JOURNAL OF THE TENNESSEE ACADEMY OF SCIENCE 76(4):91–96 OCTOBER 2001

MERCURY CONTAMINATION IN ABIOTIC AND BIOTIC COMPARTMENTS OF THE NORTH FORK HOLSTON RIVER (VIRGINIA AND TENNESSEE) ECOSYSTEM

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ABSTRACT—From 1950 to 1972, industrial activity at a now-defunct chloralkali plant in Saltville, Virginia, caused severe mercury contamination of the North Fork Holston River (NFHR) ecosystem. Water, sediment, periphyton, snails, and fishes recently were collected at 17 stations along the river's entire course and analyzed for total mercury. While the NFHR is uncontaminated or only marginally contaminated by mercury upstream of Saltville, much of the remaining ecosystem is markedly contaminated due to continued mercury leaching from terrestrial sources, downstream sediment transport, and trophic transfer. Mercury concentrations in all water samples were below the method detection limit. Of particular concern is our finding that mercury levels in some fish species known to be consumed by local anglers are above the Food and Drug Administration (FDA) action level (1.0 μg/g). Thus, mercury contamination may represent a risk to the entire NFHR ecosystem, the main Holston River into which it empties, terrestrial biota that may be linked to the NFHR, and humans that consume substantial amounts of fish taken from the NFHR.

The North Fork Holston River (NFHR) arises at Sharon Springs, Virginia, and flows southwest 210 km to its confluence with the South Fork Holston River at Kingsport, Tennessee. The resulting Holston River empties into the Cherokee Reservoir near Morristown, Tennessee. The NFHR is a clear, slow-moving, moderate-gradient river characterized by coarse, rocky substrate and extensive riffle and pool areas (Turner and Lindberg, 1978).

Mercury contamination of the lower NFHR resulted from operations at a now-defunct chloralkali plant in Saltville, Virginia, from 1951 to 1972. Mercury-laden wastewater from chlorine and sodium hydroxide production was discharged directly into the NFHR, as was the supernatant from waste slurries that had been deposited into two large settling ponds (50.6 ha [125 acres] total area) immediately adjacent to the river. The rate of mercury loss to the environment from 1951 to 1970 has been estimated to have been 45.5 kg/d (100 lb/d), and 0.11 kg/d (0.25 lb/d) from 1970 to 1972 (USEPA, 1997). Various estimates place the total amount of mercury lost to the NFHR, the chloralkali plant grounds, and the settling ponds to be 162.6 to 355.6 tons (Turner and Lindberg, 1978). In addition, mercury-contaminated debris and equipment were buried near the settling ponds and deposited in an upstream open dump after the chloralkali plant ceased operations.

In 1970, mercury levels in NFHR fish tissue exceeded 0.5 μg/g, the Food and Drug Administration action level for mercury at that time (Hildebrand et al., 1980). As a result, the Virginia State Health Board and the State of Tennessee banned all fishing in the affected section of the NFHR. Concomitant with a later increase in the FDA action level to 1.0 μg/g, both states modified their fishing bans to catch-and-release orders, which remain in effect today. The former chlorine plant site, the two large waste impoundments, and areas to which mercury contamination has migrated, including the NFHR, were placed on the National Priorities List in 1983 (USEPA, 2000).

Since 1982, remediation efforts have included an attempt to excavate and encapsulate sediments along a 305-m (1,000-ft) section of the river immediately adjacent to the former chloralkali plant site, development of a large concrete decanter system containing five settling chambers, construction of concrete channels to protect run-off from contaminated soils, and a treatment plant to process ground water collected at one of the waste ponds (USEPA, 2000). Despite these efforts, recent monitoring of mercury levels by various agencies has shown that mercury contamination in NFHR sediments, benthic invertebrates, and fishes remains significantly elevated, particularly near the former plant site and downstream reaches of the NFHR (Trivette, 1998).

The NFHR is an important recreational resource for many individuals, and many anglers acknowledge using fish taken from the NFHR as table fare for themselves and their families. This study was undertaken because no comprehensive survey of mercury levels in the entire NFHR ecosystem has ever been done.

MATERIALS AND METHODS

Study Site—Seventeen sampling stations were established over the entire reach of the NFHR. These consisted of seven stations upstream of the original impact site in Saltville, one at the impact site, and nine downstream of the site (Table 1). Stations were selected based on water level and accessibility. Average physical/chemical conditions at each station are shown in Table 2.

Sample Collection—Water, sediment, periphyton, snail (*Pleurocera canaliculatum*) and fish samples were collected from each station from May to November 1997. Water and sediment

TABLE 1. North Fork Holston River sampling station locations.

Station	River mile	Miles (km) above (−) or below (+) plant site
1	0	−27.59 (−44.5)
2	1.58	−24.03 (−38.8)
3	6.70	−18.91 (−30.5)
4	19.32	−6.29 (−10.1)
5	21.68	−3.93 (−6.3)
6	23.65	−1.96 (−3.2)
7	24.43	−1.18 (−1.9)
8	25.61	0
9	27.97	+2.36 (+3.8)
10	32.31	+6.70 (+10.8)
11	36.65	+11.04 (+17.8)
12	44.93	+19.32 (+31.2)
13	59.53	+33.92 (+54.7)
14	69.79	+44.18 (+71.3)
15	73.34	+47.73 (+77.0)
16	84.78	+59.17 (+95.4)
17	89.51	+63.90 (+103.1)

were taken from both midriver and near the bank, placed in acid-washed 250-ml polyethylene bottles, and preserved with concentrated nitric acid to pH < 2.0 (American Public Health Association, 1992). No attempt was made to sieve or size-segregate sediment samples, so mercury concentrations are for sediment types representative of each station without consideration of organic/inorganic matter content or particle size. Periphyton was manually scraped from rocks, rinsed of silt, drained of excess water, and placed in polyethylene bags. No attempt was made to determine the exact periphyton composition. Snails (*P. canaliculatum* only) were collected by hand and placed in polyethylene bags. Fishes were immobilized using a backpack electroshock unit and collected by dip net. Each individual was identified to species and placed in a polyethylene bag. This process was repeated until no new fish species were found in three consecutive samples. Fishes also were identified by principal feeding group (herbivore, insectivore, piscivores) for statistical purposes (Table 3). It should be noted, however, that at least some collected species likely do not strictly fit any one category, but rather exhibit some measure of omnivory. Moreover, because only one collecting method was used, Table 3 should not be considered an exhaustive list of all NFHR fish species. All samples were immediately placed on ice, returned to the laboratory, and stored at 4°C for later mercury analysis.

Mercury Analysis—All samples were analyzed for mercury using a Varian Spectra AA/20 atomic absorption spectrophotometer with a Varian VGA 77 cold vapor generation accessory (Varian Associates, Inc., Palo Alto, CA). Digestion and analysis of samples were conducted according to the methods of Brodie et al. (1983), Brodie (1985), Evans et al. (1986), Elrick and Horowitz (1987), and Ward and Gray (1994). Water and sediment samples were not filtered; snail and fish samples were whole-body. Snail and fish body sizes were not considered as statistical covariates.

Statistical Analysis—Mercury concentration data for each biotic and abiotic ecosystem compartment were tested for normality using the Kolmogorov-Smirnov test and the Levene median test for equal variance. Because data were not distributed normally for any compartment, all mercury concentrations were tested for differences among collection stations by the Kruskal-Wallis one-way analysis of variance on ranks. Station data also were pooled as upstream (Stations 1–7), impact (Station 8), and

TABLE 2. Physical and chemical conditions at 17 collecting stations on the North Fork Holston River.

Station number	Air temp. (°C)	Water temp. (°C)	pH	Conductivity (μS/cm)	Dissolved oxygen (mg/l)	Flow rate (m/sec)
1	15	12	6.93	250	9.6	1.0
2	18	12	7.58	250	9.6	0.9
3	15	12	6.28	711	9.4	1.2
4	14	12	7.82	212	8.9	2.0
5	32	25	7.22	209	7.0	1.0
6	24	21	7.75	234	6.2	1.5
7	21	20	7.96	244	8.1	1.9
8	23	21	7.37	369	9.2	0.3
9	26	25	7.68	1306	8.3	0.4
10	*	*	*	*	*	*
11	19	13	7.66	759	8.6	0.9
12	20	13	7.89	761	9.8	1.9
13	22	13	7.68	637	7.8	2.9
14	22	13	7.02	812	6.4	1.1
15	15	10	7.28	435	6.8	1.3
16	11	10	7.16	399	8.0	0.9
17	11	10	6.74	398	7.6	1.9

* No data collected.

TABLE 3. North Fork Holston River fish species, their feeding groups, and stations from which they were collected.

Scientific name	Common name	Feeding group	Station(s)
Semotilus atromaculatus	Creek chub	Piscivore	1, 2
Rhinichthys atratulus	Blacknose dace	Insectivore	1
Etheostoma simoterum	Tennessee snubnose darter	Insectivore	2, 4, 6
Campostoma anomalum	Central stoneroller	Herbivore	2, 4, 6, 7, 8, 10, 14, 16, 17
Cottus carolinae	Banded sculpin	Piscivore	2, 7, 12, 17
Etheostoma maculatum	Spotted darter	Insectivore	4, 7
Etheostoma rufilineatum	Redline darter	Insectivore	4
Ambloplites rupestris	Rock bass	Insectivore	4, 6, 8, 9, 10, 13, 14, 15
Etheostoma blennioides	Greenside darter	Insectivore	7, 8, 11, 13, 15, 16, 17
Micropterus dolomieu	Smallmouth bass	Piscivore	8, 17
Hypentelium nigricans	Northern hogsucker	Insectivore	8
Notropis telescopus	Telescope shiner	Insectivore	9
Lepomis auritus	Redbreast sunfish	Insectivore	11, 15, 16
Etheostoma flabellare	Fantail darter	Insectivore	15
Nocomis micropogon	River chub	Herbivore	16
Micropterus salmoides	Largemouth bass	Piscivore	12

downstream (Stations 9–17) locations and similarly tested for differences in mercury concentration for each compartment. Where significant differences among stations or locations were found, Dunn's method multiple comparison test was used to determine between which stations differences occurred. A significance level of 0.05 was used for all tests.

RESULTS

Water—Mercury concentrations in all water samples were below the method detection limit (BDL) (0.200 μg/l).

Sediment—There was no difference in total mercury concentration between sediment samples taken at midriver and samples taken near the riverbank.

Mean sediment total mercury levels were BDL (0.01 μg/g) at all upstream stations (Stations 1–7) except at Stations 6 and 7 (0.029 and 0.024 μg/g, respectively). Mercury concentrations were highest at the impact site (Station 8) (7.29 μg/g), and decreased with distance downstream (Stations 9–17) (Range = 1.66–0.022 μg/g) (Fig. 1). Median total mercury concentrations for impact site and downstream sediments were significantly higher than for upstream sediments, but did not differ from one another (Fig. 2).

Periphyton—Mean total mercury concentrations in periphyton were within detectable limits at all upstream stations except Station 3 (Fig. 3). Mercury levels were lowest at the impact site (0.053 μg/g), intermediate at the upstream location (0.139 μg/g), and highest at the downstream location (0.401 μg/g) (Fig. 4). Median downstream periphyton mercury level was significantly higher than for upstream periphyton, but levels did not differ between impact site periphyton samples and upstream or downstream samples.

Snails—Whole-body snail tissue total mercury levels were within detectable limits at all stations (Fig. 5). Mercury concen-

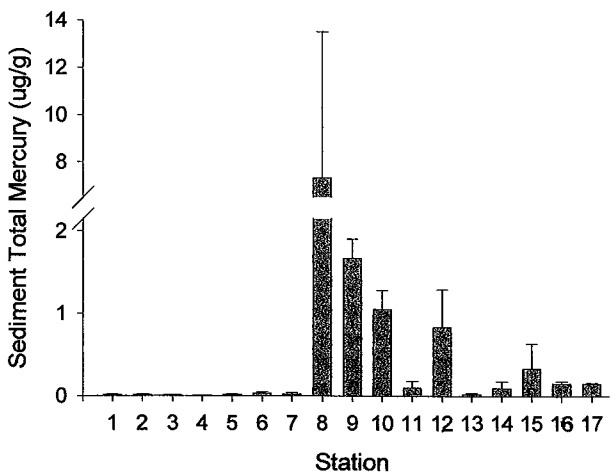

FIG. 1. Mean (± *SEM*) total mercury concentration in sediment samples from seventeen stations on the NFHR. Stations numbered from farthest upstream (Station 1) to farthest downstream (Station 17). See Table 1 for river mile locations.

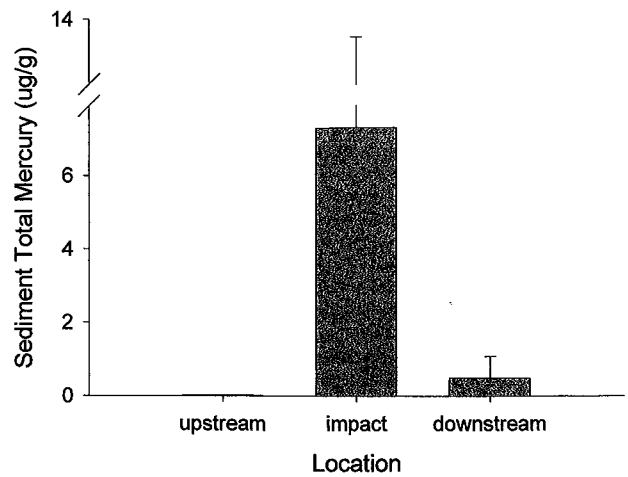

FIG. 2. Mean (± *SEM*) total mercury concentration in sediment samples from three locations on the NFHR.

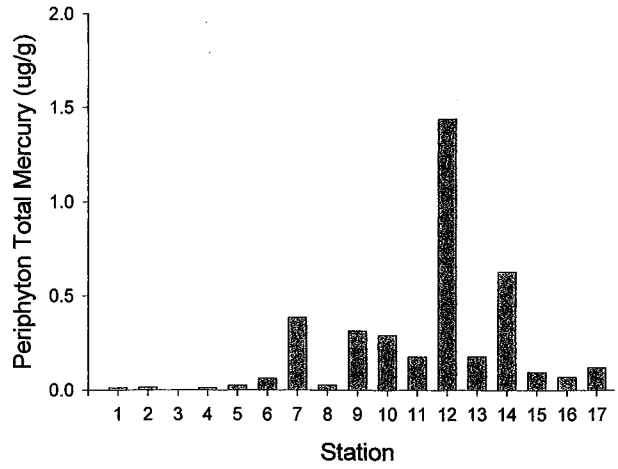

FIG. 3. Mean total mercury concentration in periphyton samples from seventeen stations on the NFHR. Stations numbered from farthest upstream (Station 1) to farthest downstream (Station 17). See Table 1 for river mile locations.

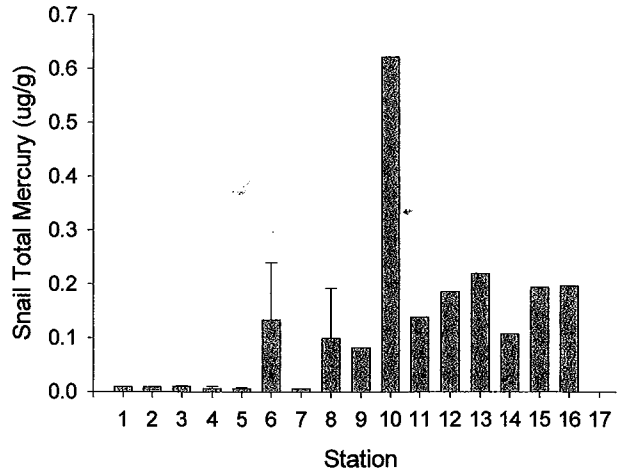

FIG. 5. Mean (± *SEM*) whole-body total mercury concentration in snail tissue from seventeen stations on the NFHR. Stations numbered from farthest upstream (Station 1) to farthest downstream (Station 17). See Table 1 for river mile locations.

trations were lowest upstream (0.050 μg/g), intermediate at the impact site (0.101 μg/g), and highest downstream (0.234 μg/g); median mercury concentrations were significantly different between upstream and downstream (Fig. 6).

Fish—Mean whole-body total mercury concentrations in fishes were within detectable limits at all stations, except Stations 3 and 5 (Fig. 7). Mean mercury level was above the FDA action limit (1.0 μg/g) at Station 11, and individual samples above the action limit were collected at Stations 12 and 15. When stations were grouped as upstream, impact, and downstream, all pairwise comparisons of median fish tissue mercury levels were significantly different, with the highest median concentration downstream and lowest upstream (Fig. 8). When fishes were classified by feeding type, insectivores had a significantly higher median tissue mercury level than herbivores for the NFHR overall (Fig. 9). Each feeding group exhibited a significantly higher median tissue mercury concentration downstream than upstream (Fig. 10). Insectivores had highest mean mercury burdens upstream and downstream, but piscivores had the highest burden at the impact site. Herbivores had the lowest mean mercury concentrations at all locations (Fig. 10).

DISCUSSION

Abiotic compartments of the NFHR ecosystem remain generally unaffected by mercury contamination upstream of the original Saltville, Virginia impact site. The exception is the two stations nearest the original impact site (Stations 6 and 7), at which sediment mercury levels were elevated. Station 6 is adjacent to the old Saltville town dump, and Station 7 is approximately 2 miles farther downstream. The dump contains mercury-contaminated demolition waste from the razed chloralkali plant, which appears to be an additional source of contamination. A recent study of the dumpsite concluded that mercury and other contaminants are leaching into the NFHR (ATSDR, 1996). Soil samples from the dump area had mercury levels ranging from 3–61 μg/g, and sediment samples from a ravine between the dump and the NFHR contained 9.7 μg Hg/g. Similarly, periphyton taken from stations upstream of the impact site generally exhibited very low (but detectable) or BDL levels of mercury, except those taken from Stations 6 and 7, which were higher. For snails, the trend was the same, but whole-body mercury levels were within the

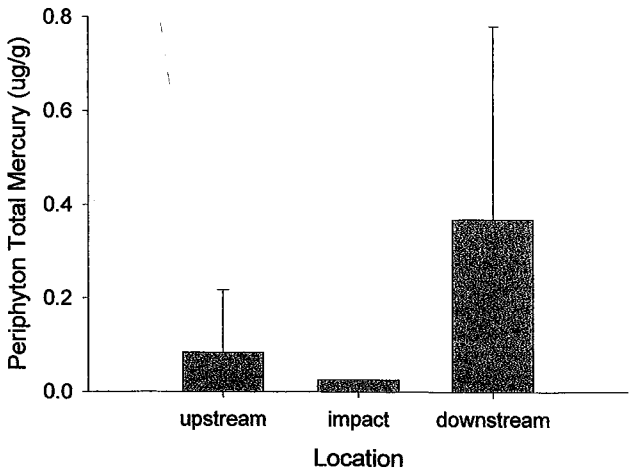

FIG. 4. Mean (± *SEM*) total mercury concentration in periphyton samples from three locations on the NFHR.

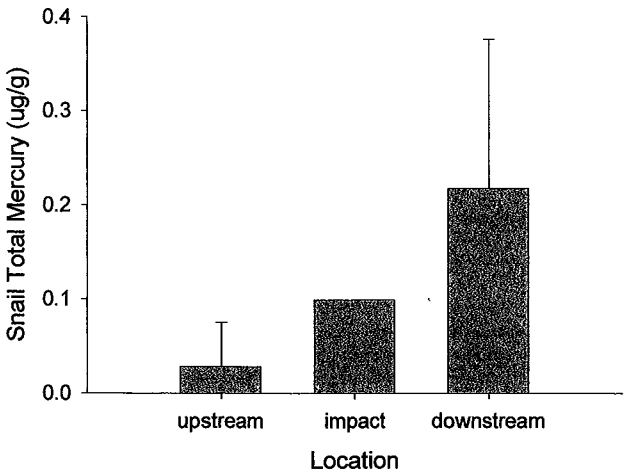

FIG. 6. Mean (± *SEM*) whole-body total mercury concentration in snail tissue samples from three locations on the NFHR.

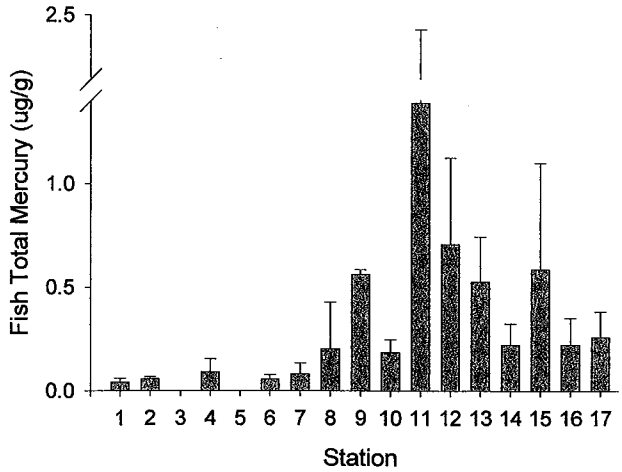

FIG. 7. Mean (± *SEM*) whole-body total mercury concentration in fish tissue samples from seventeen stations on the NFHR. Stations numbered from farthest upstream (Station 1) to farthest downstream (Station 17). See Table 1 for river mile locations.

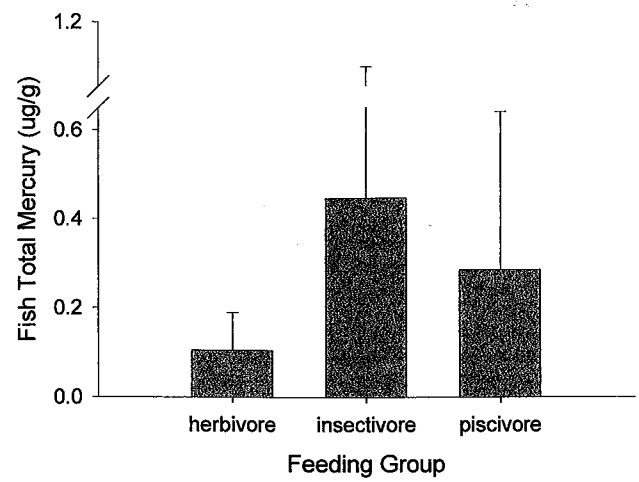

FIG. 9. Mean (± *SEM*) whole-body total mercury concentration in fish tissue from three feeding groups from the NFHR.

detectable range at all upstream stations, consistent with a pattern of mercury bioconcentration with increased trophic level. Whole-body mercury levels in upstream fishes also were consistent with this pattern, being generally low overall, but higher than in periphyton or snails. Further, tissue mercury levels in fishes classified as herbivorous were generally lower than levels in insectivores or piscivores.

At the former impact site (Station 8), total mercury concentrations in all compartments were cause for concern. The mean sediment mercury load at Station 8 was nearly 8 μg/g and was the highest measured on the entire NFHR, with individual sediment samples as high as 14 μg/g. Periphyton mercury levels at Station 8 were relatively low, but periphyton was consistently scarce at this site and therefore samples were small. Likewise, mercury concentrations in snails were relatively low at Station 8, but snails also were rare there, probably due to the very high sediment mercury concentrations and scarcity of periphyton. It seems likely that most snails collected at Station 8 were the result of drift from upstream. Fishes, however, had somewhat higher tissue mercury levels at Station 8 than at upstream stations, suggesting some measure of philopatry. Insectivorous and piscivorous fishes exhibited much higher tissue mercury levels than herbivores, consistent with a food web-mediated bioconcentration mechanism.

Sediment mercury levels generally decreased with distance downstream from the former impact site, but were detectable at all stations. This is consistent with the downstream shift in sediments from the original impact site at Station 8. The general trend in periphyton and fishes also was a decrease in tissue mercury with distance downstream of Station 8. However, mercury levels actually peaked at Stations 10, 11, and 12 for snails, fishes, and periphyton, respectively. This is probably related to the very high mercury levels in sediments at the former impact site and stations immediately downstream, which prevents long-term colonization by most biota. Mercury levels in snails are consistently elevated all the way to Station 16, possibly due to dispersal by drift and to downstream shifts in contaminated sediments and periphyton over time. High mercury levels and scarce biota at the impact site and the immediate downstream area also may represent a barrier to upstream dispersal of fishes. Fish tissue

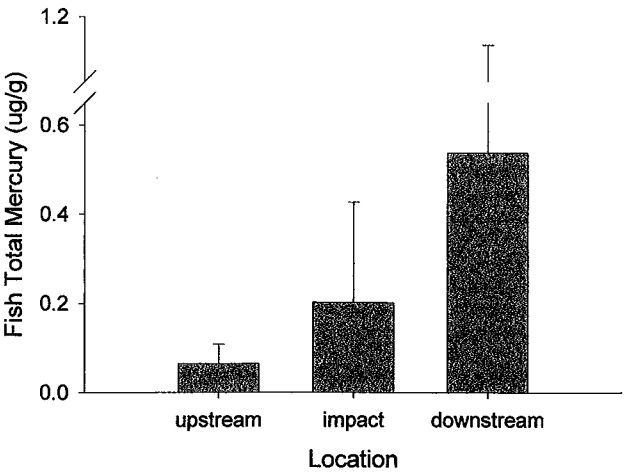

FIG. 8. Mean (± *SEM*) whole-body total mercury concentration in fish tissue samples from three locations on the NFHR.

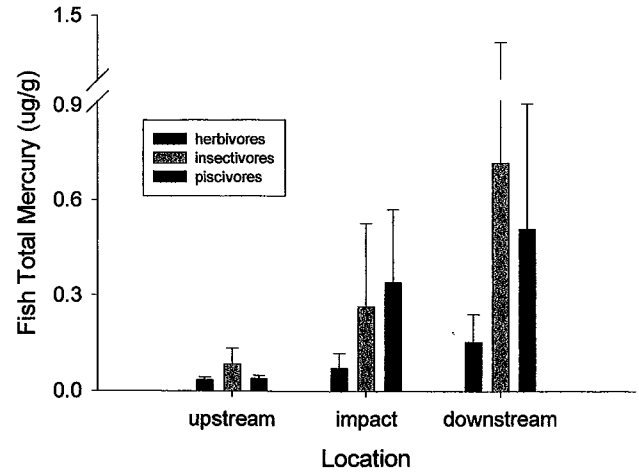

FIG. 10. Mean (± *SEM*) whole-body total mercury concentration in fish tissue from three feeding groups from three locations on the NFHR.

mercury levels downstream were as high or higher than at Station 8, but much higher than upstream, even though physical characteristics of the NFHR do not differ substantially immediately upstream of Station 8. Some fishes collected at Station 8 and downstream had tissue mercury levels over the FDA action limit of 1.0 μg/g.

We conclude that the NFHR ecosystem remains markedly contaminated with mercury in most compartments, particularly in its midreaches and points downstream from Saltville. There also may be continued input of mercury from points upstream of the original impact site, formerly thought to be relatively pristine. A recent genetic study of the aquatic snail *P. canaliculatum* from the NFHR showed both a decrease in genetic variability and an increase in DNA strand breakage in populations occupying the more highly contaminated sites (Benton et al., 2002). Of greatest concern are the elevated mercury levels in NFHR fishes, which may be used by anglers as table fare. The average percentage of the total mercury that occurs as methylmercury in fish tissue is approximately 95%, and methylmercury has been associated with central nervous system damage, developmental disorders, and genotoxicity in humans (Morel et al., 1998; Renzoni et al., 1998). Without meaningful remediation efforts, the extent of mercury contamination in the NFHR will grow as mercury continues to enter the system and sediments shift downriver. Mercury will move through the aquatic food web, possibly into terrestrial biota (e.g., riparian vegetation and related herbivores, riparian-feeding raccoons, fish-eating birds, etc), and ultimately into human consumers of contaminated fishes and other wildlife.

ACKNOWLEDGMENTS

This research was conducted in partial fulfillment of the requirements for the Master of Environmental Health degree at East Tennessee State University by S. K. Dye. This work was funded in part by intramural grants from East Tennessee State University to M. J. Benton.

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