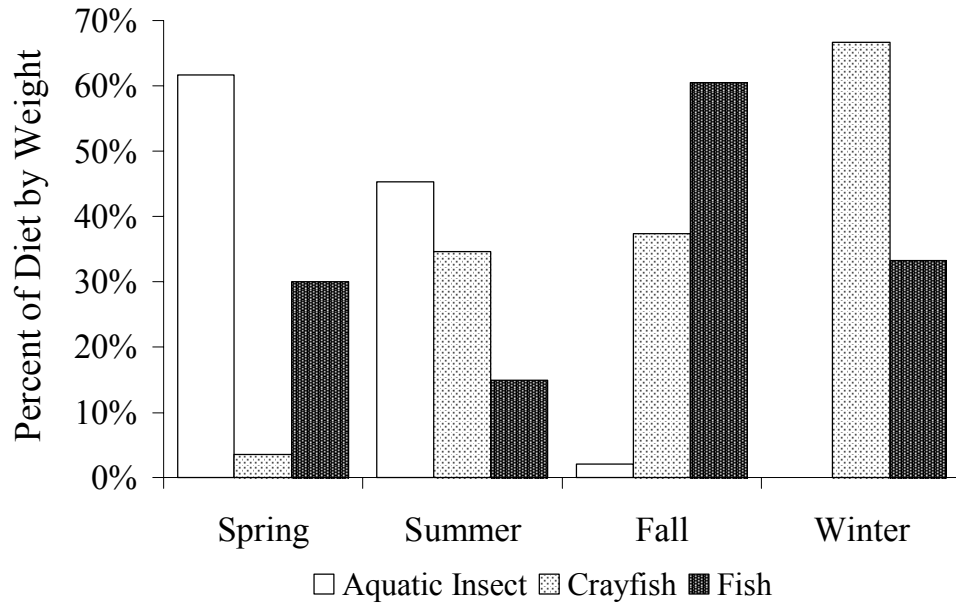


Figure 4.3. Diet composition of *Micropterus dolomieu* 200-299 mm in the South Fork of the Shenandoah River, Virginia.

Chapter 1.

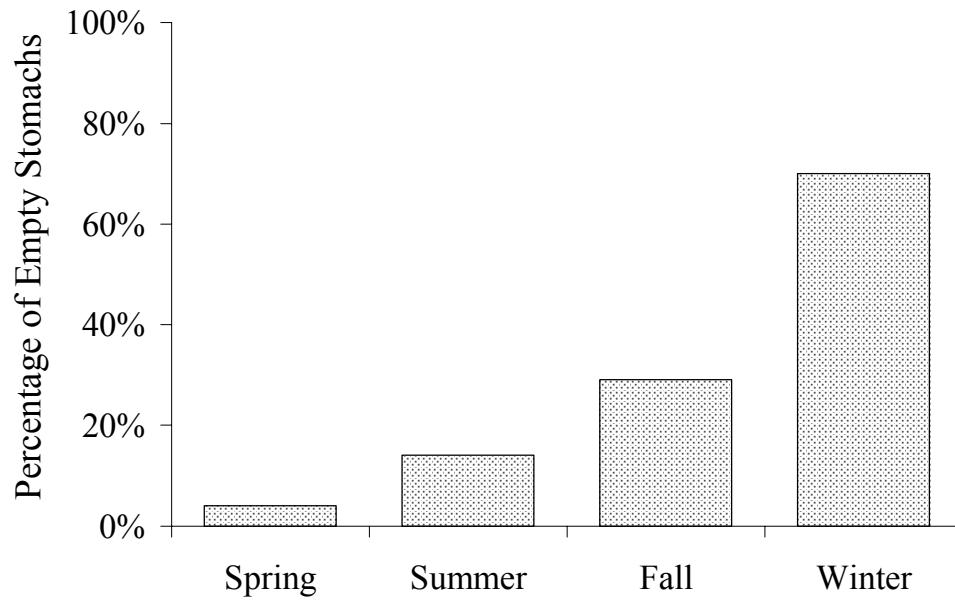


Figure 4.4. Percentage of empty stomachs for *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia.

Chapter 1.

CHAPTER 5: Summary and Management Recommendations

Food Habits of Selected Fish Species

Food habits of *Catostomus commersoni*, *Ictalurus punctatus*, *Lepomis auritus*, and *Micropterus dolomieu* were assessed during spring, summer, fall, and winter 2002 in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River, located within the Shenandoah River basin, Virginia. Algae, aquatic insects, crayfish, detritus, and fish accounted for 75-97% of the diet. Sizeable proportions of Annelida, Bivalvia, Cladocera, Gastropoda, and terrestrial insects were also consumed. As *L. auritus* and *M. dolomieu* increased in size, *L. auritus* diversified their diet, which often included larger items (e.g., crayfish and Gastropoda), and *M. dolomieu* shifted from a diet primarily composed of aquatic insects to one mainly composed of crayfish and fish. Seasonal dietary shifts included decreased consumption of aquatic insects from spring to fall by *C. commersoni* and *M. dolomieu*, increased consumption of terrestrial insects during summer and fall by *L. auritus* and *M. dolomieu*, and decreased feeding during winter by *I. punctatus*, *L. auritus*, and *M. dolomieu*. Intraspecific diet overlap between rivers was high for *C. commersoni* and *L. auritus* because of their common dependence on detritus and aquatic insects, respectively. *Micropterus dolomieu* in the South Fork of the Shenandoah River were more dependent on aquatic insects at larger sizes and for longer periods than *M. dolomieu* in the South River and North River, while *M. dolomieu* in the South River and North River consumed greater proportions of crayfish. Differences in the composition of forage fish consumed by *M. dolomieu* were also noted among rivers. Interspecific diet overlap was low, except between *L. auritus* and juvenile *M. dolomieu* on several occasions because of their common dependence on aquatic insects (i.e., Diptera, Ephemeroptera, and Trichoptera).

Resource managers interested in the bioaccumulation of chemical contaminants in fish mainly accumulated through dietary pathways, such as mercury, should seriously consider studying food habits as the foundation for their study, such as presented here, to identify dietary pathways and patterns critical to bioaccumulation processes. To better understand the bioaccumulation of mercury in *C. commersoni* and *I. punctatus* in the Shenandoah River basin, food habits of juveniles should be assessed. Because this study was conducted during drought conditions, diet items normally consumed by the selected fish species may have been inaccessible or unavailable due to hydrologic conditions. Researching food habits of the selected fish species during normal hydrologic conditions may prove worthwhile for evaluating climatic and hydrologic variability in food habits and ultimately mercury bioaccumulation.

Total Mercury and Methylmercury in Common Prey Items of Selected Fish Species

Concentrations of total mercury and methylmercury in common prey items of *C. commersoni*, *I. punctatus*, *L. auritus*, and *M. dolomieu* were assessed during spring, summer, and fall 2003 in the mercury contaminated South River and South Fork of the Shenandoah River and uncontaminated North River. Mean concentrations of total mercury in aquatic invertebrates and forage fish in contaminated rivers ranged from 66.7-398.3 and 198.0-594.9 ng/g wet weight, while mean concentrations of total mercury in aquatic invertebrates and forage fish in the reference river were 4.4 and 29.3 ng/g. Mean percentages of methylmercury in crayfish, forage fish, Gastropoda, and terrestrial Coleoptera were 78.0, 97.9, 55.3, and 5.2%, respectively. Mean percentages of methylmercury in aquatic insect larvae were 34.5% in detritivores-grazers (Ephemeroptera) and 75.6% in predators (Anisoptera and Zygoptera). Aquatic and terrestrial invertebrates closely associated with river and floodplain sediments exhibited the highest concentrations of total mercury. Concentrations of total mercury in aquatic insects, crayfish, and forage fish were significantly different among sites ($P < 0.05$) and were consistently higher in the South River, particularly at site SR6. Concentrations of total mercury in prey items were significantly different among prey taxa at all sites ($P < 0.05$) and were consistently higher in forage fish. Predacious aquatic invertebrates (e.g., Odonata) normally exhibited higher concentrations of total mercury than herbivorous and detritivorous invertebrates, while juvenile Centrarchidae (*L. auritus* and *M. dolomieu*), juvenile Ictaluridae (*Ameiurus natalis*), and Percidae (*Etheostoma spp.*) had the highest concentrations of total mercury among forage fish. No consistent seasonal patterns were found.

Although monitoring concentrations of mercury in larger sport fishes remains important, resource managers should consider monitoring concentrations of mercury in aquatic invertebrates and/or forage fish because yearly differences in factors such as flooding, water chemistry, or food web structure can change the pattern of mercury accumulation in aquatic biota and can remain unnoticed for several years if only larger sport fishes are sampled. Spatial patterns found in this study indicate that resource managers interested in identifying “hot spots” of mercury in the South River should concentrate monitoring efforts near site SR6. Further research on food habits and concentrations of mercury in diet items of aquatic invertebrates and forage fish may elucidate differences in mercury uptake between taxa and identify important pathways of mercury from the physical environment to lower trophic levels. For instance, detritus is consumed by many aquatic organisms (e.g., aquatic insect larvae, crayfish, and *C. commersoni*) and forms the foundation of most aquatic food webs. Assessing concentrations of mercury in detritus would improve the

understanding of the movement of mercury from the physical environment to lower trophic levels and ultimately the selected fish species. Further research on aquatic invertebrates closely associated with river and floodplain sediments would further improve this understanding.

Bioaccumulation Dynamics of Methylmercury in Fish Communities

A bioenergetics-based bioaccumulation model was used to describe the bioaccumulation dynamics of methylmercury in fish communities in the mercury contaminated South River and South Fork Shenandoah River and uncontaminated North River. Model-predicted concentrations of methylmercury in fish exhibited similar patterns to those observed during field studies, including size dependent patterns within species and variations between species of different trophic levels. Model-predicted concentrations of methylmercury in fish increased significantly with size and age ($P < 0.05$) and were consistently higher in *M. dolomieu* in contaminated rivers. Dietary pathways accounted for 87% of methylmercury uptake by fish in mercury contaminated rivers, but only 57% in the reference river. Graphical analyses indicated that model-predicted and observed concentrations of methylmercury in fish were comparable. Quantitative analyses indicated that mean absolute percent error between model-predicted and observed concentrations of methylmercury in fish was 52% and ranged from 17-149%. Model-predicted bioaccumulation dynamics of methylmercury in fish were sensitive to changes in food web structure, including dietary composition, average length of prey, and specific growth rate, indicating that biomanipulation of contaminated systems may ultimately affect concentrations of methylmercury in fish. Reducing concentrations of methylmercury in river sediment substantially reduced model-predicted concentrations of methylmercury in fish in the South River.

Bioaccumulation models, such as presented here, are useful tools and should be utilized for evaluating field data, identifying critical processes and pathways affecting contaminant accumulation, and comparing outcomes of alternative management options associated with pollution control, ecosystem management, and/or restoration activities for management guidance prior to costly expenditures. Population dynamics may play an integral role in understanding the bioaccumulation dynamics of methylmercury in fish communities in the Shenandoah River. To fully exercise the capabilities of the Bioaccumulation and Aquatic System Simulator (BASS), better population information needs to be collected for the simulated fish species, including population density by age class, non-predatory mortality rates, and standing stocks of dietary items. Because methylmercury accounts for 90-99% of total mercury in fish and is the underlying cause of health advisories for fish consumption, methylmercury should become the focus of future monitoring efforts. To estimate the period associated with alternative

management options and better understand the bioaccumulation dynamics of methylmercury in fish communities, the BASS model should be coupled to an existing fate and transport model, such as Water Quality Analysis Simulation Program (WASP) or Exposure Analysis Modeling Systems (EXAMS). Before remedial activities commence, such as sediment remediation, a thorough environmental impact assessment should be conducted.

Sexual and Seasonal Variations of Total Mercury in *Micropterus dolomieu*

Sexual and seasonal variations of total mercury in the muscle tissue of *M. dolomieu* were assessed during spring, summer, and fall 2002 in the mercury contaminated South Fork of the Shenandoah River. The mean concentration of total mercury in muscle tissue was 0.79 µg/g wet weight and ranged from 0.30-1.38 µg/g. There was a significant positive relationship between the concentration of total mercury and fish length, weight, and age ($P < 0.05$). Mean concentrations of total mercury were significantly different between sexes after adjustment for length and weight ($P < 0.05$) and were 19-20% higher in females than males. Mean concentrations of total mercury adjusted for length were nearly significant among seasons ($P = 0.051$) and were 14-21% higher during spring than summer and fall after adjustment for length and weight.

Resource managers should account for sexual and seasonal variations of mercury in fish by standardizing sampling periods and recording fish sex, which would assure more accurate and precise comparisons during mercury monitoring and assessment programs. In Virginia, sampling during spring would yield the highest estimate of mercury in fish, which would be a conservative estimate for the management of health advisories for fish consumption. Sampling during spring would also facilitate sexual identification of fish, depending on geographic location and species. Most state monitoring programs already target adult/edible size fish, which are normally mature. For instance, the Virginia Department of Environmental Quality samples adult/edible size *C. commersoni*, *L. auritus*, and *M. dolomieu*, which are spring or early summer spawners. Sex can easily be determined by visual analysis of the vent or by obtaining a small gonadal sample. In addition, male fish of some species (e.g., *C. commersoni*) will display tubercles during the spawning season, further simplifying sexual identification. These methods of sexual identification are noninvasive, which reduces the risk of additional contamination. Further study is recommended to assess the consistency and magnitude of sexual and seasonal variations in concentrations of total mercury among other fish species (e.g., *Ictalurus punctatus*) and to identify the mechanisms causing these differences.

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APPENDIX A.

Table 1.1. Diet composition of *Catostomus commersoni* in the South River, Virginia.

	<u>Spring</u>	<u>Summer</u>	<u>Fall</u>	<u>Winter</u>
No. intestines examined	35	35	32	35
No. empty intestines	3	7	10	9
Total length range (mm)	169-497	176-480	215-472	105-491
Mean total length (\pm SE) (mm)	359 (\pm 14)	347 (\pm 15)	369 (\pm 14)	339 (\pm 20)
<i>Taxa</i>	%	%	%	%
Annelida	0.8	-	-	0.2
Aquatic Insect	27.8	18.5	17.7	15.0
Coleoptera	-	-	-	0.1
Diptera	14.6	6.2	4.1	8.3
Ephemeroptera	6.3	5.2	12.4	0.9
Lepidoptera	0.1	0.1	0.1	-
Megaloptera	-	0.7	-	-
Odonata	0.1	-	0.2	1.7
Plecoptera	-	-	-	-
Trichoptera	6.7	6.3	0.9	3.9
Crustacea	0.1	2.9	0.7	10.1
Amphipoda	-	0.6	0.7	0.7
Cladocera	0.1	2.2	-	9.3
Copepoda	-	-	-	-
Mollusca	0.8	8.4	1.0	7.4
Bivalvia	0.8	7.5	1.0	5.9
Gastropoda	-	0.9	-	1.5
Other	70.4	73.3	81.3	67.5
Detritus	70.3	68.5	79.9	64.1
Vegetation	-	1.8	1.4	3.4
Miscellaneous	0.1	-	-	-

Table 1.2. Diet composition of *Catostomus commersoni* in the South Fork of the Shenandoah River, Virginia. PDUI = partially digested unidentifiable insect matter.

	<u>Spring</u>	<u>Summer</u>	<u>Fall</u>	<u>Winter</u>
No. intestines examined	30	30	27	18
No. empty intestines	0	6	6	2
Total length range (mm)	389-509	402-496	310-503	334-510
Mean total length (\pm SE) (mm)	448 (\pm 6)	429 (\pm 4)	443 (\pm 7)	449 (\pm 9)
<i>Taxa</i>	%	%	%	%
Annelida	0.3	-	-	0.3
Aquatic Insect	28.4	26.6	23.7	20.5
Coleoptera	-	-	0.1	0.4
Diptera	5.5	1.6	8.1	0.6
Ephemeroptera	9.0	2.6	11.7	0.6
Lepidoptera	-	-	1.0	0.2
Megaloptera	-	-	0.1	0.3
Odonata	0.2	-	0.4	7.3
Plecoptera	0.1	-	-	-
Trichoptera	13.5	22.4	2.4	11.1
PDUI	0.2	-	-	-
Crustacea	0.4	-	0.3	2.9
Amphipoda	0.2	-	-	2.6
Cladocera	0.2	-	0.3	0.1
Copepoda	-	-	-	-
Decapoda	-	-	-	0.2
Mollusca	5.2	2.4	2.1	2.6
Bivalvia	4.0	0.8	2.1	2.1
Gastropoda	1.2	1.6	-	0.5
Other	65.7	70.9	73.8	73.7
Detritus	65.7	70.9	73.1	51.2
Vegetation	-	-	0.7	22.5

Table 1.3. Diet composition of *Catostomus commersoni* in the North River, Virginia. PDUI = partially digested unidentifiable insect matter.

	<u>Spring</u>	<u>Summer</u>	<u>Fall</u>	<u>Winter</u>
No. intestines examined	30	30	31	27
No. empty intestines	0	5	7	4
Total length range (mm)	186-483	211-531	256-490	313-492
Mean total length (\pm SE) (mm)	415 (\pm 10)	400 (\pm 13)	362 (\pm 13)	429 (\pm 7)
<i>Taxa</i>	%	%	%	%
Annelida	0.1	0.2	-	0.3
Aquatic Insect	24.6	16.3	26.6	25.4
Coleoptera	0.3	0.1	0.3	2.1
Diptera	9.3	4.2	10.2	17.1
Ephemeroptera	9.0	1.5	7.1	0.2
Lepidoptera	-	-	0.1	-
Megaloptera	-	-	-	0.2
Odonata	0.2	-	2.9	2.7
Trichoptera	5.8	10.5	6.1	3.1
Crustacea	1.4	3.6	2.6	0.3
Amphipoda	0.1	0.1	0.2	0.3
Cladocera	0.3	3.5	1.6	-
Ostracoda	1.0	-	0.8	-
Mollusca	0.3	1.1	9.1	7.5
Bivalvia	0.2	0.8	8.3	5.5
Gastropoda	0.1	0.2	0.8	2.0
Other	73.6	78.9	61.6	66.4
Detritus	73.6	78.6	61.6	66.4
Vegetation	-	0.3	-	-

Table 1.4. Diet composition of *Ictalurus punctatus* in the South Fork of the Shenandoah River, Virginia. PDUI and PDUF = partially digested unidentifiable insect and fish matter, respectively.

	<u>Spring</u>	<u>Summer</u>	<u>Fall</u>
No. stomachs examined	1	38	26
No. empty stomachs	0	8	8
Total length range (mm)	708	197-827	179-783
Mean total length (\pm SE) (mm)	708 (\pm 0)	556 (\pm 22)	577 (\pm 29)
<i>Taxa</i>	%	%	%
Aquatic Insect	-	6.8	0.2
Diptera	-	0.3	0.2
Ephemeroptera	-	0.4	-
Megaloptera	-	3.4	-
Trichoptera	-	1.7	-
PDUI	-	1.0	-
Crustacea	-	4.9	6.8
Crayfish	-	4.9	6.8
Fish	30.8	11.7	21.6
<i>Lepomis auritus</i>	-	4.1	-
<i>Lepomis spp.</i>	-	2.9	-
<i>Micropterus dolomieu</i>	14.4	3.3	10.9
<i>Noturus insignis</i>	-	-	0.2
PDUF	16.5	1.3	10.5
Mollusca	-	0.1	-
Gastropoda	-	0.1	-
Terrestrial Biota	69.2	3.9	-
Coleoptera	-	3.9	-
<i>Microtus pennsylvanicus</i>	69.2	-	-
PDUI	-	-	-
Other	-	72.5	71.5
Detritus	-	8.7	0.1
Vegetation	-	63.8	71.4

Table 1.5. Diet composition of *Lepomis auritus* in the South River, Virginia. PDUI = partially digested unidentifiable insect matter.

Total length class (mm)	Spring			Summer			Fall			Winter		
	<100	100-150	>150	<100	100-150	>150	<100	100-150	>150	<100	100-150	>150
No. stomachs examined	2	18	14	6	11	15	9	11	14	5	9	17
No. empty stomachs	0	0	0	1	0	1	2	2	4	5	7	16
<i>Taxa</i>	%	%	%	%	%	%	%	%	%	%	%	%
Annelida	-	5.2	1.3	-	4.0	-	-	-	-	-	34.3	-
Aquatic Insect	100.0	78.8	68.5	80.0	73.5	47.5	92.5	63.1	69.9	-	50.0	100.0
Coleoptera	11.9	2.9	7.5	4.4	0.7	9.5	-	0.8	10.4	-	-	-
Diptera	42.2	22.9	8.3	5.1	2.4	0.3	11.3	17.5	0.3	-	-	-
Ephemeroptera	28.3	18.7	24.6	30.3	19.7	8.6	52.5	22.3	28.1	-	-	-
Hemiptera	-	0.1	2.2	-	-	-	-	-	-	-	-	-
Lepidoptera	-	-	-	1.9	-	-	-	2.1	9.8	-	-	-
Megaloptera	-	1.9	-	-	-	-	-	-	-	-	-	-
Odonata	-	1.2	3.5	-	-	-	2.9	-	-	-	50.0	100.0
Plecoptera	-	-	-	-	1.2	0.2	-	-	-	-	-	-
Trichoptera	-	7.7	6.7	8.1	14.7	8.6	14.9	6.0	3.0	-	-	-
PDUI	17.6	22.3	15.2	30.2	34.8	20.3	10.9	14.4	18.2	-	-	-
Crustacea	-	4.11	1.1	-	7.6	8.0	2.4	0.5	-	-	11.9	-
Amphipoda	-	-	-	-	-	-	2.4	-	-	-	-	-
Cladocera	-	-	0.1	-	-	-	-	0.5	-	-	-	-
Crayfish	-	-	1.0	-	7.6	8.0	-	-	-	-	-	-
Isopoda	-	4.1	-	-	-	-	-	-	-	-	11.9	-
Mollusca	-	-	8.8	-	10.8	3.7	-	7.6	0.1	-	-	-
Bivalvia	-	-	-	-	4.9	-	-	-	-	-	-	-
Gastropoda	-	-	8.8	-	5.9	3.7	-	7.6	0.1	-	-	-
Terrestrial Insect	-	0.8	1.8	-	2.0	37.1	0.4	-	16.2	-	-	-
Araneae	-	-	1.0	-	-	-	-	-	-	-	-	-
Chilopoda/Diplopoda	-	0.4	0.3	-	-	-	-	-	-	-	-	-
Coleoptera	-	0.2	0.3	-	-	33.9	-	-	3.5	-	-	-
Hymenoptera	-	0.2	0.2	-	2.0	3.2	0.4	-	12.7	-	-	-
Other	-	11.1	18.3	20.0	2.1	3.7	4.8	28.9	13.8	-	3.9	-
Detritus	-	10.4	9.4	20.0	2.1	1.8	4.8	17.9	13.2	-	3.9	-
Vegetation	-	0.7	2.7	-	-	1.9	-	11.0	0.5	-	-	-
Miscellaneous	-	-	6.2	-	-	-	-	-	0.1	-	-	-

Table 1.6. Diet composition of *Lepomis auritus* in the South Fork of the Shenandoah River, Virginia. PDUI and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Taxa	Spring			Summer			Fall			Winter		
	<100	100-150	>150	<100	100-150	>150	<100	100-150	>150	<100	100-150	>150
Total length class (mm)	2	10	27	6	11	18	11	17	14	2	17	11
No. stomachs examined	0	1	0	0	0	2	1	2	1	1	16	11
No. empty stomachs	%	%	%	%	%	%	%	%	%	%	%	%
Annelida	-	-	0.1	9.6	-	-	-	-	-	-	-	-
Aquatic Insect	79.6	93.1	87.9	86.8	99.1	69.8	87.7	75.3	78.7	100.0	100.0	-
Coleoptera	-	0.9	2.5	-	-	0.1	-	0.1	1.2	-	-	-
Diptera	39.4	6.4	6.0	20.1	11.6	1.4	9.0	4.1	5.0	-	-	-
Ephemeroptera	-	35.2	31.7	30.5	23.1	10.2	38.0	41.2	10.6	-	-	-
Hemiptera	-	-	0.1	-	-	-	-	0.6	8.4	-	-	-
Lepidoptera	-	-	0.3	-	1.1	0.3	-	0.4	10.1	-	-	-
Megaloptera	-	-	-	-	-	4.2	-	-	-	-	-	-
Odonata	-	6.0	1.6	1.2	-	5.0	10.0	2.7	3.8	100.0	100.0	-
Plecoptera	-	9.4	4.7	-	1.5	-	-	-	7.9	-	-	-
Trichoptera	26.3	3.9	21.9	21.4	44.9	25.9	12.0	15.7	16.3	-	-	-
PDUI	13.9	31.4	19.1	13.7	16.9	22.9	18.7	10.5	15.4	-	-	-
Crustacea	-	-	0.1	-	-	6.1	-	-	-	-	-	-
Cladocera	-	-	0.1	-	-	-	-	-	-	-	-	-
Crayfish	-	-	-	-	-	6.1	-	-	-	-	-	-
Fish	-	-	0.7	-	-	5.2	-	-	-	-	-	-
<i>Lepomis spp.</i>	-	-	0.7	-	-	-	-	-	-	-	-	-
PDUF	-	-	-	-	-	5.2	-	-	-	-	-	-
Mollusca	-	-	1.3	1.7	-	1.3	1.9	4.7	2.7	-	-	-
Gastropoda	-	-	1.3	1.7	-	1.3	1.9	4.7	2.7	-	-	-
Terrestrial Insect	-	-	-	-	-	8.8	-	-	5.0	-	-	-
Araneae	-	-	-	-	-	-	-	-	1.8	-	-	-
Coleoptera	-	-	-	-	-	8.8	-	-	-	-	-	-
Hymenoptera	-	-	-	-	-	-	-	-	3.2	-	-	-
Other	20.4	6.9	9.9	1.9	0.8	8.7	10.4	20.0	13.6	-	-	-
Detritus	20.4	6.9	8.3	1.9	0.2	0.3	3.9	13.6	6.9	-	-	-
Vegetation	-	-	1.6	-	0.6	8.4	6.5	6.4	6.7	-	-	-

Table 1.7. Diet composition of *Lepomis auritus* in the North River, Virginia. PDUI and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Taxa	Spring			Summer			Fall			Winter		
	<100 %	100-150 %	>150 %	<100 %	100-150 %	>150 %	<100 %	100-150 %	>150 %	<100 %	100-150 %	>150 %
Total length class (mm)												
No. stomachs examined	0	11	19	3	7	14	6	12	13	3	3	17
No. empty stomachs	0	0	0	0	0	0	1	3	2	3	3	15
Aquatic Insect	-	93.8	83.8	100.0	89.8	66.3	94.9	82.6	75.5	-	-	100.0
Coleoptera	-	-	0.7	7.4	2.2	12.6	11.5	3.9	1.0	-	-	-
Diptera	-	39.7	14.4	17.1	22.6	0.7	15.9	8.9	22.9	-	-	-
Ephemeroptera	-	17.2	28.3	28.2	25.5	11.4	41.2	13.0	2.6	-	-	-
Hemiptera	-	0.1	-	-	0.2	-	-	-	0.1	-	-	50.0
Lepidoptera	-	-	-	4.4	1.0	-	-	7.9	14.0	-	-	-
Odonata	-	5.0	2.7	-	-	-	2.1	-	9.1	-	-	50.0
Plecoptera	-	-	0.3	-	-	-	-	-	-	-	-	-
Trichoptera	-	14.5	20.7	22.4	28.1	21.7	16.2	27.8	2.0	-	-	-
PDUI	-	17.3	16.7	20.4	10.1	19.9	8.1	21.0	23.6	-	-	-
Crustacea	-	0.1	3.6	-	5.0	5.7	-	-	-	-	-	-
Amphipoda	-	0.1	-	-	-	-	-	-	-	-	-	-
Crayfish	-	-	2.8	-	5.0	5.7	-	-	-	-	-	-
Isopoda	-	-	0.8	-	-	-	-	-	-	-	-	-
Fish	-	-	-	-	-	1.8	-	-	-	-	-	-
PDUF	-	-	-	-	-	1.8	-	-	-	-	-	-
Mollusca	-	0.8	5.5	-	-	0.1	-	8.9	10.9	-	-	-
Gastropoda	-	0.8	5.5	-	-	0.1	-	8.9	10.9	-	-	-
Terrestrial Insect	-	0.1	1.1	-	5.17	25.0	-	-	7.9	-	-	-
Araneae	-	-	0.1	-	-	-	-	-	5.4	-	-	-
Coleoptera	-	-	0.2	-	4.8	25.0	-	-	0.5	-	-	-
Hymenoptera	-	0.1	0.8	-	0.4	-	-	-	-	-	-	-
PDUI	-	-	-	-	-	-	-	-	1.9	-	-	-
Other	-	5.2	6.0	-	-	1.0	5.1	8.4	5.8	-	-	-
Detritus	-	3.0	3.3	-	-	1.0	5.1	5.9	2.5	-	-	-
Vegetation	-	2.0	2.7	-	-	-	-	2.5	3.3	-	-	-
Miscellaneous	-	0.2	-	-	-	-	-	-	-	-	-	-

Table 1.8. Diet composition of *Micropterus dolomieu* in the South River, Virginia. PDUJ and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Total length class (mm)	Spring				Summer				Fall				Winter			
	100 >	100-199	200-299	<299	100 >	100-199	200-299	<299	100 >	100-199	200-299	<299	100 >	100-199	200-299	<299
No. stomachs examined	2	13	12	8	11	13	11	7	10	15	16	3	6	6	4	4
No. empty stomachs	0	0	0	1	1	2	1	0	1	5	4	1	4	6	4	2
<i>Taxa</i>	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Annelida	-	4.3	-	-	10.0	9.1	-	-	-	-	-	-	-	-	-	-
Aquatic Insect	92.4	36.5	28.2	18.8	83.5	39.1	-	-	75.4	42.5	-	-	-	-	-	-
Coleoptera	-	0.4	-	-	-	1.2	-	-	-	-	-	-	-	-	-	-
Diptera	50.6	10.2	6.7	14.5	14.3	-	-	-	2.6	-	-	-	-	-	-	-
Ephemeroptera	-	10.1	3.9	-	45.1	22.7	-	-	47.7	37.5	-	-	-	-	-	-
Hemiptera	41.8	-	-	-	-	0.1	-	-	-	1.9	-	-	-	-	-	-
Lepidoptera	-	0.1	-	-	-	3.0	-	-	-	-	-	-	-	-	-	-
Odonata	-	4.9	-	-	-	-	-	-	1.2	0.5	-	-	-	-	-	-
Plecoptera	-	-	-	-	-	9.1	-	-	-	-	-	-	-	-	-	-
Trichoptera	-	6.0	12.4	0.7	3.8	1.4	-	-	4.9	-	-	-	-	-	-	-
PDUJ	-	4.9	5.2	3.6	20.3	1.7	-	-	18.9	2.6	-	-	-	-	-	-
Crustacea	-	3.3	16.4	21.2	-	34.9	85.2	41.8	4.7	10.0	91.7	50.0	-	-	-	-
Cladocera	-	-	-	-	-	-	-	-	4.7	-	-	-	-	-	-	-
Crayfish	-	3.1	16.4	21.2	-	34.9	85.2	41.8	-	10.0	91.7	50.0	-	-	-	-
Isopoda	-	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fish	6.3	44.2	26.7	25.9	6.5	15.6	3.4	53.2	10.4	38.9	8.3	50.0	50.0	-	100.0	-
Centrarchidae PDUF	-	-	-	-	-	1.3	-	-	-	-	-	-	50.0	-	-	-
Cyprinidae PDUF	-	-	-	-	-	4.8	-	13.4	-	-	-	-	-	-	95.7	-
<i>Etheostoma flabellare</i>	-	7.5	-	-	-	-	-	-	-	10.0	-	-	-	-	-	-
<i>Etheostoma</i> spp.	-	10.8	8.1	-	-	-	-	-	-	-	-	-	-	-	-	-
<i>Exoglossum maxillingua</i>	-	-	-	12.7	-	-	-	-	-	-	-	-	-	-	-	-
Ictaluridae PDUF	-	-	-	-	-	6.1	-	-	-	-	-	-	-	-	-	-
<i>Lepomis</i> spp.	-	-	-	-	-	-	-	-	-	-	-	38.3	-	-	-	-
PDUF	6.3	25.9	18.6	13.1	6.5	3.4	3.4	39.9	10.4	28.9	8.3	11.7	-	-	-	4.3

Table 1.8. (continued) Diet composition of *Micropterus dolomieu* in the South River, Virginia. PDUJ and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Total length class (mm)	Spring			Summer			Fall			Winter		
	<100	100-199	200-299	<299	>100	100-199	200-299	<299	>100	100-199	200-299	<299
<i>Taxa</i>	%	%	%	%	%	%	%	%	%	%	%	%
Terrestrial Insect	1.3	-	-	-	-	10.0	4.9	8.9	7.6	-	-	-
Araneae	-	-	-	-	-	-	-	7.1	-	-	-	-
Coleoptera	-	-	-	-	-	10.0	4.9	-	-	-	-	-
Hymenoptera	-	-	-	-	-	-	-	1.7	-	-	-	-
PDUJ	1.3	-	-	-	-	-	-	-	7.6	-	-	-
Other	-	11.7	28.7	34.2	-	1.3	1.4	-	0.7	0.9	-	50.0
Detritus	-	10.9	13.6	8.6	-	1.3	1.4	-	-	0.9	-	50.0
Vegetation	-	0.8	15.1	25.6	-	-	-	-	0.7	-	-	-

Table 1.9. Diet composition of *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia. PDUJ and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Total length class (mm)	Spring						Summer						Fall						Winter					
	100	100-199	200-299	299<	100	100-199	200-299	299<	100	100-199	200-299	299<	100	100-199	200-299	299<	100	100-199	200-299	299<				
No. stomachs examined	1	13	27	15	4	17	28	9	0	23	20	6	0	6	4	0	6	15	16					
No. empty stomachs	0	1	1	0	0	0	5	3	0	6	4	4	0	5	4	0	5	12	9					
<i>Taxa</i>	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%				
Annelida	-	-	3.8	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Aquatic Insect	100.0	78.8	61.7	24.4	100.0	79.4	45.3	16.7	-	74.1	2.1	-	-	-	-	-	-	-	-	-				
Coleoptera	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Diptera	9.4	7.7	2.9	5.6	2.8	1.3	-	-	-	1.1	-	-	-	-	-	-	-	-	-	-				
Ephemeroptera	64.1	12.2	25.2	8.4	82.3	55.0	29.9	-	-	43.8	-	-	-	-	-	-	-	-	-	-				
Hemiptera	-	-	-	-	-	-	-	-	-	22.5	0.2	-	-	-	-	-	-	-	-	-				
Lepidoptera	-	-	0.02	-	-	0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Megaloptera	-	-	9.7	-	-	5.9	5.7	16.7	-	-	-	-	-	-	-	-	-	-	-	-				
Neuroptera	-	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Odonata	-	6.6	3.8	0.4	-	0.9	6.3	-	-	5.8	1.9	-	-	-	-	-	-	-	-	-				
Plecoptera	-	20.8	0.2	0.9	2.0	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Trichoptera	-	18.9	13.4	3.1	10.5	7.4	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-				
PDUJ	26.6	12.5	6.5	5.9	2.4	8.3	3.3	-	-	1.0	0.1	-	-	-	-	-	-	-	-	-				
Crustacea	-	-	3.6	20.6	-	13.6	34.6	45.7	-	-	37.4	50.0	-	-	66.7	28.6	-	-	-	-				
Crayfish	-	-	3.6	20.6	-	13.6	34.6	45.7	-	-	37.4	50.0	-	-	66.7	28.6	-	-	-	-				
Fish	-	8.2	30.0	45.5	-	5.9	14.9	36.8	-	23.8	60.5	50.0	-	100.0	33.3	61.7	-	-	-	-				
<i>Ambloplites rupestris</i>	-	-	-	2.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-				
Centrarchidae PDUF	-	8.2	1.4	5.7	-	-	-	-	-	-	6.3	-	-	-	-	14.3	-	-	-	-				
<i>Cyprinella analostana</i>	-	-	-	-	-	-	8.0	-	-	-	-	-	-	-	-	-	-	-	-	-				
Cyprinidae PDUF	-	-	-	-	-	4.7	-	-	-	6.3	6.25	-	-	-	-	-	-	-	-	-				
<i>Lepomis auritus</i>	-	-	7.5	0.2	-	-	-	-	-	5.6	-	-	-	-	33.3	-	-	-	-	-				
<i>Lepomis spp.</i>	-	-	2.4	5.6	-	-	-	-	-	7.3	14.8	50.0	-	100.0	-	22.2	-	-	-	-				
<i>Noturus insignis</i>	-	-	10.2	25.1	-	-	4.4	-	-	-	-	-	-	-	-	2.9	-	-	-	-				

Table 1.9. (continued) Diet composition of *Micropterus dolomieu* in the South Fork of the Shenandoah River, Virginia. PDUI and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Total length class (mm)	Spring			Summer			Fall			Winter		
	>100	100-199	200-299	>299	>100	100-199	200-299	>299	>100	100-199	200-299	>299
<i>Taxa</i>	%	%	%	%	%	%	%	%	%	%	%	%
<i>Micropterus dolomieu</i>	-	-	3.1	-	-	-	-	16.7	-	-	-	-
<i>Nocomis spp.</i>	-	-	-	-	-	-	-	13.6	-	-	-	-
PDUF	-	-	5.4	6.1	-	1.1	2.5	6.5	-	4.7	33.1	-
Mollusca	-	-	-	-	-	0.2	3.0	-	-	-	-	22.3
Bivalvia	-	-	-	-	-	-	-	-	-	-	-	0.9
Gastropoda	-	-	-	-	-	0.2	3.0	-	-	-	-	0.9
Terrestrial Insect	-	-	-	0.1	-	0.2	-	-	-	0.4	-	-
Araneae	-	-	-	0.1	-	-	-	-	-	0.3	-	-
Coleoptera	-	-	-	-	-	-	-	-	-	0.1	-	-
Hymenoptera	-	-	-	-	-	0.2	-	-	-	-	-	-
Other	-	13.0	0.9	9.3	-	0.7	2.2	0.9	-	1.6	-	8.8
Detritus	-	8.3	0.8	6.7	-	0.2	2.1	0.9	-	-	-	4.9
Vegetation	-	4.7	0.1	2.6	-	0.5	0.1	-	-	1.6	-	3.9

Table 1.10. Diet composition of *Micropterus dolomieu* in the North River, Virginia. PDUI and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Total length class (mm)	Spring				Summer				Fall				Winter			
	100 >	100-199	200-299	>299	100 >	100-199	200-299	>299	100 >	100-199	200-299	>299	100 >	100-199	200-299	>299
No. stomachs examined	2	8	14	6	1	13	13	4	7	11	13	6	1	6	10	4
No. empty stomachs	1	0	2	1	0	1	4	2	0	3	3	2	1	6	5	3
<i>Taxa</i>	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Annelida	-	-	-	-	-	-	3.1	-	-	-	-	-	-	-	-	-
Aquatic Insect	100.0	88.2	33.5	0.6	100.0	51.1	10.4	-	100.0	63.3	0.2	-	-	-	-	-
Coleoptera	-	12.2	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-
Diptera	16.7	6.5	0.1	-	-	-	-	-	10.3	0.6	-	-	-	-	-	-
Ephemeroptera	-	55.4	19.8	0.2	100.0	40.7	-	-	66.6	48.7	-	-	-	-	-	-
Hemiptera	-	0.1	0.6	-	-	0.7	-	-	13.1	-	-	-	-	-	-	-
Lepidoptera	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-
Megaloptera	-	-	4.6	0.4	-	-	-	-	-	-	-	-	-	-	-	-
Odonata	-	-	1.8	-	-	-	-	-	-	12.5	-	-	-	-	-	-
Trichoptera	75.0	7.5	5.2	-	-	0.7	0.6	-	-	1.0	-	-	-	-	-	-
PDUI	8.3	6.6	1.4	-	-	4.8	-	-	10.0	0.4	0.2	-	-	-	-	-
Crustacea	-	0.8	24.2	56.6	-	8.3	59.6	50.0	-	12.0	70.5	89.0	-	-	20.0	100.0
Crayfish	-	-	23.9	56.6	-	8.3	59.6	50.0	-	12.0	70.5	89.0	-	-	20.0	100.0
Isopoda	-	0.8	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-
Fish	-	-	22.4	42.4	-	31.7	9.3	-	-	24.6	29.3	10.3	-	-	80.0	-
Centrarchidae PDUF	-	-	3.1	-	-	5.4	-	-	-	12.1	1.7	-	-	-	-	-
Cyprinidae PDUF	-	-	4.3	-	-	-	-	-	-	-	-	-	-	-	-	-
Ictaluridae PDUF	-	-	-	-	-	-	5.3	-	-	-	-	-	-	-	-	-
<i>Lepomis gibbosus</i>	-	-	-	-	-	-	-	-	-	8.4	-	-	-	-	-	-
<i>Lepomis spp.</i>	-	-	-	-	-	-	-	-	-	4.1	-	-	-	-	35.4	-
<i>Micropterus dolomieu</i> .	-	-	-	4.2	-	-	4.0	-	-	-	-	-	-	-	-	-
<i>Notropis amoenus</i>	-	-	-	10.4	-	-	-	-	-	-	-	-	-	-	20.0	-
<i>Noturus insignis</i>	-	-	-	26.0	-	-	-	-	-	-	-	-	-	-	-	-
PDUF	-	-	15.0	1.9	-	26.2	-	-	-	27.6	10.3	-	-	-	24.6	-

Table 1.10. (continued) Diet composition of *Micropterus dolomieu* in the North River, Virginia. PDU1 and PDUF = partially digested unidentifiable insect and fish matter, respectively.

Total length class (mm)	Spring			Summer			Fall			Winter		
	<100	100-199	200-299	<299	>100	100-199	200-299	<299	>100	100-199	200-299	>299
Taxa	%	%	%	%	%	%	%	%	%	%	%	%
Mollusca	-	-	0.2	-	-	1.3	-	-	-	-	-	-
Gastropoda	-	-	0.2	-	-	1.3	-	-	-	-	-	-
Terrestrial Insect	-	0.8	-	-	-	8.6	15.8	50.0	-	-	-	-
Coleoptera	-	-	-	-	-	15.8	50.0	-	-	-	-	-
Hymenoptera	-	0.8	-	-	-	8.6	-	-	-	-	-	-
Other	-	10.1	19.6	0.4	-	0.2	1.8	-	-	-	-	-
Detritus	-	7.9	17.3	0.3	-	-	1.8	-	-	-	-	-
Vegetation	-	2.2	2.3	0.1	-	0.2	-	-	-	-	-	0.7

Table 3.1. Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR3 on the South River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	61.50	0.32	5.16	29.80	6.14
2	184.00	0.44	13.60	63.20	18.70
3	337.00	0.54	20.10	87.20	32.10
4	497.00	0.61	26.00	108.00	45.80
5	662.00	0.67	31.30	128.00	59.70
6	832.00	0.72	36.40	146.00	73.80
7	1,006.00	0.76	41.20	163.00	87.90
8	1,184.00	0.80	45.90	180.00	102.00
9	1,364.00	0.84	50.30	196.00	116.00
10	1,548.00	0.87	54.70	212.00	130.00
11	1,733.00	0.89	58.90	227.00	144.00
<i>Etheostoma flabellare</i>					
1	0.47	0.33	0.04	0.19	0.02
2	1.18	0.54	0.13	0.52	0.12
3	2.07	0.77	0.21	0.77	0.27
4	2.96	0.94	0.29	1.02	0.43
5	3.84	1.09	0.36	1.24	0.62
<i>Lepomis auritus</i>					
1	6.80	0.26	0.36	2.47	0.15
2	19.60	0.45	1.35	7.01	0.91
3	37.60	0.59	2.01	9.70	1.76
4	55.30	0.69	2.54	11.90	2.66
5	72.80	0.82	3.00	19.40	3.78
6	89.90	1.02	3.41	25.00	5.50
7	107.00	1.19	3.79	27.50	7.26
8	124.00	1.33	4.14	29.80	9.04
9	140.00	1.44	4.47	32.00	10.80
<i>Luxilus cornutus</i>					
1	2.12	0.21	0.07	0.56	0.03
2	6.59	0.33	0.41	1.91	0.24
3	13.30	0.47	0.79	3.21	0.62
4	20.70	0.59	1.19	4.54	1.15
5	28.40	0.70	1.60	5.91	1.81
<i>Micropterus dolomieu</i>					
1	14.10	0.37	0.69	10.40	0.50
2	48.50	0.79	2.33	34.70	3.04
3	101.00	0.92	3.65	37.80	5.23
4	160.00	0.97	4.83	49.50	7.16
5	224.00	1.05	5.93	68.10	9.26
6	292.00	1.21	6.97	95.20	12.20

Table 3.1. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR3 on the South River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
7	363.00	1.38	7.96	114.00	15.70
8	438.00	1.53	8.91	132.00	19.30
9	515.00	1.68	9.83	149.00	23.10
10	595.00	1.80	10.70	166.00	27.00
<i>Noturus insignis</i>					
1	2.28	0.19	0.05	0.58	0.02
2	7.57	0.29	0.30	1.85	0.13
3	16.00	0.38	0.59	2.99	0.31
4	25.50	0.47	0.89	4.13	0.55

Table 3.2. Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR4 on the South River, Virginia, where WT = mean body weight, MeHg = mean body concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	61.50	0.41	6.13	38.80	7.90
2	184.00	0.56	16.10	82.30	24.00
3	337.00	0.69	23.90	114.00	41.10
4	497.00	0.78	30.90	141.00	58.70
5	662.00	0.86	37.30	167.00	76.60
6	832.00	0.92	43.30	190.00	94.50
7	1,006.00	0.98	49.00	213.00	113.00
8	1,184.00	1.03	54.50	235.00	131.00
9	1,364.00	1.07	59.90	256.00	149.00
10	1,548.00	1.11	65.00	276.00	167.00
11	1,733.00	1.14	70.10	296.00	184.00
<i>Etheostoma flabellare</i>					
1	0.47	0.48	0.04	0.28	0.03
2	1.18	0.78	0.16	0.77	0.18
3	2.07	1.09	0.26	1.16	0.38
4	2.96	1.34	0.34	1.51	0.62
5	3.84	1.55	0.43	1.85	0.88
<i>Lepomis auritus</i>					
1	6.80	0.38	0.43	3.62	0.22
2	19.60	0.65	1.60	10.30	1.30
3	37.60	0.84	2.39	14.20	2.50
4	55.30	0.99	3.02	17.40	3.78
5	72.80	1.14	3.57	25.00	5.28
6	89.90	1.36	4.06	30.80	7.31
7	107.00	1.55	4.51	33.90	9.41
8	124.00	1.70	4.92	36.80	11.50
9	140.00	1.83	5.31	39.50	13.70
<i>Luxilus cornutus</i>					
1	2.12	0.31	0.08	0.83	0.04
2	6.59	0.47	0.49	2.85	0.35
3	13.30	0.67	0.94	4.78	0.89
4	20.70	0.84	1.42	6.77	1.64
5	28.40	1.00	1.90	8.80	2.58
<i>Micropterus dolomieu</i>					
1	14.10	0.52	0.83	14.80	0.71
2	48.50	1.11	2.77	49.40	4.29
3	101.00	1.29	4.34	53.80	7.37
4	160.00	1.36	5.74	70.60	10.10
5	224.00	1.48	7.05	97.30	13.00
6	292.00	1.71	8.28	136.00	17.20
7	363.00	1.94	9.46	162.00	22.10
8	438.00	2.16	10.60	187.00	27.20
9	515.00	2.36	11.70	211.00	32.50

Table 3.2. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR4 on the South River, Virginia, where WT = mean body wet weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
10	595.00	2.54	12.80	234.00	37.90
<i>Noturus insignis</i>					
1	2.28	0.28	0.06	0.87	0.03
2	7.57	0.42	0.36	2.75	0.19
3	16.00	0.55	0.70	4.45	0.45
4	25.50	0.67	1.06	6.14	0.80

Table 3.3. Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	61.50	0.73	8.63	70.90	14.00
2	184.00	0.99	22.70	150.00	42.40
3	337.00	1.21	33.70	208.00	72.30
4	497.00	1.37	43.40	258.00	103.00
5	662.00	1.50	52.40	304.00	134.00
6	832.00	1.62	60.90	348.00	166.00
7	1,006.00	1.71	69.00	389.00	197.00
8	1,184.00	1.80	76.70	429.00	228.00
9	1,364.00	1.88	84.20	467.00	260.00
10	1,548.00	1.94	91.50	504.00	291.00
11	1,733.00	2.00	98.60	540.00	322.00
<i>Etheostoma flabellare</i>					
1	0.47	1.08	0.06	0.68	0.07
2	1.18	1.73	0.23	1.84	0.40
3	2.07	2.42	0.36	2.75	0.85
4	2.96	2.96	0.49	3.59	1.38
5	3.84	3.39	0.60	4.39	1.95
<i>Lepomis auritus</i>					
1	6.80	0.85	0.61	8.46	0.51
2	19.60	1.44	2.25	24.00	2.89
3	37.60	1.85	3.36	33.20	5.53
4	55.30	2.18	4.25	40.70	8.35
5	72.80	2.46	5.02	48.50	11.40
6	89.90	2.73	5.71	55.20	14.70
7	107.00	2.97	6.34	60.80	18.10
8	124.00	3.18	6.93	65.90	21.60
9	140.00	3.36	7.48	70.80	25.30
<i>Luxilus cornutus</i>					
1	2.12	0.71	0.12	1.99	0.11
2	6.59	1.06	0.69	6.77	0.79
3	13.30	1.49	1.33	11.40	1.99
4	20.70	1.86	1.99	16.10	3.64
5	28.40	2.21	2.68	20.90	5.71
<i>Micropterus dolomieu</i>					
1	14.10	1.13	1.17	32.90	1.55
2	48.50	2.43	3.89	110.00	9.35
3	101.00	2.81	6.10	120.00	16.00
4	160.00	2.96	8.08	157.00	21.80
5	224.00	3.20	9.92	217.00	28.20
6	292.00	3.71	11.70	303.00	37.40
7	363.00	4.22	13.30	358.00	48.00
8	438.00	4.68	14.90	412.00	59.10
9	515.00	5.10	16.40	463.00	70.50

Table 3.3. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
10	595.00	5.49	17.90	512.00	82.10
<i>Noturus insignis</i>					
1	2.28	0.65	0.09	2.07	0.07
2	7.57	0.95	0.51	6.54	0.44
3	16.00	1.25	0.99	10.60	1.03
4	25.50	1.52	1.49	14.60	1.81

Table 3.4. Model-predicted bioaccumulation dynamics of methylmercury in fish in the South Fork of the Shenandoah River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	69.80	0.22	5.04	23.20	5.58
2	199.00	0.31	12.60	48.10	16.80
3	359.00	0.38	18.50	66.30	28.80
4	524.00	0.43	23.70	82.30	41.00
5	694.00	0.48	28.50	97.10	53.30
6	868.00	0.51	33.00	111.00	65.60
7	1,046.00	0.54	37.20	124.00	77.80
8	1,227.00	0.56	41.40	137.00	90.00
9	1,411.00	0.59	45.30	149.00	102.00
10	1,598.00	0.61	49.20	161.00	114.00
11	1,788.00	0.62	53.00	172.00	126.00
<i>Cyprinella analostana</i>					
1	1.76	0.13	0.03	0.24	0.01
2	5.56	0.20	0.29	1.08	0.15
3	11.80	0.30	0.58	1.89	0.42
<i>Ictalurus punctatus</i>					
1	96.20	0.08	1.02	9.53	0.80
2	311.00	0.13	5.95	48.30	5.12
3	664.00	0.22	11.60	93.70	13.70
4	1,055.00	0.30	17.40	149.00	25.40
5	1,472.00	0.38	23.30	204.00	41.30
6	1,909.00	0.46	29.30	258.00	59.80
7	2,365.00	0.52	35.30	280.00	80.70
8	2,836.00	0.55	41.50	294.00	98.90
9	3,321.00	0.58	47.70	289.00	117.00
10	3,818.00	0.59	53.90	335.00	135.00
11	4,326.00	0.61	60.20	389.00	154.00
12	4,844.00	0.64	66.50	447.00	176.00
<i>Lepomis auritus</i>					
1	10.40	0.14	0.33	1.86	0.11
2	30.40	0.23	1.22	5.19	0.60
3	60.60	0.29	1.86	7.40	1.14
4	92.00	0.34	2.40	9.46	1.72
5	124.00	0.38	2.88	11.10	2.32
6	157.00	0.42	3.32	12.50	2.93
7	190.00	0.45	3.73	14.10	3.55
8	223.00	0.49	4.11	15.70	4.20
<i>Micropterus dolomieu</i>					
1	34.60	0.13	0.85	6.77	0.33
2	99.90	0.23	2.51	17.40	1.38
3	187.00	0.32	3.70	28.50	2.68
4	279.00	0.39	4.70	38.40	4.12
5	373.00	0.48	5.61	52.80	5.88

Table 3.4. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish in the South Fork of the Shenandoah River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
6	468.00	0.56	6.44	61.90	7.78
7	566.00	0.64	7.22	71.90	9.77
8	664.00	0.71	7.96	80.30	11.80
9	764.00	0.77	8.67	88.70	13.90
10	865.00	0.83	9.34	96.90	16.00
11	967.00	0.89	9.99	105.00	18.10
<i>Noturus insignis</i>					
1	2.32	0.12	0.04	0.34	0.01
2	7.31	0.18	0.21	1.05	0.08
3	15.30	0.23	0.41	1.70	0.19
4	24.30	0.29	0.62	2.35	0.34

Table 3.5. Model-predicted bioaccumulation dynamics of methylmercury in fish in the North River, Virginia, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	69.60	0.12	3.32	12.30	2.67
2	207.00	0.17	8.52	25.60	8.06
3	378.00	0.21	12.60	35.20	13.90
4	558.00	0.24	16.20	43.70	19.80
5	745.00	0.27	19.60	51.50	25.90
6	936.00	0.29	22.70	58.90	32.10
7	1,132.00	0.31	25.80	65.90	38.30
8	1,332.00	0.32	28.70	72.60	44.50
9	1,536.00	0.34	31.50	79.10	50.70
10	1,743.00	0.35	34.20	85.40	56.90
<i>Lepomis auritus</i>					
1	11.10	0.03	0.27	0.28	0.02
2	33.50	0.06	1.04	0.83	0.16
3	66.30	0.08	1.59	1.26	0.34
4	99.40	0.09	2.03	1.71	0.56
5	132.00	0.11	2.42	2.00	0.82
6	165.00	0.12	2.76	2.26	1.10
7	198.00	0.13	3.08	2.54	1.40
<i>Micropterus dolomieu</i>					
1	17.10	0.03	0.44	0.61	0.04
2	53.10	0.06	1.38	1.45	0.23
3	103.00	0.08	2.08	2.50	0.46
4	157.00	0.10	2.68	3.40	0.70
5	214.00	0.11	3.23	4.25	0.96
6	272.00	0.13	3.73	5.29	1.26
7	332.00	0.14	4.21	6.05	1.55
8	393.00	0.16	4.67	6.76	1.86
9	455.00	0.17	5.11	7.44	2.16
<i>Notropis amoenus</i>					
1	1.86	0.03	0.03	0.03	0.03
2	5.77	0.05	0.21	0.13	0.03
3	11.90	0.08	0.40	0.22	0.09
<i>Noturus insignis</i>					
1	2.30	0.02	0.03	0.04	0.00
2	7.56	0.04	0.17	0.14	0.01
3	16.00	0.06	0.33	0.22	0.04
4	25.40	0.07	0.49	0.31	0.08

Table 3.6. Model-predicted bioaccumulation dynamics of methylmercury in *Ictalurus punctatus* in the South Fork of the Shenandoah River, Virginia for diets composed of 19.5, 50.0, and 75.0% fish, where WT = mean body wet, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<u>19.5% Piscivory</u>					
1	96.20	0.08	1.02	9.53	0.80
2	311.00	0.13	5.95	48.30	5.12
3	664.00	0.22	11.60	93.70	13.70
4	1,055.00	0.30	17.40	149.00	25.40
5	1,472.00	0.38	23.30	204.00	41.30
6	1,909.00	0.46	29.30	258.00	59.80
7	2,365.00	0.52	35.30	280.00	80.70
8	2,836.00	0.55	41.50	294.00	98.90
9	3,321.00	0.58	47.70	289.00	117.00
10	3,818.00	0.59	53.90	335.00	135.00
11	4,326.00	0.61	60.20	389.00	154.00
12	4,844.00	0.64	66.50	447.00	176.00
<u>50.0% Piscivory</u>					
1	96.20	0.12	1.02	14.80	0.81
2	311.00	0.22	5.95	86.20	5.92
3	664.00	0.39	11.60	174.00	17.30
4	1,055.00	0.55	17.40	282.00	33.30
5	1,472.00	0.71	23.30	390.00	56.00
6	1,909.00	0.86	29.30	496.00	82.80
7	2,365.00	0.99	35.30	536.00	114.00
8	2,836.00	1.06	41.50	557.00	141.00
9	3,321.00	1.10	47.70	540.00	167.00
10	3,818.00	1.14	53.90	631.00	194.00
11	4,326.00	1.17	60.20	738.00	221.00
12	4,844.00	1.22	66.50	851.00	254.00
<u>75.0% Piscivory</u>					
1	96.20	0.14	1.02	18.00	0.69
2	311.00	0.28	5.95	109.00	5.48
3	664.00	0.50	11.60	221.00	16.80
4	1,055.00	0.70	17.40	361.00	33.10
5	1,472.00	0.92	23.30	499.00	56.50
6	1,909.00	1.12	29.30	637.00	84.60
7	2,365.00	1.29	35.30	687.00	117.00
8	2,836.00	1.38	41.50	712.00	147.00
9	3,321.00	1.45	47.70	688.00	176.00
10	3,818.00	1.49	53.90	805.00	205.00
11	4,326.00	1.53	60.20	943.00	234.00
12	4,844.00	1.61	66.50	1,089.00	269.00

Table 3.7. Model-predicted bioaccumulation dynamics of methylmercury in *Micropterus dolomieu* at site SR3 on the South River, Virginia for average lengths of prey of 9.5, 25.0, and 42.6%, where WT = mean body wet, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<u>9.5% Average Prey Length</u>					
1	14.10	0.24	0.69	5.20	0.32
2	48.50	0.40	2.33	16.50	1.56
3	101.00	0.50	3.65	24.70	2.91
4	160.00	0.62	4.83	41.40	4.62
5	224.00	0.79	5.93	65.20	6.99
6	292.00	1.01	6.97	91.30	10.20
7	363.00	1.20	7.96	108.00	13.70
8	438.00	1.37	8.91	124.00	17.30
9	515.00	1.52	9.83	139.00	21.00
10	595.00	1.65	10.70	153.00	24.70
<u>25.0% Average Prey Length</u>					
1	14.10	0.37	0.69	10.40	0.50
2	48.50	0.79	2.33	34.70	3.04
3	101.00	0.92	3.65	37.80	5.23
4	160.00	0.97	4.83	49.50	7.16
5	224.00	1.05	5.93	68.10	9.26
6	292.00	1.21	6.97	95.20	12.20
7	363.00	1.38	7.96	114.00	15.70
8	438.00	1.53	8.91	132.00	19.30
9	515.00	1.68	9.83	149.00	23.10
10	595.00	1.80	10.70	166.00	27.00
<u>42.6% Average Prey Length</u>					
1	14.10	0.44	0.69	13.10	0.60
2	48.50	1.03	2.33	47.00	3.98
3	101.00	1.16	3.65	40.20	6.64
4	160.00	1.03	4.83	31.40	7.63
5	224.00	1.00	5.93	72.50	8.81
6	292.00	1.30	6.97	132.00	13.20
7	363.00	1.61	7.96	158.00	18.40
8	438.00	1.88	8.91	185.00	23.80
9	515.00	2.12	9.83	210.00	29.30
10	595.00	2.33	10.70	232.00	34.90

Table 3.8. Model-predicted bioaccumulation dynamics of methylmercury in *Catostomus commersoni* at site SR6 on the South River, Virginia for adjusted specific growth rates, where WT = mean body wet, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<u>25% Decreased Specific Growth Rate</u>					
1	45.10	0.77	7.03	55.50	11.70
2	135.00	1.04	18.50	120.00	36.10
3	247.00	1.28	27.50	166.00	61.90
4	365.00	1.46	35.50	207.00	88.40
5	487.00	1.59	42.80	245.00	115.00
6	612.00	1.71	49.70	281.00	142.00
7	741.00	1.82	56.40	314.00	169.00
8	872.00	1.89	62.70	347.00	196.00
9	1,005.00	1.97	68.80	378.00	222.00
10	1,140.00	2.04	74.80	409.00	249.00
11	1,278.00	2.10	80.60	438.00	276.00
<u>Observed Specific Growth Rate</u>					
1	61.50	0.73	8.63	70.90	14.00
2	184.00	0.99	22.70	150.00	42.40
3	337.00	1.21	33.70	208.00	72.30
4	497.00	1.37	43.40	258.00	103.00
5	662.00	1.50	52.40	304.00	134.00
6	832.00	1.62	60.90	348.00	166.00
7	1,006.00	1.71	69.00	389.00	197.00
8	1,184.00	1.80	76.70	429.00	228.00
9	1,364.00	1.88	84.20	467.00	260.00
10	1,548.00	1.94	91.50	504.00	291.00
11	1,733.00	2.00	98.60	540.00	322.00
<u>25% Increased Specific Growth Rate</u>					
1	78.20	0.69	10.10	85.90	16.10
2	233.00	0.95	26.60	180.00	48.10
3	428.00	1.14	39.40	247.00	81.70
4	631.00	1.31	50.90	306.00	116.00
5	841.00	1.43	61.40	360.00	151.00
6	1,057.00	1.55	71.30	411.00	186.00
7	1,277.00	1.64	80.70	459.00	222.00
8	1,502.00	1.73	89.80	506.00	257.00
9	1,730.00	1.80	98.50	551.00	293.00
10	1,962.00	1.86	107.00	594.00	328.00
11	2,189.00	1.92	115.00	636.00	364.00

Table 3.9. Model-predicted bioaccumulation dynamics of methylmercury in *Lepomis auritus* at site SR6 on the South River, Virginia for adjusted specific growth rates, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<u>25% Decreased Specific Growth Rate</u>					
1	5.07	0.89	0.51	6.69	0.43
2	14.60	1.53	1.89	19.40	2.52
3	28.20	1.98	2.82	27.00	4.82
4	41.60	2.33	3.58	33.10	7.25
5	54.90	2.61	4.23	38.50	9.79
6	68.00	2.88	4.82	44.20	12.40
7	80.90	3.12	5.36	49.80	15.30
8	93.80	3.36	5.86	54.10	18.20
9	106.00	3.56	6.33	58.10	21.20
<u>Observed Specific Growth Rate</u>					
1	6.80	0.85	0.61	8.46	0.51
2	19.60	1.44	2.25	24.00	2.89
3	37.60	1.85	3.36	33.20	5.53
4	55.30	2.18	4.25	40.70	8.35
5	72.80	2.46	5.02	48.50	11.40
6	89.90	2.73	5.71	55.20	14.70
7	107.00	2.97	6.34	60.80	18.10
8	124.00	3.18	6.93	65.90	21.60
9	140.00	3.36	7.48	70.80	25.30
<u>25% Increased Specific Growth Rate</u>					
1	8.55	0.83	0.70	10.20	0.58
2	24.60	1.37	2.59	28.50	3.24
3	46.90	1.77	3.85	39.20	6.19
4	68.80	2.09	4.86	48.90	9.42
5	90.40	2.39	5.73	57.80	13.00
6	112.00	2.64	6.51	64.80	16.80
7	132.00	2.87	7.22	71.20	20.80
8	153.00	3.05	7.88	77.20	25.00
9	173.00	3.23	8.50	82.80	29.30

Table 3.10. Model-predicted bioaccumulation dynamics of methylmercury in *Micropterus dolomieu* at site SR6 on the South River, Virginia for adjusted specific growth rates, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<u>25% Decreased Specific Growth Rate</u>					
1	9.78	1.16	0.93	23.20	1.24
2	33.60	2.48	3.12	86.30	7.49
3	69.90	3.39	4.89	112.00	15.40
4	111.00	3.47	6.48	118.00	20.40
5	155.00	3.59	7.96	145.00	25.60
6	203.00	3.77	9.35	176.00	31.00
7	253.00	4.17	10.70	255.00	38.20
8	305.00	4.67	12.00	296.00	47.30
9	358.00	5.12	13.20	336.00	56.80
10	414.00	5.54	14.40	375.00	66.60
<u>Observed Specific Growth Rate</u>					
1	14.10	1.13	1.17	32.90	1.55
2	48.50	2.43	3.89	110.00	9.35
3	101.00	2.81	6.10	120.00	16.00
4	160.00	2.96	8.08	157.00	21.80
5	224.00	3.20	9.92	217.00	28.20
6	292.00	3.71	11.70	303.00	37.40
7	363.00	4.22	13.30	358.00	48.00
8	438.00	4.68	14.90	412.00	59.10
9	515.00	5.10	16.40	463.00	70.50
10	595.00	5.49	17.90	512.00	82.10
<u>25% Increased Specific Growth Rate</u>					
1	18.70	1.14	1.39	45.10	1.91
2	64.30	2.39	4.62	126.00	11.00
3	134.00	2.58	7.24	151.00	17.60
4	212.00	2.79	9.59	218.00	24.40
5	296.00	3.29	11.80	323.00	34.10
6	387.00	3.81	13.80	395.00	45.70
7	481.00	4.28	15.80	463.00	57.90
8	580.00	4.71	17.70	527.00	70.40
9	682.00	5.10	19.50	588.00	83.30
10	787.00	5.45	21.30	646.00	96.30

Table 3.11. Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia for 25% reduced concentrations of methylmercury in river sediment, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	61.50	0.55	6.22	51.20	10.10
2	184.00	0.74	16.40	108.00	30.60
3	337.00	0.91	24.30	150.00	52.20
4	497.00	1.03	31.30	186.00	74.40
5	662.00	1.13	37.80	220.00	96.80
6	832.00	1.21	43.90	251.00	119.00
7	1,006.00	1.28	49.80	281.00	142.00
8	1,184.00	1.35	55.40	309.00	165.00
9	1,364.00	1.40	60.80	337.00	187.00
10	1,548.00	1.45	66.00	364.00	210.00
11	1,733.00	1.50	71.10	390.00	233.00
<i>Etheostoma flabellare</i>					
1	0.47	0.81	0.04	0.49	0.05
2	1.18	1.30	0.16	1.33	0.29
3	2.07	1.82	0.26	1.98	0.61
4	2.96	2.22	0.35	2.59	0.99
5	3.84	2.55	0.43	3.17	1.41
<i>Lepomis auritus</i>					
1	6.80	0.64	0.44	6.13	0.37
2	19.60	1.08	1.63	17.40	2.10
3	37.60	1.39	2.43	24.10	4.00
4	55.30	1.64	3.07	29.50	6.05
5	72.80	1.86	3.62	37.20	8.29
6	89.90	2.12	4.12	43.50	10.90
7	107.00	2.33	4.58	47.80	13.70
8	124.00	2.51	5.00	51.90	16.50
9	140.00	2.66	5.39	55.70	19.40
<i>Luxilus cornutus</i>					
1	2.12	0.54	0.09	1.44	0.08
2	6.59	0.80	0.50	4.88	0.57
3	13.30	1.12	0.95	8.19	1.44
4	20.70	1.40	1.44	11.60	2.63
5	28.40	1.65	1.93	15.10	4.12
<i>Micropterus dolomieu</i>					
1	14.10	0.86	0.84	23.90	1.13
2	48.50	1.83	2.81	79.50	6.79
3	101.00	2.12	4.40	87.10	11.60
4	160.00	2.22	5.83	114.00	15.90
5	224.00	2.42	7.16	157.00	20.50
6	292.00	2.79	8.41	219.00	27.20
7	363.00	3.18	9.60	260.00	34.90
8	438.00	3.53	10.80	299.00	42.90

Table 3.11. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia for 25% reduced concentrations of methylmercury in river sediment, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
9	515.00	3.86	11.90	337.00	51.20
10	595.00	4.14	12.90	373.00	59.60
<i>Noturus insignis</i>					
1	2.28	0.49	0.06	1.50	0.05
2	7.57	0.72	0.37	4.72	0.32
3	16.00	0.94	0.71	7.62	0.74
4	25.50	1.13	1.08	10.50	1.31

Table 3.12. Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia for 50% reduced concentrations of methylmercury in river sediment, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	61.50	0.36	4.31	35.50	7.00
2	184.00	0.49	11.30	75.20	21.20
3	337.00	0.60	16.80	104.00	36.20
4	497.00	0.69	21.70	129.00	51.50
5	662.00	0.75	26.20	152.00	67.10
6	832.00	0.81	30.50	174.00	82.80
7	1,006.00	0.86	34.50	195.00	98.50
8	1,184.00	0.90	38.40	214.00	114.00
9	1,364.00	0.94	42.10	234.00	130.00
10	1,548.00	0.97	45.70	252.00	146.00
11	1,733.00	1.00	49.30	270.00	161.00
<i>Etheostoma flabellare</i>					
1	0.47	0.54	0.03	0.34	0.03
2	1.18	0.86	0.11	0.92	0.20
3	2.07	1.21	0.18	1.38	0.42
4	2.96	1.48	0.24	1.80	0.68
5	3.84	1.70	0.30	2.20	0.97
<i>Lepomis auritus</i>					
1	6.80	0.43	0.30	4.28	0.26
2	19.60	0.73	1.13	12.20	1.46
3	37.60	0.94	1.68	16.80	2.79
4	55.30	1.10	2.13	20.60	4.22
5	72.80	1.27	2.51	28.20	5.85
6	89.90	1.49	2.86	34.10	7.98
7	107.00	1.67	3.17	37.60	10.20
8	124.00	1.83	3.46	40.70	12.40
9	140.00	1.95	3.74	43.70	14.70
<i>Luxilus cornutus</i>					
1	2.12	0.36	0.06	0.99	0.05
2	6.59	0.53	0.34	3.38	0.39
3	13.30	0.74	0.66	5.68	0.99
4	20.70	0.93	0.99	8.03	1.82
5	28.40	1.10	1.34	10.50	2.85
<i>Micropterus dolomieu</i>					
1	14.10	0.58	0.58	16.70	0.79
2	48.50	1.23	1.95	55.60	4.75
3	101.00	1.43	3.05	61.20	8.14
4	160.00	1.50	4.04	80.10	11.10
5	224.00	1.64	4.96	110.00	14.40
6	292.00	1.88	5.83	153.00	19.00
7	363.00	2.15	6.66	182.00	24.40
8	438.00	2.37	7.45	210.00	30.00

Table 3.12. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia for 50% reduced concentrations of methylmercury in river sediment, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
9	515.00	2.60	8.22	236.00	35.90
10	595.00	2.79	8.97	262.00	41.80
<i>Noturus insignis</i>					
1	2.28	0.33	0.04	1.04	0.03
2	7.57	0.48	0.25	3.27	0.22
3	16.00	0.62	0.49	5.28	0.51
4	25.50	0.75	0.74	7.29	0.90

Table 3.13. Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia for 75% reduced concentrations of methylmercury in river sediment, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
<i>Catostomus commersoni</i>					
1	61.50	0.18	2.16	17.70	3.50
2	184.00	0.25	5.67	37.60	10.60
3	337.00	0.30	8.42	51.90	18.10
4	497.00	0.34	10.90	64.50	25.80
5	662.00	0.38	13.10	76.10	33.60
6	832.00	0.40	15.20	86.90	41.40
7	1,006.00	0.43	17.20	97.30	49.30
8	1,184.00	0.45	19.20	107.00	57.10
9	1,364.00	0.47	21.10	117.00	65.00
10	1,548.00	0.48	22.90	126.00	72.80
11	1,733.00	0.50	24.60	135.00	80.60
<i>Etheostoma flabellare</i>					
1	0.47	0.27	0.01	0.17	0.01
2	1.18	0.43	0.05	0.46	0.10
3	2.07	0.60	0.09	0.68	0.21
4	2.96	0.74	0.12	0.89	0.34
5	3.84	0.85	0.15	1.10	0.48
<i>Lepomis auritus</i>					
1	6.80	0.22	0.15	2.19	0.13
2	19.60	0.37	0.56	6.23	0.74
3	37.60	0.48	0.84	8.62	1.43
4	55.30	0.56	1.06	10.50	2.16
5	72.80	0.67	1.26	18.10	3.10
6	89.90	0.86	1.43	23.60	4.64
7	107.00	1.02	1.59	25.90	6.21
8	124.00	1.14	1.73	28.10	7.80
9	140.00	1.25	1.87	30.20	9.40
<i>Luxilus cornutus</i>					
1	2.12	0.18	0.03	0.49	0.02
2	6.59	0.27	0.17	1.69	0.19
3	13.3	0.37	0.33	2.84	0.49
4	20.7	0.47	0.49	4.02	0.91
5	28.4	0.55	0.67	5.23	1.43
<i>Micropterus dolomieu</i>					
1	14.10	0.30	0.29	8.68	0.41
2	48.50	0.64	0.97	28.60	2.45
3	101.00	0.74	1.53	31.80	4.20
4	160.00	0.78	2.02	41.60	5.75
5	224.00	0.84	2.48	56.90	7.43
6	292.00	0.97	2.91	78.90	9.82
7	363.00	1.10	3.33	94.00	12.60
8	438.00	1.23	3.73	109.00	15.50

Table 3.13. (continued) Model-predicted bioaccumulation dynamics of methylmercury in fish at site SR6 on the South River, Virginia for 75% reduced concentrations of methylmercury in river sediment, where WT = mean body weight, MeHg = mean concentration of methylmercury wet weight in muscle tissue, GU = gill uptake of methylmercury, I = ingested methylmercury, and EE = egested and excreted methylmercury.

Age (yr)	WT (g)	MeHg ($\mu\text{g/g}$)	GU ($\mu\text{g/yr}$)	I ($\mu\text{g/yr}$)	EE ($\mu\text{g/yr}$)
9	515.00	1.34	4.11	123.00	18.50
10	595.00	1.45	4.49	137.00	21.70
<i>Noturus insignis</i>					
1	2.28	0.16	0.02	0.51	0.01
2	7.57	0.24	0.12	1.64	0.11
3	16.00	0.31	0.24	2.64	0.25
4	25.50	0.38	0.37	3.65	0.45

VITA

Gregory W. Murphy was born on May 16, 1979 in Easton, Pennsylvania. He moved with his family from Phillipsburg, New Jersey to Tatamy, Pennsylvania when he was nine years old. Greg graduated from Nazareth Area Senior High School in 1997. After attending Millersville University and Northampton Community College in Pennsylvania, Greg finished his undergraduate education in 2001 with a Bachelor of Science degree in Fisheries Science from Unity College in Maine. While living in Maine, Greg held fisheries positions with Acheron Engineering, Environmental, and Geologic Consultants, FPL Energy, and the Maine Atlantic Salmon Commission and routinely volunteered for the Maine Department of Marine Resources. Thereafter, Greg traveled south to the Virginia Polytechnic Institute and State University to pursue a Master of Science degree in Fisheries and Wildlife Sciences studying trophic dynamics and bioaccumulation of mercury in fish communities in the Shenandoah River basin, Virginia.