

Total and Methyl Mercury in the Neversink Reservoir Watershed

by

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November 21, 2006

ABSTRACT

Recent monitoring of fish has identified mercury as a contaminant of concern in the Neversink Reservoir. The Neversink is located in the Catskill Park and is one of six reservoirs west of the Hudson River that are part of the New York City water supply system. High mercury levels in smallmouth bass (*Micropterus dolomieu*) from the Neversink Reservoir were detected in 1998 and all six reservoirs currently have fish consumption advisories for various species based on elevated mercury levels. The Neversink was selected for further assessment because mercury concentrations in standard-length brown trout (*Salmo trutta*) and smallmouth bass were higher than in any other New York City reservoir and it is also the most acidic of the reservoirs, a characteristic that may be positively influencing mercury transformation and uptake. The distribution of total and methyl mercury concentrations in water, sediments, benthic macroinvertebrates, and fish from different aquatic habitat types (i.e., streams, ponds, and the reservoir) throughout the upper Neversink watershed was examined. Also, methylation efficiencies in water and sediment, and accumulation patterns in biota were documented.

Total and methyl mercury concentrations in water and sediment samples were lowest in headwater streams and highest in a beaver pond. Methylation efficiencies in water were higher in the reservoir and ponds than they were in streams. This was in contrast to methylation efficiencies in sediments where the highest rates were detected in streams. There was no correlation between methylation efficiencies in water and sediments ($r = 0.33$, $P = 0.276$).

Benthic macroinvertebrate mercury concentrations also varied by habitat type, generally being lower in stream ecosystems and higher in natural (beaver) and man-made ponds (Lake Cole). Invertebrate predators had higher mean mercury levels ($\bar{x} = 60 \pm 87$ ng/g total, $\bar{x} = 29 \pm 29$ ng/g methyl), with a higher mean percentage of methyl mercury ($\bar{x} = 66 \pm 20\%$ methyl), than detritivores ($\bar{x} = 27 \pm 19$ ng/g total, $\bar{x} = 15 \pm 20$ ng/g methyl, $\bar{x} = 41 \pm 29\%$ methyl).

Mercury concentrations in fish ranged from 19 ± 7 ng/g in forage fish from headwater streams to $1,303 \pm 630$ ng/g in predatory species from the reservoir. Trophic patterns of mercury concentrations in fish varied by habitat type, with an inverse sequence (i.e., mercury levels were higher in forage vs. predatory fish) documented at the beaver pond. Because species assemblages varied among habitat types, few direct species-habitat comparisons could be made. However, where comparisons could be made, blacknose dace (*Rhinichthys atratulus*) from the beaver pond area were found to have over 5 times higher mercury levels than those of a similar size from mid-order streams. Also, similar-size slimy sculpins (*Cottus cognatus*) and one-year-old brook trout (*Salvelinus fontinalis*) had mercury concentrations 2-3 times higher in mid-order vs. headwater streams. These comparisons suggest a ranking of the bioaccumulation potential for these three habitat types of: beaver pond > mid-order streams > headwater streams. Also, mercury concentrations in standard length smallmouth bass and

brown trout from the Neversink reservoir remained high, relative to the other reservoirs in the New York City system.

Accumulation of mercury from water and sediment to biota was influenced by trophic level. Total mercury bioaccumulation factors (BAF, water to biota) ranged from 11,915 in headwater stream invertebrate detritivores to 654,060 in large predatory fish from the reservoir. Methyl mercury BAFs ranged from 155,926 in beaver pond invertebrate detritivores to 20,406,667 in predatory fish from the reservoir. Total mercury biota-sediment accumulation factors (BSAFs) ranged from 0.3 in beaver pond invertebrate detritivores to 36.7 in smallmouth bass from the reservoir. Methyl mercury BSAFs ranged from 7.7 in beaver pond invertebrate detritivores to 3,401 in predatory fish from the reservoir. BAFs and BSAFs did not exclusively identify areas where mercury bioaccumulation was most problematic. Comparatively high water and sediment mercury concentrations in the beaver pond area resulted in lower accumulation factor values, even though concentrations in biota were consistently high, relative to similar biota from other areas.

Mercury concentrations in water, and forage and top trophic level fish from throughout much of the watershed were found to be above effects criteria for the protection of human and/or wildlife health. The extent of the mercury problem in the watershed and evidence of similar situations throughout the Catskill Mountains suggests that further food-web related research and monitoring in this region is warranted. This study highlights the complex nature of mercury in the environment and demonstrates the need to consider a complex array of criteria, including abiotic and biotic mercury concentrations, mercury species, trophic status, site characteristics, and regional geography, to improve our understanding of how mercury moves through the food chain.

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INTRODUCTION

Mercury is a neurotoxic metal that is ubiquitous throughout the environment. It occurs in the earth's crust and is released into the environment through a variety of natural and anthropogenic processes. Emissions from burning coal for energy production, industrial boiler operations, and waste incineration are primary airborne sources of mercury to the environment (EPA 1999, Evers 2005). Typically, this airborne mercury is transported via wind currents and deposited over the landscape. Transport distance from the source is largely dependent on the species, or form, of mercury (e.g., elemental, reactive gaseous, and particulate), but much of it falls out of the atmosphere within 500 km and all species can potentially deposit close to the source (Evers 2005). Therefore, areas downwind of mercury-emitting combustors and incinerators are often subject to high rates of atmospheric deposition of this contaminant. Once mercury is deposited from the atmosphere much of it flows into the aquatic environment where it becomes available to fish and, subsequently, to human and wildlife fish consumers; although recent research has found that the terrestrial ecosystem is also subject to mercury processes that put it at risk (Rimmer et al. 2005).

Most mercury from the atmosphere is in an inorganic form that must be converted by bacteria or other processes to organic methyl mercury before it bioaccumulates in biota (Compeau and Bartha 1985, Watras et al. 1998). Methyl mercury is one of the most toxic forms of mercury and it readily moves across biological membranes (Lindqvist and Rodhe 1985, WHO 1990, 1991). Initial, bottom of the food chain, uptake of methyl mercury occurs in aquatic environments through passive diffusion from water to phytoplankton (Mason et al. 1995). At subsequent trophic levels, diet is the primary exposure pathway and concentrations tend to increase in biota from one trophic level to the next (Rogers 1994). Methyl mercury tends to bind to protein sulfhydryl groups and hence is typically sequestered in the muscle tissue of fish (Wiener and Spry 1996). Bloom (1992) documented that approximately 95% of the mercury in predatory fish muscle tissue is comprised of methyl mercury. The capacity of methyl mercury to bioaccumulate and its high toxicity makes it the primary mercury species of concern regarding ecosystem and human health.

Mercury levels in biota are controlled by a complex set of environmental factors, some of which remain poorly understood. Much of the current knowledge about patterns of mercury contamination in biota was derived from research and monitoring of large mid- and top-trophic level fish. Fish tissue monitoring has typically focused on these fish because of the potential human health risk (EPA 2000). Bioaccumulation of mercury in these types of fish is influenced by many factors including food web complexity (Chen et al. 2000), trophic level (Wren et al. 1983, Spry and Weiner 1991), growth rate, body size (Loukmas and Skinner 2005), age (Simonin et al. 1994) and the bioavailability of methyl mercury, which in turn is controlled by biogeochemical characteristics of the aquatic environment such as pH (Cope et al. 1990), dissolved organic carbon (Driscoll et al. 1994), presence of wetlands (Jackson 1988), and watershed extent in relation to waterbody size (Evers 2005).

Much less is known about how mercury is accumulated and transferred in other aquatic biota, including benthic macroinvertebrates (Pennuto et al. 2005) and small forage fish species (Yearly 2000). Benthic invertebrates, which comprise a major dietary component of many fish (Cooper 1983, Werner 2004), are important links between sediments and fish, and small forage fish often represent an intermediate trophic level between invertebrates and larger predatory species. A literature review of mercury patterns in benthic macroinvertebrates found a paucity of available information regarding this important trophic link (Pennuto et al. 2005). Also, a comprehensive summary of fish monitoring databases throughout the Northeast indicated that forage fish are rarely analyzed for mercury (Kamman et al. 2005), despite their utility as ecological indicators of contamination (Yearly 2000). Thus, it is necessary to more extensively examine mercury uptake and movement throughout these lower food webs in order to thoroughly understand bioaccumulation patterns in aquatic systems.

The Catskill Mountains of New York represent an area of great potential impairment due to high levels of mercury deposition. A model developed by Miller et al. (2005) estimated that the Catskill Mountains have one of the highest mercury deposition rates in northeastern North America. A recent assessment suggested that 60 percent of the total amount of mercury deposition in the Catskills is from local and regional anthropogenic sources, with natural sources (16%) and Asia (13%) being other large contributors (Seignour et al. 2002). Current knowledge of the extent of the mercury problem in the Catskills is sparse, but despite limited monitoring, evidence is mounting that mercury may be having a pervasive impact on the area's fish and wildlife resources. Mercury concentrations detected in certain fish from some Catskill-area lakes and reservoirs were high enough to prompt the New York State Department of Health to issue region-wide consumption advice for this area (NYSDOH 2005). Further, mercury concentrations in standard-length yellow perch and smallmouth bass from New York City drinking water reservoirs in and around the Catskills were always higher than levels in these species from reservoirs east of the Hudson River (Loukmas and Skinner 2005).

Mercury contamination became an important issue in the Neversink Reservoir when in 1998, smallmouth bass from the reservoir were shown to have mercury levels above the NYSDOH action limit. It is also the most acidic of the Catskill region reservoirs and has a largely acidic upper watershed (Ollinger et al. 1993, Lawrence et al. 2001), which may be contributing to the observed mercury levels in fish. Because of these factors, the Neversink watershed was selected as a suitable site to investigate mercury distribution, methylmercury transformation, uptake into biota and movement through the food chain.

The objectives of this study were to: 1) document mercury and methyl mercury levels in water, sediments, macroinvertebrates, and fish in a variety of different aquatic habitats throughout the upper Neversink Reservoir watershed; 2) determine the influence of habitat type on mercury transformation by calculating methylation efficiencies (i.e., methylmercury concentrations/total mercury concentrations) in water and sediments from a variety of sites; and 3) assess biological transfer of mercury by determining bioaccumulation factors.

STUDY AREA

The Neversink Reservoir became operational in 1953 and is one of four New York City water supply reservoirs in the Delaware River drainage. Its watershed is located in Sullivan and Ulster counties, NY and covers an area of 238 km². The reservoir and upper watershed are physiographically diverse and are located in 3 different ecological zones: the primary headwater streams in the Catskill Peaks, the main branch of the Neversink River and the upper ½ of the reservoir in the Delaware Hills, and the southern ½ of the reservoir in the Neversink Highlands (Reschke 1990). Detailed descriptions of these ecozones are available in Dickinson (1983). Human development in the watershed is minimal and the area is primarily forested with sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), and beech (*Fagus grandifolia*). Further details of watershed land use, cover types, climate, elevation, precipitation, physiography, and geology are available in Lawrence et al. (2001).

METHODS

Site selection

Seventeen sites within the upper Neversink Reservoir watershed were chosen for assessment (Figure 1). Sites were selected to represent 5 unique ecosystem types within the upper watershed: headwater and mid-order streams, a man-made pond (Lake Cole), a beaver pond, and the Reservoir. Three sites were categorized as headwater streams: Tison (East Branch), Winnisook (West Branch), and Biscuit Brook. Five sites were categorized as mid-order streams: Aden Brook, Main Branch, East Branch, and West Branch of the Neversink River, and Claryville (East Branch). Six sites were selected from the reservoir, two sites were from the beaver pond, and the remaining site was Lake Cole. Not all parameters (water, sediment, biota) were collected from every site.

Water sampling

All water column mercury sampling conducted for this study adhered to published EPA guidelines, "EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels" (EPA 1996). Water samples were collected from 13 sites; 2 reservoir and 2 mid-order stream sites were not sampled. Water column samples for mercury were collected at four different times from the reservoir; once during spring isothermic conditions and three times in late summer and fall during stratified water column conditions. A peristaltic pump and hose apparatus were used to collect water column samples at each location in the reservoir. Water was sampled twice from riparian and pond sites; once during general high flow conditions in the spring and again in the fall during general base flow conditions. Surface water samples from the Reservoir, pond, Lake Cole, and streams were made by a hand grab. Water samples were preserved at 4 °C in laboratory-prepared 1-liter Teflon bottles.

Standard water chemistry parameters (Table 1) were measured from the Reservoir

according to New York City Department of Environmental Protection (NYCDEP) protocols (Effler and Bader 1998). Sampling teams also used the guidance of NYSDEC SOP #203-02 “Standard Operating Procedure: Collection of Lake Water Quality Samples” (Rev. 0.0 8/6/02) and NYSDEC SOP # 201-02 “Standard Operating Procedure: Collection of Ambient Water Quality Samples” (Rev. 0.0 8/8/02).

Table 1. NYCDEP water sampling program measurements (adapted from Effler and Bader 1998).

Field Measurements	Chemical/Physical Analysis
temperature	turbidity
pH	color
dissolved oxygen	ammonia
conductivity	nitrate/nitrite
Secchi depth	total nitrogen
	soluble reactive, total dissolved, and total phosphorus
	dissolved organic carbon
	total organic carbon
	chlorophyll <i>a</i>

Sediment sampling

Sediment sampling was conducted in adherence to NYSDEC SOP # 207-02 “Standard Operating Procedure: Collection of Sediment Samples” (Rev 0.0 8/8/02). Surficial samples provide an accurate representation of current ambient conditions; therefore, sediment was sampled only once, during summer at low water conditions.

Sediments were collected from 16 sites; one beaver pond site was not sampled. Stream and beaver pond samples were collected using a Teflon scoop and represented the top 2 to 4 cm of sediments. Sediments were collected from the reservoir and Lake Cole using a stainless steel Petite Ponar dredge and represented the top 4 to 6 cm of sediments. The Ponar was cleaned prior to use by rinsing in ambient water three times. The sediments were removed with a clean, stainless steel scoop, away from the sides of the ponar. All samples were placed into clean bottles, which were prepared by Frontier Geosciences, Inc.. At least 20 g of sediments were collected from each site for both total and methyl mercury analyses.

All sample containers were labeled using a permanent marker to indicate the date, time, and sampling location. This information was then recorded in a field logbook and on a chain-of-custody form. Additional field data recorded included site and sample ID, date, time, location, bottom depth, sediment characterization, and sampling personnel. The custody form accompanied the samples during shipment to the contract labs. Sediment material not placed in sample bottles was returned to the location of collection. After collection, sample bottles were placed in coolers with ice and shipped overnight to Frontier Geosciences, Inc. for analysis.

Macroinvertebrate sampling

Macroinvertebrates were collected from 11 sites; four reservoir and 2 mid-order stream sites were not sampled. Using 0.5 m wide x 0.3 m high rectangular dip nets, macroinvertebrates were collected by kick sampling a 50 m reach at riverine sites and scoop netting a 50 m section of shoreline at lacustrine sites. Macroinvertebrates were removed from the nets and placed in 30 x 15 x 10 cm clear plastic trays, where the organisms were found, removed with forceps, and placed in glass jars filled with water from the site. Data recorded in field logbooks included site and sample ID, date, location, stream habitat description, and sampling personnel. The samples were then delivered in ice-filled coolers back to the laboratory where they were immediately sorted into taxonomic groups, counted, weighed, and placed in clean sample jars as composites if the total weight of the group approximated or exceeded 1.0 g. Macroinvertebrates were identified with the aid of reference guides from Peckarsky et al. (1990) and Voshell (2002). The samples were then frozen until they were shipped via overnight delivery to Cebam Analytical, Inc. for analyses. At seven sites (3 mid-order streams, 2 headwater streams, 1 beaver pond site, and Lake Cole) a few amphibians were opportunistically collected during macroinvertebrate sampling and kept for mercury analysis.

Fish sampling

Five individuals of a top trophic level predator (brook [*Salvelinus fontinalis*] and brown trout [*Salmo trutta*] in riverine sites; smallmouth bass [*Micropterus dolomieu*] and brown trout in lacustrine sites) and lower trophic level species (slimy sculpins [*Cottus cognatus*], blacknose dace [*Rhinichthys atratulus*], and golden shiners [*Notemigonus crysoleucas*] from riverine sites; alewives [*Alosa pseudoharengus*], rainbow smelt [*Osmerus mordax*], and pumpkinseeds [*Lepomis gibbosus*] from lacustrine sites) were targeted for collection. Fish were collected from 12 sites; 2 reservoir, 2 mid-order and 1 headwater stream were not sampled. Fish were captured by using gill nets in the reservoir and by electrofishing at other sites.

In the reservoir, 12 nets of various mesh sizes (2-10 cm) were set in order to capture a variety of different-sized fish. At least one small stretch mesh (2-4 cm) and one large stretch mesh net (5-10 cm) was set at each of 4 reservoir sites. Nets were checked within 24 hours after being set and were pulled if the necessary quota of fish were collected; or, if fish were still needed, the nets were set for one additional night. All nets were pulled within 48 hours of their initial set.

For the riverine and beaver pond sites a backpack electrofishing device was used for fish collection. Each site was sampled until either the collection goal was achieved, or a 100 m section upstream and downstream of each site was thoroughly sampled. On Lake Cole, a small 3 m aluminum electrofishing boat was used for sample collection by making one pass of the entire shoreline of the lake.

Fish were handled according to standard NYSDEC fish collection and handling procedures (Appendix A). This required recording the date of collection, a unique identification number, the location including GIS coordinates, species, length in millimeters, weight in grams, and method of collection on standard specimen collection forms. In addition, fish scales were collected for aging. Chain-of-custody forms were maintained and samples kept cool and then frozen immediately after handling on the same day of collection.

Fish samples were prepared for analysis by experienced NYSDEC personnel at the Hale Creek Field Station, in Gloversville, NY following standard NYSDEC procedures (Appendix A). For larger, top-trophic level fish this involved using a standard fillet for analysis. Forage species and some of the smaller trout were processed as whole fish.

Mercury analyses

Water and sediment samples were analyzed according to EPA approved protocols for total mercury (EPA Method 1631, EPA 2002) and methyl mercury (EPA Method 1630, EPA 2001). Macroinvertebrates and a subset of 30 fish (15 each of top and lower trophic level fish) were simultaneously analyzed for total and methyl mercury using a method developed by Liang et al. (1994). Biota samples were analyzed on a wet weight basis. All samples were shipped by overnight courier to the analytical laboratories (water and sediments to Frontier Geosciences, Inc; macroinvertebrates and fish to Cebam Analytical, Inc.).

Data analyses

Summary data reporting and statistics

Site data were pooled within each unique habitat type for summary reporting and qualitative/statistical comparisons. Summary descriptive statistics, calculated using Microsoft Excel[®], were reported in tabular format and typically include sample sizes, lengths, weights, and mercury concentration means, standard deviations, and ranges. All summary figures were similarly composed using Excel[®].

Statistix[®] 8 software (Analytical Software 2003) was used to perform all statistical tests. The Shapiro-Wilk test was used to assess data for normality. Wilcoxon Rank Sum tests were used to compare mercury concentrations between macroinvertebrate and fish groups. Spearman Rank correlations were used to test for relationships between mercury in sediment and water. Linear regressions were also performed using mercury concentrations and fish length as the dependent and independent variables, respectively, with subsequent regression-

based predictions made for average-sized fish of certain species in order to make intra-specific comparisons among reservoirs. Regression line comparisons were conducted to compare groups of fish mercury concentration data plotted by length. Minor and infrequent departures from normality were considered acceptable.

Methylation efficiencies

Methylation efficiency was measured as the ratio of methyl mercury concentrations to total mercury concentrations in water and sediment (Ayers, et al. 2000). When methyl mercury was not detected in a sample, ½ the detection limit was used in the calculation.

Bioaccumulation factors

Bioaccumulation factors for total and methyl mercury were calculated and combined for the 5 aquatic habitat types within the watershed. Bioaccumulation factors were determined from mercury concentrations in both water (BAF) and sediment (BSAF) to biota. Biota used in the bioaccumulation determinations were categorized into 4 trophic groups: invertebrate detritivores, invertebrate predators, forage fish and predatory fish. The following equation was used to calculate bioaccumulation factors:

$$\text{BAF or BSAF} = \frac{\text{mean mercury concentration in biota}}{\text{mean mercury concentration in water or sediment}}$$

When methyl mercury was not detected in a sample, ½ the detection limit was used in the calculation.

RESULTS and DISCUSSION

Analytical quality assurance

Quality assurance checks of total and methyl mercury data for all media were deemed acceptable (Appendix B). For biota, neither total nor methyl mercury was detected in any method blank (Appendices B-1 and B-2). Also, percent recoveries of reference materials and calibration and check standards were within acceptable ranges. The relative percent difference between sample duplicates was within guidelines for all but one methyl mercury sample. For sediments and water, calibration and check standards, reference materials, and sample duplicates were all within acceptable limits (Appendices B-3 and B-4).

Water

General limnology of Neversink Reservoir

The bathymetry of the Neversink Reservoir is shown in Figure 2. The general morphometry of the Reservoir is shown in Table 2. There are no point-source discharges of

wastewater in the Neversink Reservoir watershed. Data presented by NYCDEP in its phosphorus Total Maximum Daily Load (TMDL) documents (Kane et al. 1999) indicated that the reservoir was not water-quality restricted. The phosphorus TMDL of 22,553 kg/yr was based on the 20 µg/L guidance value and included a 10% margin of safety of 2,255 kg/yr. The current load of 6,863 kg/yr is well below the available load capacity. The mean total phosphorus concentration for the reservoir for the period 1996-2001 was 4.97 µg/L. These values are consistent with an oligotrophic condition.

Table 2. Neversink Reservoir morphometric information.

Surface Area	595.7 hectares
Shoreline Length	28.4 kilometers
Elevation	439 meters
Mean Depth	22.1 meters
Maximum Depth	43.0 meters
Volume	1342.4 x 10 ⁵ meters ³
Watershed Area	233.4 kilometers
Hydrolic Retention Time	0.59 years
Outlet Dam	Yes
Water Quality Class	A(T)

Although the reservoir was sampled in a number of locations, the general limnologic data are summarized for Station 2 (Figure 2). Figure 3 shows the time series of water temperature (°C), dissolved oxygen concentration (mg/L), and percent of saturation of oxygen at this location, with depth, for the study period. The reservoir was thermally stratified for most of the growing season and there was very little oxygen depletion with depth and limited supersaturation in the photic zone.

Table 3 shows summary statistics for each nutrient component and other water chemistry parameters for the study period. Generally, during the study period, the reservoir continued to exhibit water chemistry indicative of a low-productivity, dilute system. This result is consistent with the facts that the watershed is mostly forested and undeveloped and has no major wastewater treatment facility discharges.

Figure 4 shows the time series for total phosphorus, chlorophyll *a* and Secchi disk depth at Site 2 (epilimnion) for the period 1997-2003. Results for these trophic state indicators were similar at the other Reservoir sampling locations during the study period.

Therefore, overall conventional water chemistry results during the study period were indicative of a low-productivity waterbody and were consistent with previous field studies conducted by NYCDEP.

Table 3. Summary statistics for Neversink Reservoir water chemistry parameters for 2002-2003: Site 2.

Sample Parameter	Valid N	Mean	Minimum	Maximum	Std.Dev.
Total phosphorus ($\mu\text{g/L}$)	44	5.68	<2.6	15.40	2.80
Total dissolved phosphorus ($\mu\text{g/L}$)	20	<1.8	<2.6	3.00	1.96
Soluble reactive phosphorus ($\mu\text{g/L}$)	20	<0.82	<1.2	4.10	1.27
Chlorophyll a ($\mu\text{g/L}$)	9	3.71	1.60	7.60	1.81
Turbidity (NTU)	57	0.98	0.40	2.60	0.45
Total organic carbon (mg/L)	20	1.73	1.03	2.27	0.36
Dissolved organic carbon (mg/L)	20	1.71	1.05	2.26	0.35
True color (Pt-Co, mg/L)	57	13.58	8.00	24.00	3.14
Total nitrogen (mg/L)	20	0.24	0.13	0.32	0.07
Total dissolved nitrogen (mg/L)	20	0.24	0.13	0.32	0.07
NH ₄ -N (mg/L)	20	0.01	0.00	0.02	0.01
NO ₃ +NO ₂ -N (mg/L)	20	0.16	0.04	0.28	0.08
Water temperature ($^{\circ}\text{C}$)	57	9.98	4.40	23.92	5.78
pH (SU)	57	5.88	5.27	6.90	0.41
Dissolved oxygen (mg/l)	57	9.40	6.38	12.30	1.61
Specific conductance ($\mu\text{mho/cm}$)	57	29.57	25.00	32.80	2.04

Mercury

Mean total mercury in water ranged from 0.95 ± 0.19 ng/L in mid-order streams to 2.54 ± 0.93 ng/L in the beaver pond area (Appendix C-1, Figure 5). Mean total mercury concentrations were similar among the reservoir, Lake Cole, and the headwater sites. Methyl mercury was not detected in water from any of the headwater or mid-order streams. Mean methyl mercury concentrations from lacustrine sites ranged from 0.04 ± 0.03 ng/L in Lake Cole to 0.25 ± 0.12 ng/L in the beaver pond area.

Water quality criteria for the protection of wildlife

Total mercury and methyl mercury water quality criteria (WQC) for the protection of wildlife have been developed by EPA (1997b). The WQC for methyl mercury is 0.05 ng/L and the WQC for total mercury is 0.641 ng/L. The methyl mercury criterion was met or exceeded in the beaver pond ($\bar{x} = 0.25 \pm 0.12$ ng/L) and reservoir ($\bar{x} = 0.05 \pm 0.03$ ng/L). The total mercury criterion was exceeded in all five habitat types. Therefore, the two most likely habitats to pose a risk to wildlife due to high mercury exposure were the reservoir and beaver pond; however, the extent of potential risk also may encompass the entire upper watershed if

the total mercury criterion is used for assessment.

Sediment

Total mercury was detected in every sediment sample from all habitat types. Concentrations varied by habitat type and ranged from 4.6 ± 3.0 ng/g in headwater sites to 187 ng/g in the beaver pond (Figure 6). Methyl mercury was not detected in sediments from all headwater streams and 1 mid-order stream. At sites where it was detected, concentrations ranged from 0.1 ng/g in Lake Cole to 5.5 ng/g in the beaver pond. Both total and methyl mercury concentrations were typically higher in the lacustrine *vs.* the riverine sites, which was similar to patterns found in water. Total and methyl mercury levels also were related to the percentage of total solids in the sediments ($r = -0.8725$, $P < 0.0001$, total; $r = -0.7868$, $P = 0.0013$, methyl).

Methylation efficiencies

Methylation efficiencies were determined for water and sediments for all habitat types (Figure 7). In water, mean mercury methylation efficiencies ranged from 0.009 ± 0.001 in headwater streams to 0.13 in the beaver pond. Lacustrine sites had higher mean methylation efficiencies in water than riverine locations. In contrast, mean sediment methylation efficiencies were highest at mid-order stream sites ($\bar{x} = 0.04 \pm 0.01$). There was no relationship between methylation efficiencies in water and sediments ($r = 0.33$, $P = 0.276$).

Methylation efficiency is an important criteria in determining the bioaccumulative nature of aquatic ecosystems (Krabbenhoft et al. 1999). Ecosystems with low methylation efficiencies typically show low to moderate mercury bioaccumulation (Turner et al. 1993); while high methylation efficiencies have been linked to ecosystems with substantial bioaccumulation (i.e., high mercury levels in fish; Wiener et al. 1990, Lamborg et al. 1995, Krabbenhoft et al. 1999). Krabbenhoft et al. (1999) conducted a pilot study of watersheds throughout the United States and concluded that methylation efficiencies ≥ 0.06 were indicative of areas of high bioaccumulation. In this study, methylation efficiencies of this magnitude were only seen in water samples in the vicinity of the beaver pond, which would indicate that this area is the most susceptible to enhanced mercury bioaccumulation. A ranking of bioaccumulation potential based on water and sediment methyl mercury concentrations and combined methylation efficiencies for unique aquatic habitat types suggest that biota from the beaver pond area should have the highest mercury concentrations relative to similar types from other habitats; headwater streams should have the lowest (Table 4). Biota mercury concentrations from the other habitat types should be somewhere in between, however, the specific order was unclear.

Table 4. Patterns of bioaccumulation potential of five habitat types in the Neversink Reservoir watershed, 2003.

Parameter	Ranking of bioaccumulation potential
Water MeHg	Beaver pond area > reservoir > Lake Cole > mid-order streams = headwater streams
Sediment MeHg	Beaver pond area > reservoir > mid-order streams > Lake Cole > headwater streams
Methylation efficiency	Beaver pond area > reservoir = mid-order streams > Lake Cole > headwater streams

Macroinvertebrates

Patterns of mercury concentrations by habitat

Mean total mercury concentrations for all macroinvertebrate samples ranged from 17.5 ± 5.4 at headwater sites to 61.1 ± 30.5 from the beaver pond area (Figure 8). Mean methyl mercury concentrations ranged from 4.6 ± 4.3 from headwater sites to 51.7 ± 30.0 from the beaver pond area. Macroinvertebrates from lacustrine sites generally had higher mercury levels than those from riverine locations, particularly the headwater stream reaches. This pattern was consistent for both predatory and detritivorous invertebrates (Figure 8).

Taxonomic/trophic patterns of mercury concentrations

Predatory macroinvertebrates had higher mean total ($\bar{x} = 60 \pm 87$ ng/g) and methyl mercury concentrations ($\bar{x} = 29 \pm 29$ ng/g) than detritivores ($\bar{x} = 27 \pm 19$ ng/g total, $P = 0.013$; $\bar{x} = 15 \pm 20$ ng/g methyl, $P = 0.055$). The percentage of mercury in the methylated form also was greater in predators ($\bar{x} = 66 \pm 20\%$) vs. detritivores ($\bar{x} = 41 \pm 29\%$, $P = 0.011$). Because of this, taxonomic patterns of accumulation often differed between rankings based on total and methyl mercury (Table 5). Methyl mercury concentrations were more likely to exhibit a pattern of biomagnification in the invertebrates, whereas total mercury measurements were more often higher in detritivores vs. predators, especially in the stream habitats. Crayfish typically had higher mercury levels than other detritivores and most predators, likely due to their larger size and longer life span (Martin 1997).

Table 5. Patterns of total and methyl mercury concentrations in benthic macroinvertebrates from five habitat types in the Neversink Reservoir watershed, 2003.

Habitat	Mercury species	Taxonomic ranking of mercury concentrations ¹
Headwater streams	total mercury	dragonflies > caddisflies > mayflies > stoneflies
	methyl mercury	dragonflies > stoneflies > caddisflies > mayflies
Mid-order streams	total mercury	mayflies > dragonflies > crayfish > true flies > stoneflies > caddisflies
	methyl mercury	crayfish > dragonflies > true flies > stoneflies > mayflies > caddisflies
Beaver pond	total mercury	crayfish > hellgrammites > dragonflies > caddisflies > true flies > aquatic sow bugs
	methyl mercury	crayfish > hellgrammites > dragonflies > caddisflies > true flies > aquatic sow bugs
Lake Cole	total mercury	crayfish > dragonflies
	methyl mercury	dragonflies > crayfish
Neversink Reservoir	total mercury	mayflies > caddisflies > aquatic sow bugs
	methyl mercury	mayflies > aquatic sow bugs > caddisflies

¹ Predators: dragonflies, stoneflies, hellgrammites; detritivores: crayfish, mayflies, caddisflies, true flies, aquatic sow bugs.

Comprehensive studies of mercury in aquatic macroinvertebrates are scarce (Pennuto et al. 2005), but the few that do exist indicate the importance of trophic status in determining mercury burdens (Tremblay et al. 1995, Tremblay and Lucotte 1997, Tremblay 1999, Mason et al. 2000, Gorski et al. 2003). Most studies suggest that patterns of methyl mercury concentrations are more reliably indicative of biomagnification in the macroinvertebrate food chain than total mercury levels, and this concept is supported by results of this study. Also in

accordance with this research, other studies have found that the percent of the total mercury body burden that is in the methylated form increases with the trophic position of invertebrate group (Tremblay et al. 1995, Tremblay and Lucotte 1997, Tremblay 1999, Appendix C-4). This suggests that relying exclusively on total mercury measurements to describe and understand accumulation patterns in invertebrates and their connection to higher trophic levels is inadequate.

Amphibians

Thirteen amphibian samples (3 species: northern two-lined salamander (*Eurycea bislineata*), red-spotted newt (*Notophthalmus viridescens*), and green frog tadpole (*Rana clamitans*)) from four habitat types were collected during macroinvertebrate sampling (Appendices C-4 and C-5). Amphibians were not part of the original collection protocol, but were opportunistically collected because of their availability. Northern two-lined salamanders were collected from headwater and mid-order stream sites whereas red-spotted newts and green frog tadpoles were captured from lacustrine locations. Total and methyl mercury concentrations ranged from 17.0 ng/g (total) and 8.0 ng/g (methyl) in a green frog tadpole from the beaver pond area to 70.9 ng/g (total) and 55.6 ng/g (methyl) in a northern two-lined salamander from a mid-order stream (Figure 9). For northern two-lined salamanders, mercury concentrations were higher in mid-order streams vs headwater streams. The range of total mercury concentrations found in northern two-lined salamanders (18.1-70.9 ng/g) was similar to those detected in Maine and Virginia (21.4-79.5 ng/g, Bank et al. 2005); although the percentage of methyl mercury in the samples was generally less in the Neversink samples (22-83% vs. 73-97%). From lacustrine sites, red-spotted newts (adult) had higher mercury concentrations than green frog tadpoles, which is likely a reflection of and dietary differences (i.e., tadpoles are primarily plankton feeders, while newts typically consume small aquatic invertebrates) and age (i.e., newts were likely > 2 years old, tadpoles were < 1 year old).

Fish

One hundred and twenty-five fish were collected from throughout the watershed (Appendix C-6). Total mercury was detected in all samples and mean concentrations ranged from 19 ± 7 ng/g in forage fish from headwater sites to 1303 ± 630 ng/g in predatory fish from the reservoir (Figure 10). Methyl mercury was detected in all 30 analyzed samples and mean values ranged from 15 ng/g in forage fish from headwater sites to 839 ± 545 ng/g in predatory fish from the reservoir.

The portion of total mercury that was methylated differed between trophic groups ($P < 0.001$). Mean methyl mercury percentages were significantly higher in predatory fish ($\bar{x} = 92 \pm 10\%$) vs. forage species ($\bar{x} = 63 \pm 8\%$). The percent of methyl mercury in lower trophic level fish was similar to that in predatory benthic macroinvertebrates and amphibians (Figure 11). One caveat to these clear trophic patterns is that percent methyl mercury may have been influenced by the type of tissues analyzed because most mid- and low-trophic level fish were small (< 6 in) and were therefore analyzed as whole fish whereas only fillet tissue was

analyzed for larger high-trophic level fish. However, for brook trout, 4 individuals were analyzed whole and 4 were analyzed as fillets and only a very slight difference was observed (e.g., 86% fillet vs. 84% whole).

Fish could not be reliably compared among all the habitat types because mercury accumulation is typically affected by size, age, and species. Habitat comparisons were limited to instances where there were same-size or same-age fish of a particular species at multiple sites. Blacknose dace (62-86 mm) were compared between the beaver pond area and mid-order stream sites (Figure 12). Total mercury concentrations were over five times higher in blacknose dace from the beaver pond than those from the streams. Also, mercury concentrations in one-year-old brook trout and similar-sized slimy sculpins were higher in mid-order streams than headwater sites. Based on these comparisons, a subsequent ranking of the bioaccumulation potential of mercury in fish for these three habitat types is:

beaver pond area > mid-order stream > headwater stream

A comparison of mercury concentrations for the lower trophic level species within the reservoir, alewife and smelt, determined that there were slight differences between species (Figure 13). The limited data indicate that mercury concentrations increased to a greater extent with size in smelt vs. alewives.

For the top-trophic level fish in the reservoir, previously collected smallmouth bass and brown trout mercury data from 1998 (NYSDEC unpublished data) were compared to this study's data to determine if there was a recent temporal change in mercury concentrations. Regression line comparisons indicated that there was no discernable change for either smallmouth bass or brown trout (Figure 14) in the reservoir over this five-year time period. Therefore, the 1998 and 2003 data were combined to increase sample sizes for subsequent comparisons.

A comparison of mercury concentrations between smallmouth bass and brown trout revealed that at similar lengths smallmouth bass always had higher mercury levels. For example, the regression-predicted mercury value at 400 mm was 262 ng/g for brown trout and 1,732 ng/g for smallmouth bass; not until a brown trout reaches 655 mm in length would it have this mercury concentration. These differences are almost certainly influenced by the dissimilar ages and growth rates of the fish. A meaningful comparison between smallmouth bass from the reservoir and Lake Cole could not be made because the number of samples of same-sized fish from these two waters were too few (i.e., only two fish from each site between 293-297 mm in length).

Reservoir comparison

The magnitude of the mercury problem in Neversink Reservoir fish was determined by comparing this study's data with that from other reservoirs in the region. From 1998-2003 NYSDEC collected mercury concentration data for a variety of fish species, including

smallmouth bass and brown trout, from all 19 of the New York City water supply reservoirs (Loukmas and Skinner 2005). Smallmouth bass were collected from 16 of these reservoirs and brown trout were sampled from 9. Regression-predicted mercury concentrations at standard lengths (381 mm (15 inches) for smallmouth bass and 457 mm (18 inches) for brown trout) indicated that fish from the Neversink Reservoir were some of the most highly contaminated throughout the entire reservoir system. Neversink Reservoir smallmouth bass exhibited the second highest mercury concentrations in the reservoir system, slightly lower than those from Schoharie Reservoir (Figure 15). Further, the 6 Catskill region reservoirs all had higher mercury levels in 381 mm smallmouth bass than any of the 10 reservoirs analyzed for this species east of the Hudson River. Similarly, Neversink Reservoir brown trout had the highest predicted mercury concentration of the 9 New York City reservoirs sampled for this species (Figure 16). However, in contrast to smallmouth bass, brown trout mercury concentrations in Catskill region reservoirs were not different from east of Hudson reservoirs.

Human fish consumption guidelines

The NYSDOH uses a criterion of 1.0 ug/g mercury in fish tissue as the basis for issuing health advice. Prior to this study, the health advice for the Neversink Reservoir was to limit smallmouth bass (all sizes) consumption to one meal per month. Based on a review of data from this project, NYSDOH decided to add the same advice for brown trout over 24 inches. These advisories were reported in the statewide publication, *Chemicals in Sportfish and Game: 2004-05 Health Advisories* (NYSDOH 2004a) and a smaller bulletin specific to the New York City reservoirs, *2004 Health Advisories on Eating Sportfish: New York City Reservoir System* (NYSDOH 2004b).

Wildlife health implications

For the protection of fish-eating wildlife from mercury contamination, EPA (1997b) developed a criterion to determine potential risk to wildlife from mercury concentrations in water and used this value to express corresponding risk levels in fish. Fish tissue criteria formulated by EPA (1997b) for the protection of piscivorous wildlife are 77 ng/g for mercury levels in forage fish and 346 ng/g in larger, higher trophic level fish. Mercury concentrations at or below these levels were assumed to be protective of wildlife health. For forage fish, a documented effect level was found in loons at 300 ng/g (Barr 1986) and EPA (1997b) suggested that a specific adverse effects level for mercury in forage fish is between 77 ng/g and 300 ng/g.

Mean total mercury concentrations in upper trophic level fish exceeded the 346 ng/g threshold in the reservoir and Lake Cole, likely because these are the only two habitats in the watershed that provide enough space and resources for predatory fish to grow old and large enough to accumulate such levels. Because the percentage of methyl mercury in these fish is near 100%, there was no need to use this measurement for comparison.

Mean total mercury levels in forage fish exceeded the 77 ng/g threshold from all habitat types except headwater streams (19.2 ± 6.9 ng/g). Further, mean mercury

concentrations in forage fish from the beaver pond and Lake Cole also exceeded 300 ng/g. Because methyl mercury makes up only about 63% of the total amount of mercury, on average, in forage fish, a more appropriate measure may be to use these measurements instead. For this, forage fish mean methyl mercury concentrations exceeded 77 ng/g in 3 habitats (beaver pond, reservoir, and Lake Cole (assuming 63% methyl mercury)), but none were above 300 ng/g. These data suggest that there were potential risks to piscivorous wildlife that feed in the lacustrine and palustrine areas of the Neversink watershed, and these risks may extend into some of the near-reservoir streams.

While mercury data for both trophic groups of fish was important in this analysis, more emphasis needs to be placed on the forage species because of their prevalence in the diets of wildlife piscivores. EPA's (1997a) exposure parameters for fish-eating wildlife indicate that the majority of piscivorous wildlife consume small, low-trophic level fish (planktivores and insectivores), almost exclusively. These parameters seem to be overly generic and simplistic for most species, but the concept that fish-eating wildlife feed more heavily on smaller fish versus large predatory fish is appropriate (e.g., Barr 1986, Barr 1996). In addition, as indicated by a paucity of studies (Yearly 2000, Kamman et al. 2005), there is an underappreciation of mercury contamination in lower-trophic level fish, and thus, a very limited amount of information regarding realistic dietary risks to piscivorous wildlife. The extent of potentially deleterious mercury levels in forage fish in the upper Neversink Reservoir watershed indicates that further work on this subject is warranted.

Bioaccumulation factors

Total and methyl mercury bioaccumulation factors between water and biota (BAF) and sediment and biota (BSAF) varied by habitat type and generally increased with advancing trophic levels. For total mercury, BAFs ranged from 11,915 in invertebrate detritivores in headwater streams to 654,059 in predatory fish from the reservoir (Table 3, Figure 17). Trophic level patterns for total mercury BAFs were consistent throughout the habitats with the greatest increases generally occurring between the invertebrate groups and forage fish. BAF values for methyl mercury ranged from 155,926 in beaver pond invertebrate detritivores to 20,406,667 in large predatory fish from the reservoir (Table 6, Figure 18). Trophic level BAF patterns for total and methyl mercury were similar among habitat types except for predatory fish from the beaver pond, which had lower mercury levels, and thus a lower BAF, than the forage fish. This may be reflective of higher site fidelity of forage fish, making it more indicative of mercury conditions near the beaver pond than more mobile predatory fish, which may be spending time in the nearby reservoir or other habitats.

BSAFs for total mercury ranged from 0.3 in invertebrate detritivores from the beaver pond area to 36.7 in predatory fish from the reservoir (Table 7, Figure 19). BSAFs for methyl mercury ranged from 7.7 in invertebrate detritivores from the beaver pond area to 3,401 in predatory fish from the reservoir (Figure 20). BSAFs for total and methyl mercury were lowest in the beaver pond environment, which was due to the relatively high mercury levels detected in the sediments. These low BSAFs indicate that high sediment concentrations did

not translate into correspondingly high levels in biota.

Table 6. Bioaccumulation factors (BAFs) for total and methyl mercury in water to biota.

Habitat type	Invertebrate - detritivore		Invertebrate - predator		Fish - forage		Fish - predator	
	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg
Headwater streams	11915	160000	12979	616000	13475	912000	17730	1700000
Mid-order streams	19684	472000	24632	1216000	88948	4384000	101737	6570000
Lake Cole	18865	440540	28298	759459	230496	8783784	419149	15972973
Reservoir	16095	292000	-	-	176603	3790000	654060	20406667
Beaver pond	21311	155926	29795	284436	169058	1029630	90847	766667

Table 7. Biota - sediment accumulation factors (BSAFs) for total and methyl mercury.

Habitat type	Invertebrate - detritivore		Invertebrate - predator		Fish - forage		Fish - predator	
	THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg
Headwater streams	3.7	200	3.9	770	4.1	1140	5.4	2125
Mid-order streams	3.6	36.9	4.5	95	16.3	342	18.6	513
Lake Cole	1.1	163	1.6	281	13	3250	24	5910
Reservoir	0.9	49	-	-	10	632	36.7	3401
Beaver pond	0.3	7.7	0.4	12	2.3	50.6	1.3	37.6

CONCLUSIONS

This study represents an initial examination of how mercury is distributed in Catskill environments and lends insight into the processes of mercury uptake, pathways, and bioavailability in aquatic biota. The results of this study suggest that abiotic (i.e., water and sediment) mercury conditions are indicative of mercury concentrations in lower trophic level biota at specific sites and habitat types. Among the upper watershed sites, total and methyl mercury concentrations were uniformly high in water and sediments from the beaver pond area and consistently low in headwater stream habitats. This pattern also was reflected in lower trophic level biota (i.e., macroinvertebrates, amphibians, and forage fish), which are likely to be more indicative of site-level conditions than larger, and more mobile, top-trophic level fish. Comparisons between the biota from the reservoir and other habitat types were not direct because of the differences in species assemblages or fish sizes. However, the highest mercury concentrations in the Neversink watershed were found in top-trophic level fish from the reservoir.

Mercury concentrations were related to trophic level in all habitat types, with the lone exception from the beaver pond, where forage fish had higher concentrations than predatory fish. The lower site fidelity of predatory fish, and thus the likelihood that they spend time in other habitat types may explain this pattern deviation. This study also highlights the importance of using methyl mercury as a more appropriate measure than total mercury for detailing accumulation patterns in lower trophic level food webs. Methyl mercury percentages and concentrations increased with each successive trophic level, suggesting that the relative bioavailability of mercury is different at each level. Information on the bioavailability of mercury at any one trophic stage, or even an individual species within a trophic level, is crucial to understanding mercury impacts further down the chain.

Caution should be exercised not to directly equate bioaccumulation factors with actual biota mercury concentrations. Some of the highest concentrations were measured in biota from the beaver pond area, but BAFs and BSAFs at this site were low. The relatively high abiotic mercury levels in this area resulted in lower bioaccumulation factor calculations. In other words, accumulation rates decreased when abiotic mercury concentrations reached relatively high levels. Therefore, while water and sediment mercury concentrations were indicative of mercury levels in biota, this relationship was not linear.

Potential human and environmental risks due to high mercury concentrations were documented in water and fish from throughout the Neversink watershed. High rates of deposition (Miller et al. 2005) and elevated fish mercury concentrations from other Catskill waters (Loukmas and Skinner 2005) suggest that similar risks may be widespread throughout the region. Despite these potential risks, information regarding mercury concentrations in insectivorous and piscivorous wildlife from this area remain unknown. Future research focusing on these trophic groups of wildlife, as well as expanding the extent of the base of information concerning the lower food webs are logical and appropriate extensions of this study.

ACKNOWLEDGMENTS

We were fortunate to have assistance from a very skilled and enthusiastic group of project personnel, all of whom made important contributions to this study. We thank Robert Angyal and Tony Zerkle for their substantial help with fish collections. We are indebted to Jessica Bennett for her work with invertebrate collections and identifications. Bob Bode provided laboratory space and also assisted Jessica with identifications. Kathy Skinner assisted with invertebrate collections. Jim Swart and Frank Estabrooks helped plan and conduct the sediment work. Kim Nezelek provided valuable assistance with reservoir access, water sampling, and data acquisition. Andrew Bader supplied us with NYCDEP water chemistry data. Anthony Gudlewski assisted with sample processing and shipment. Cebam Analytical, Inc. and Frontier Geosciences provided exceptional analytical service. We also thank Larry Skinner and Tim Sinnott for providing advice and giving direction to the project. This project was funded as part of the New York City Watershed Program by a federal Safe Drinking Water Act grant (FY 2002 EPA cooperative agreement X-98255002-0). We appreciate the management of the grant within NYSDEC by Kenneth Markussen, Bruce Mussett, and Laura Stetson. This report was reviewed and helpful comments were made by Larry Skinner, Kathy Skinner, Howard Simonin, and Robert Angyal.

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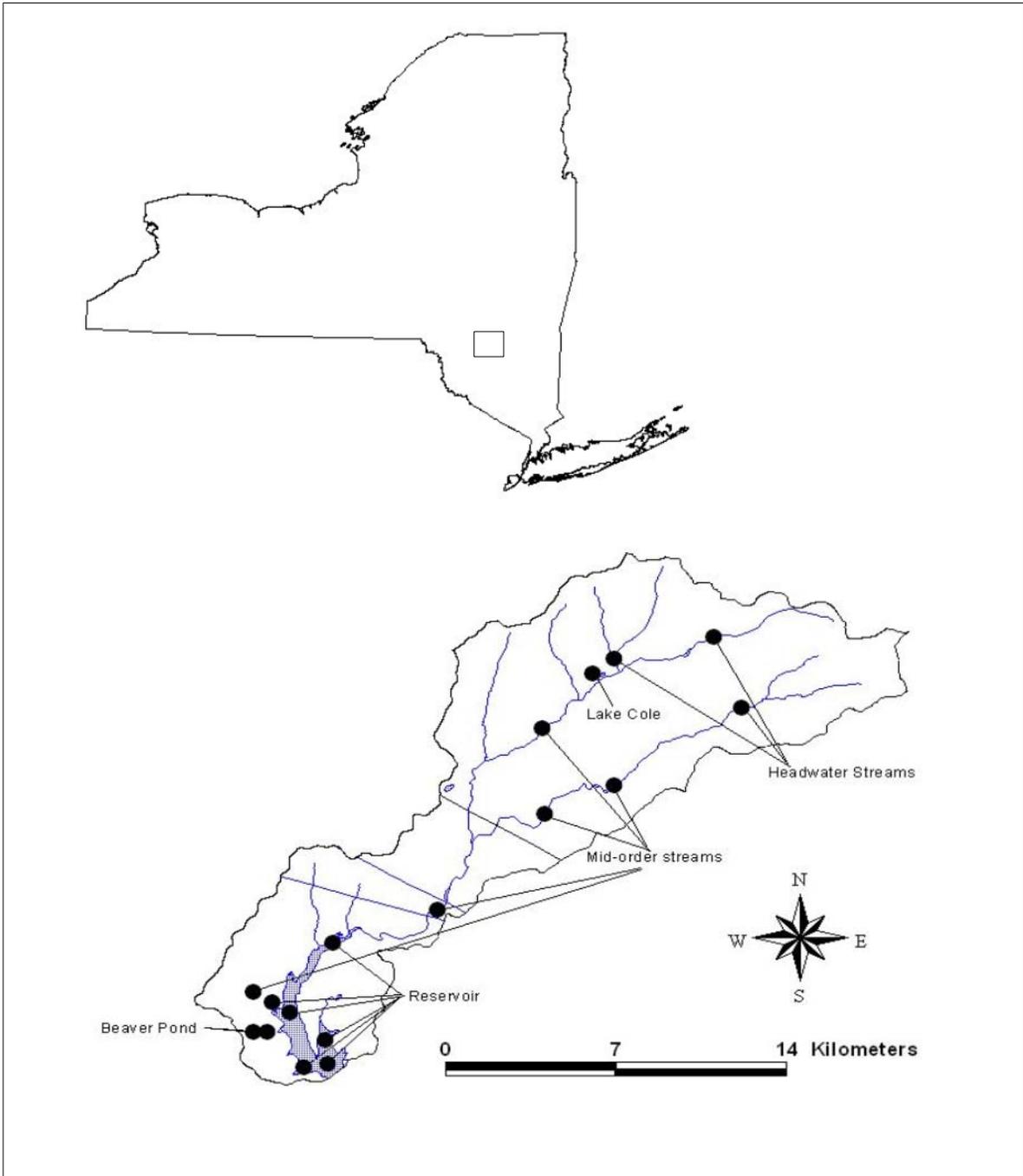


Figure 1. Map of the Neversink Reservoir Watershed study sites.

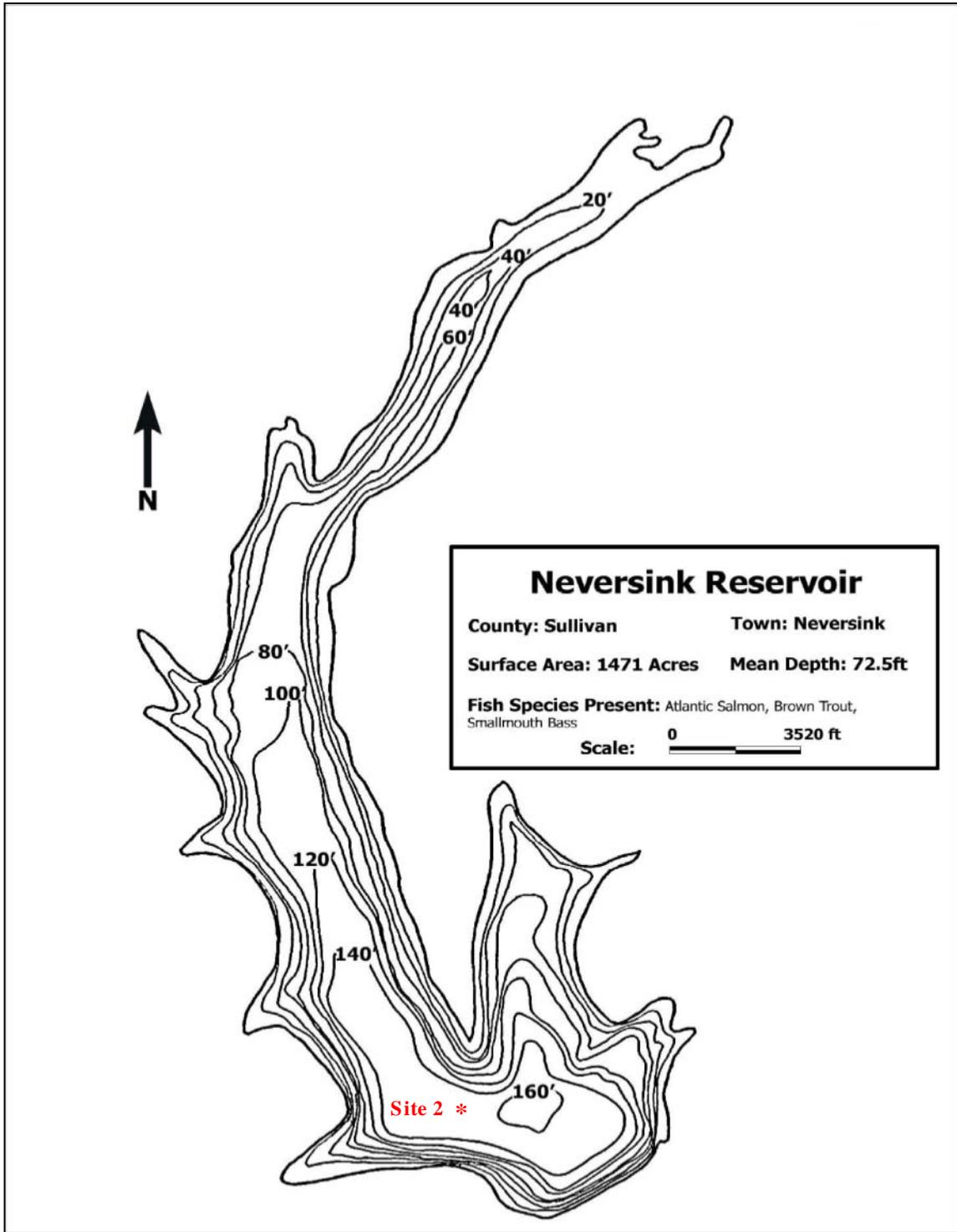


Figure 2. Neversink Reservoir bathymetric map (Swart et al. 1989).

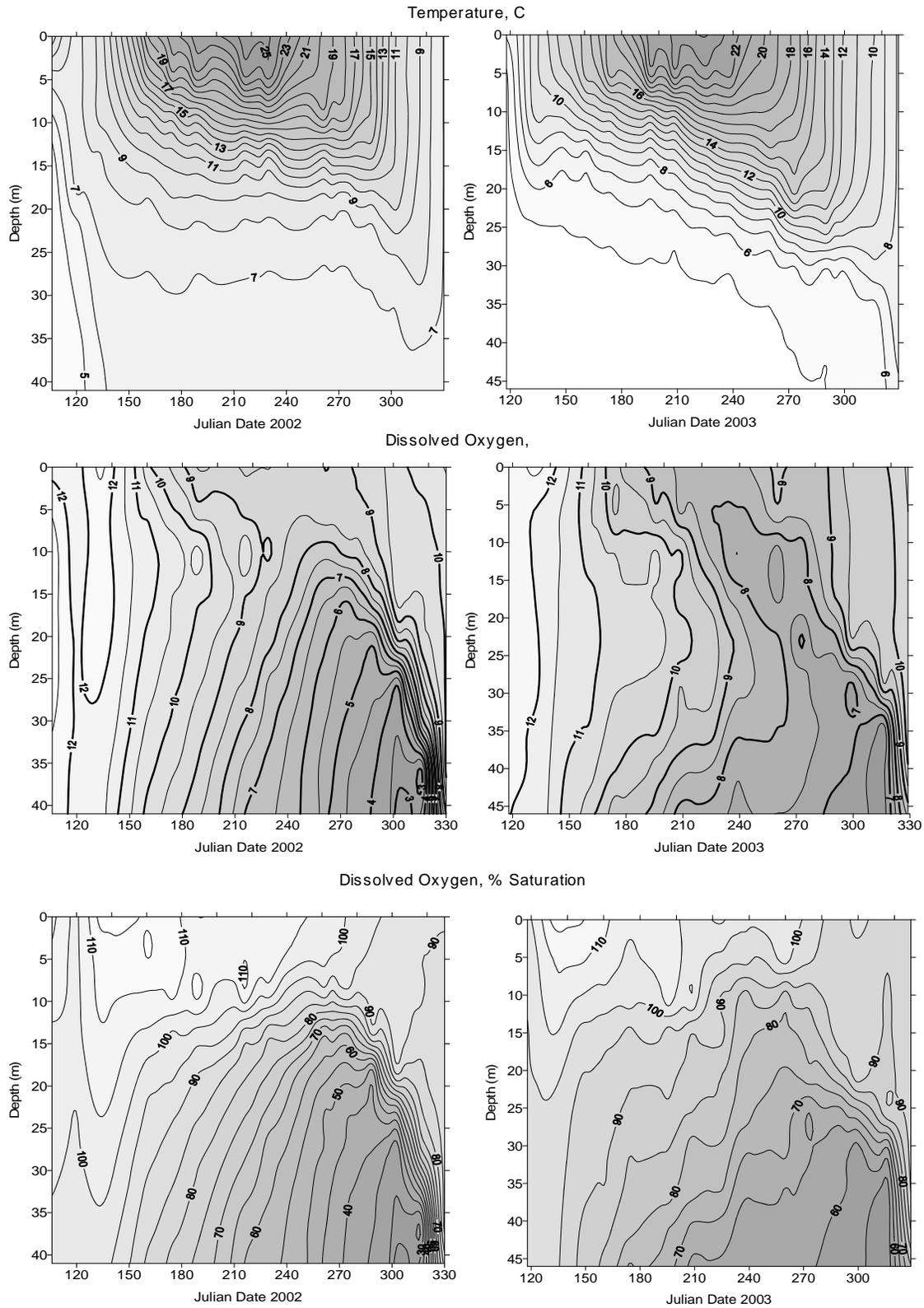


Figure 3. Time series of water temperature (C), dissolved oxygen concentration (mg/L), and percent of saturation of oxygen at site 2, with depth, 2002 - 2003.

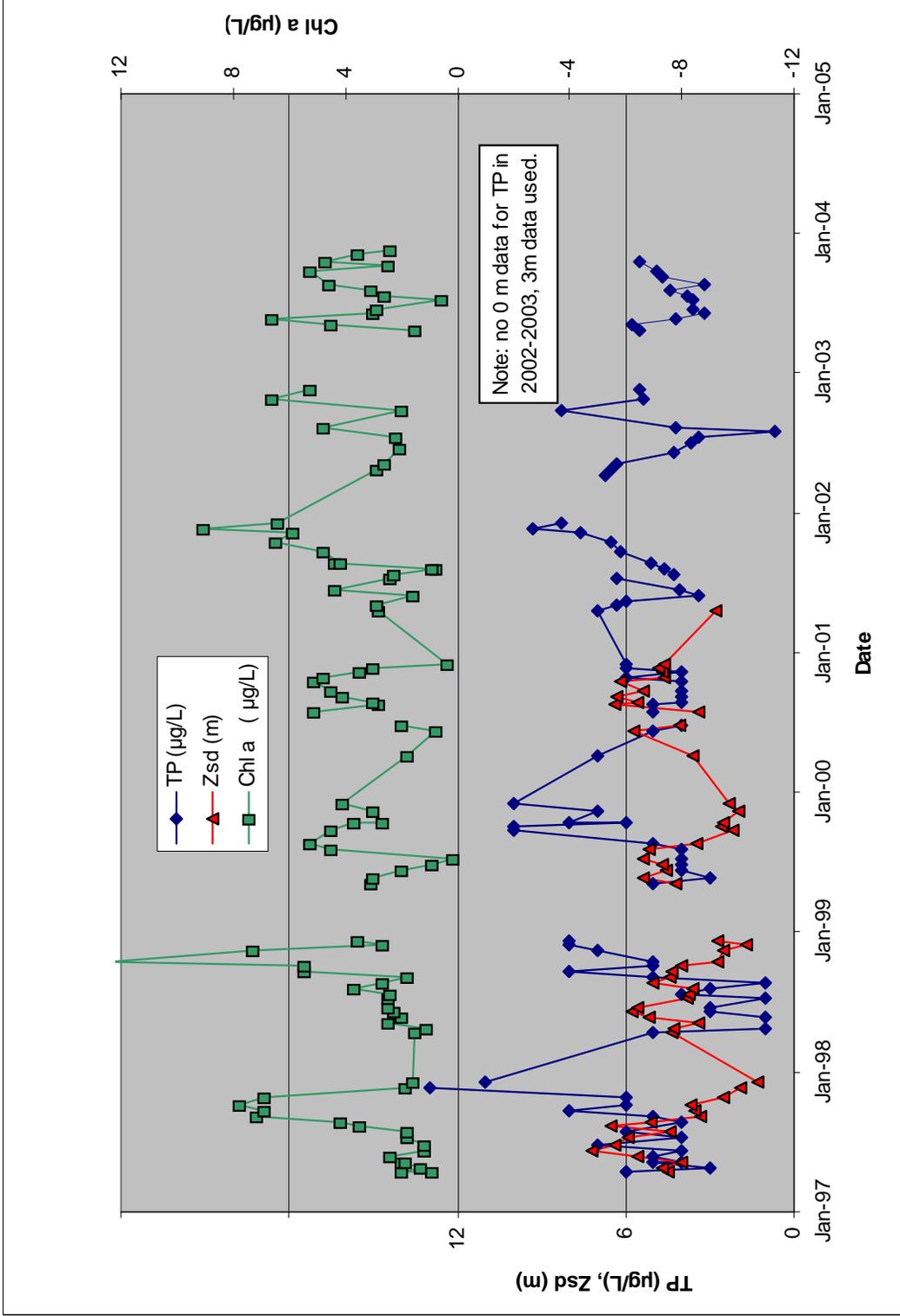


Figure 4. Neversink Reservoir surface (0 m) total phosphorus, chlorophyll *a*, and secchi disk transparency: Time series, 1997-2003

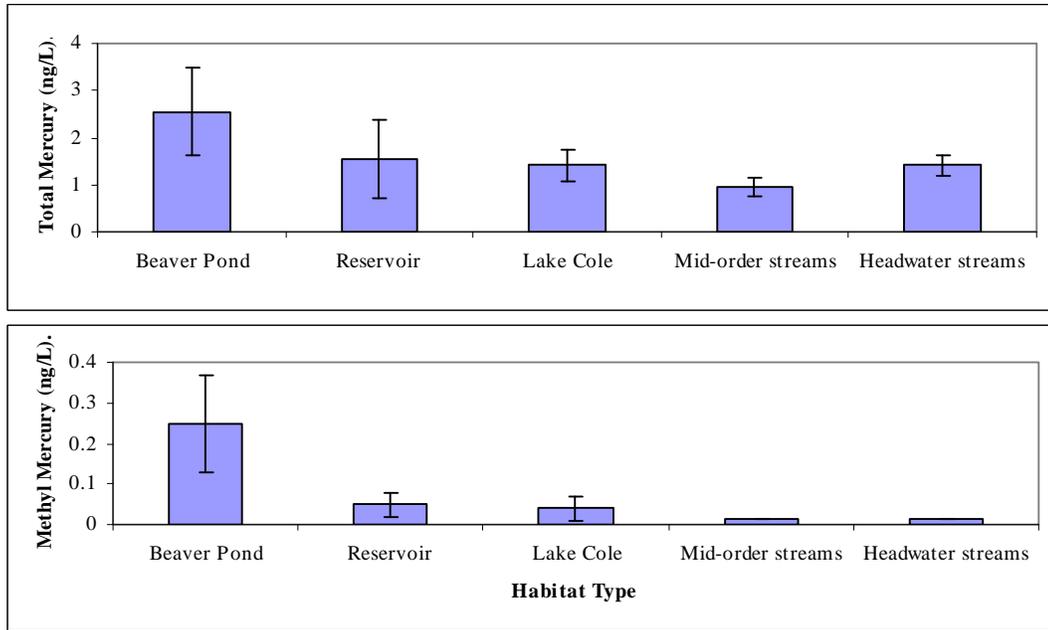


Figure 5. Mean total and methyl mercury concentrations (ng/L) in water collected from the Neversink Reservoir watershed, 2003.

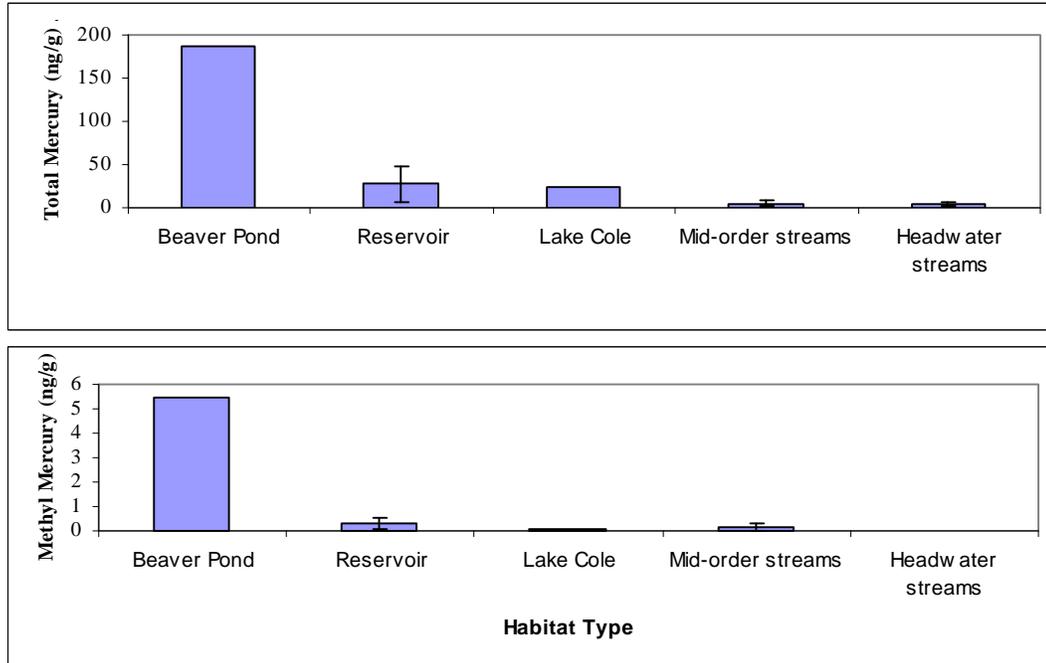


Figure 6. Mean total and methyl mercury concentrations (ng/g) in sediment collected from the Neversink Reservoir watershed, 2003.

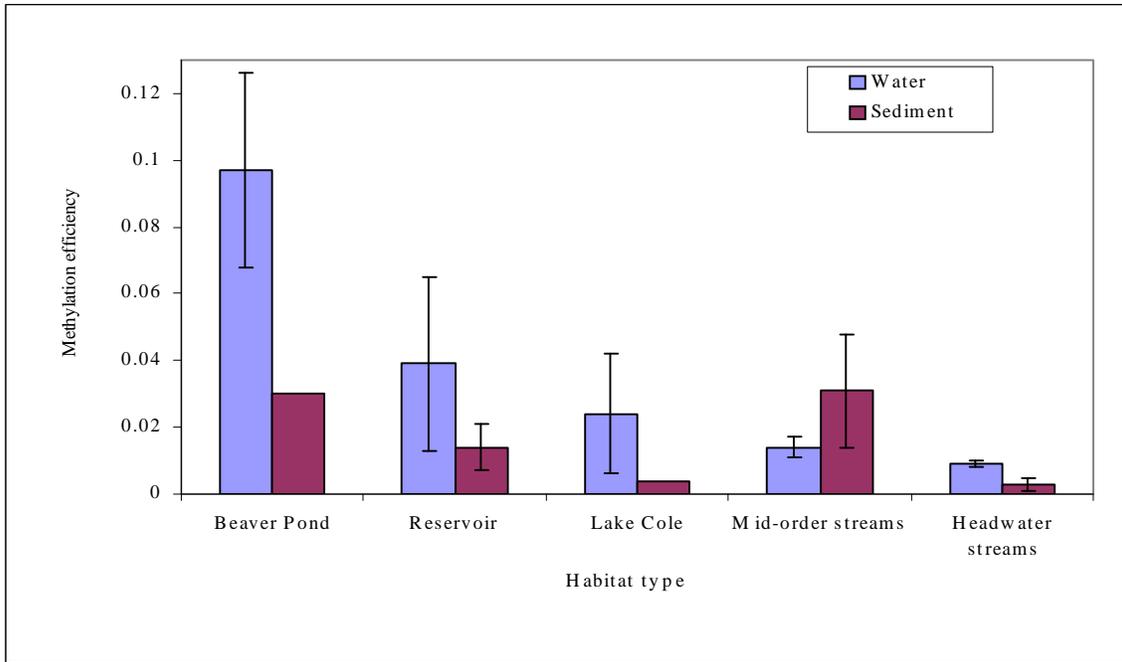


Figure 7. Mercury methylation efficiencies (ratio of methyl mercury to total mercury) for sediment and water from 5 habitat types within the NRW, 2003.

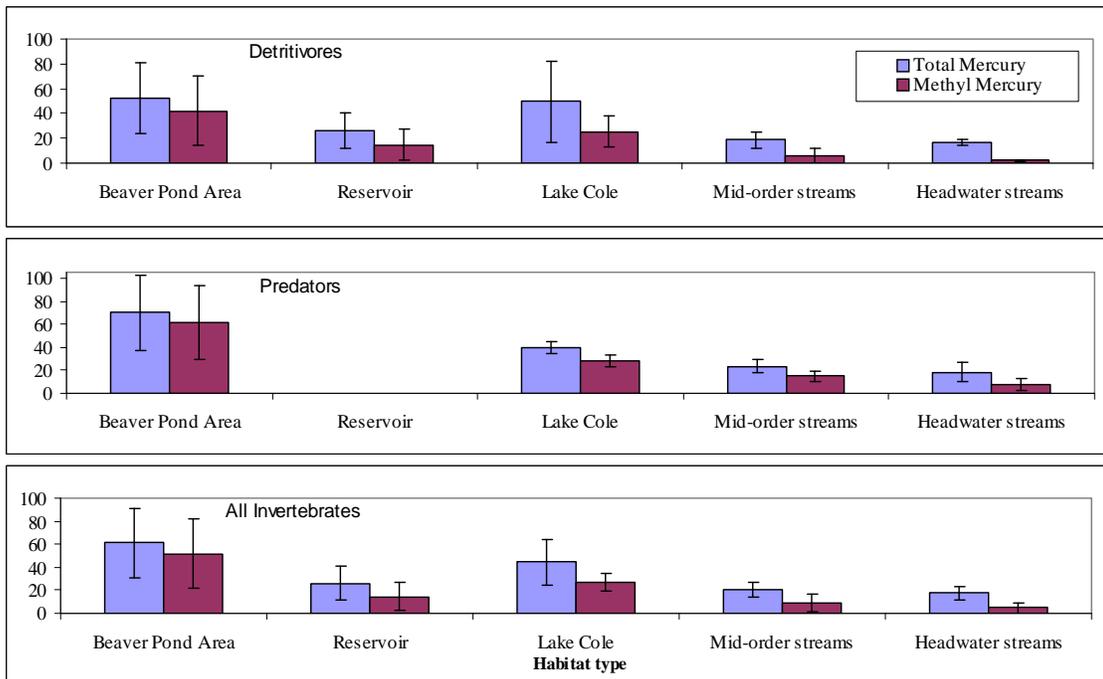


Figure 8. Mean total and methyl mercury concentrations in macroinvertebrates from the Neversink Reservoir watershed, 2003.

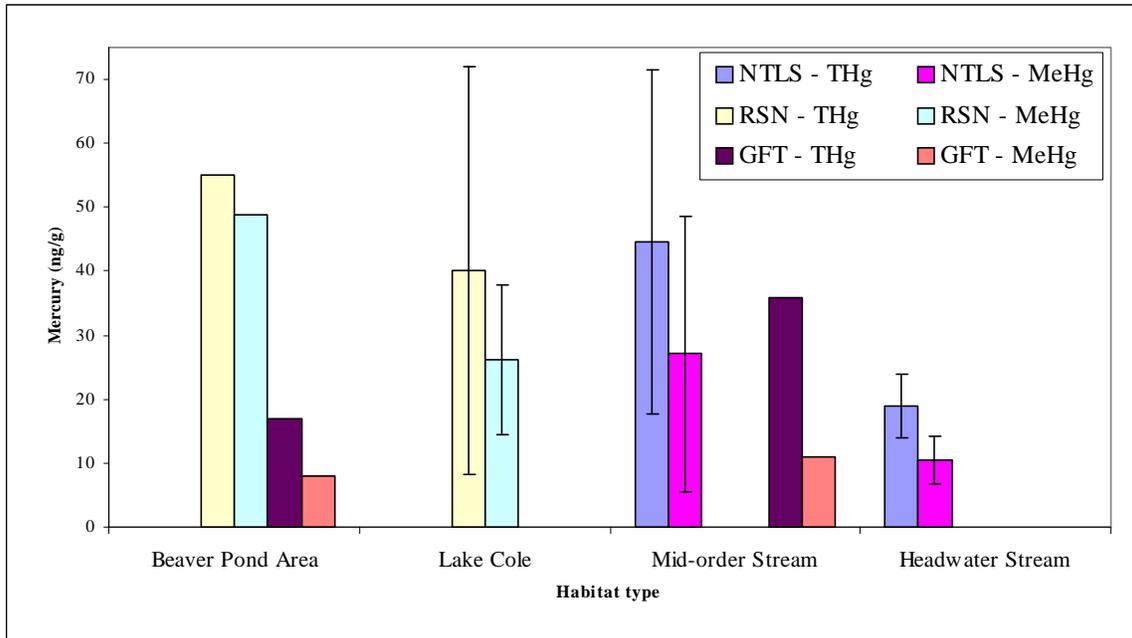


Figure 9. Mean total and methyl mercury concentrations in amphibians from the Neversink Reservoir watershed, 2003. NTLS = Northern two-lined salamander, RSN = Red-spotted newt, GFT = Green frog tadpole.

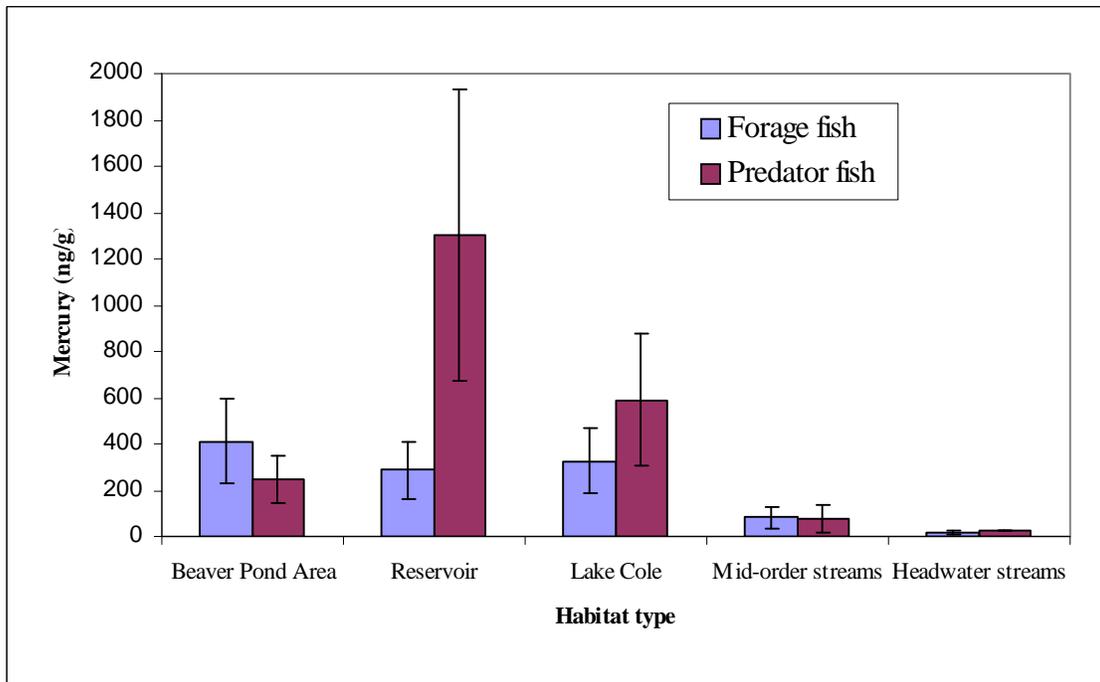


Figure 10. Mean mercury concentrations in forage and predator fish species in the Neversink Reservoir watershed, 2003.

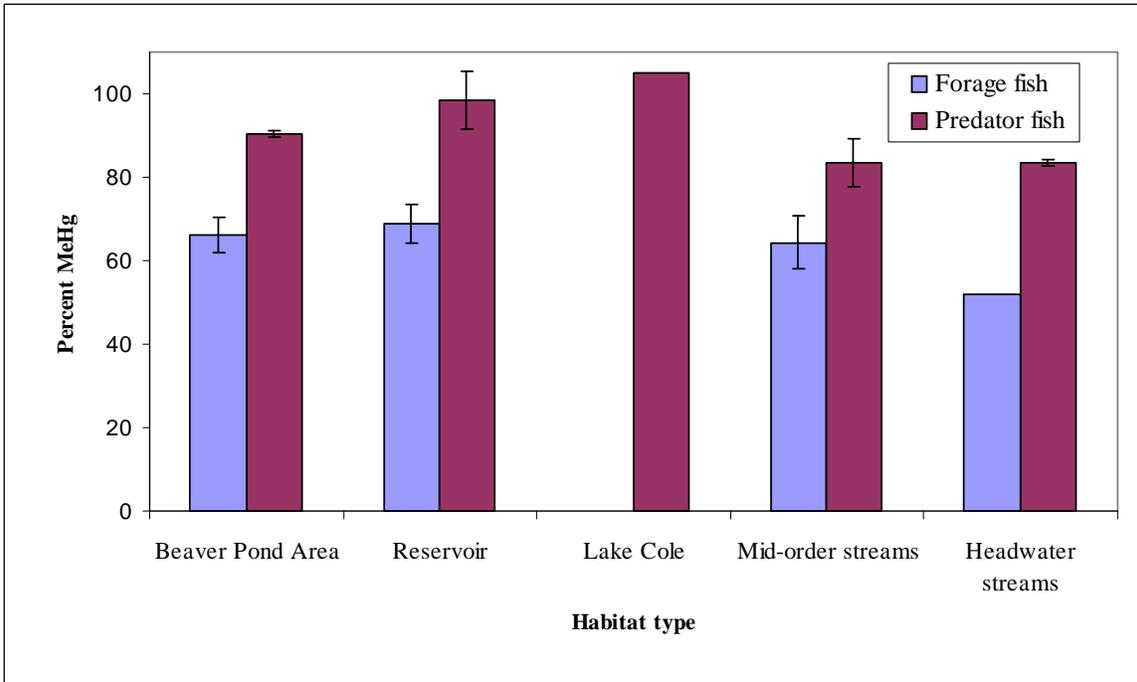


Figure 11. Percent methyl mercury (of total mercury) in forage and predator fish from the Neversink Reservoir watershed, 2003.

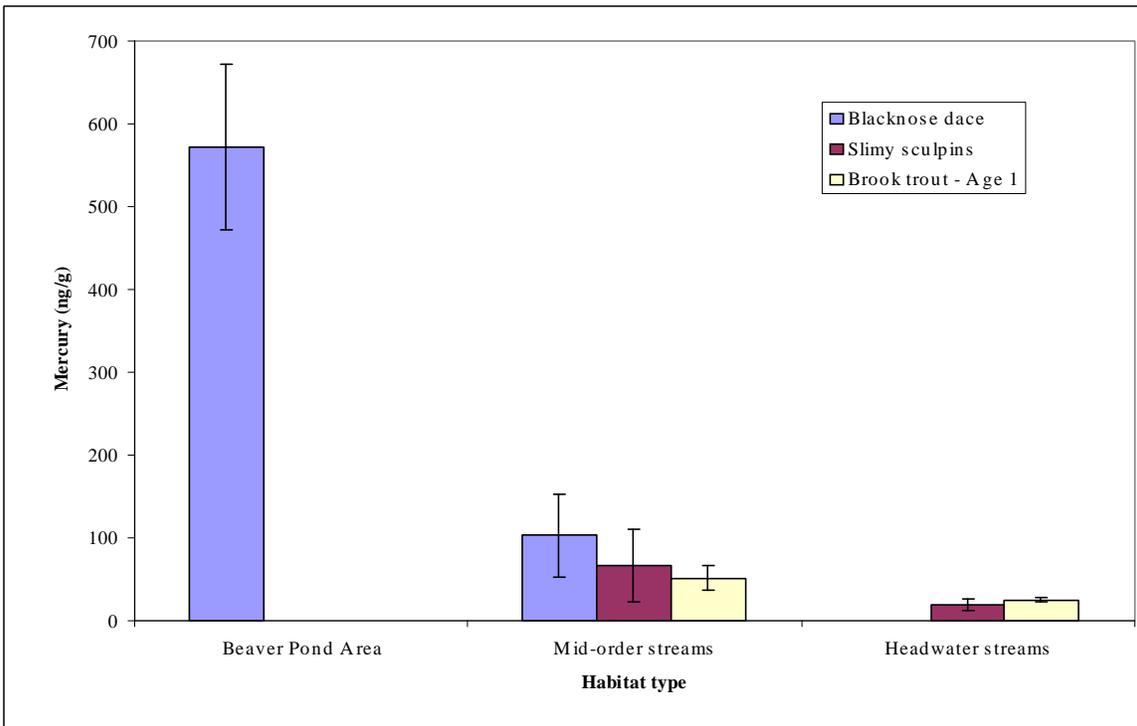


Figure 12. Mean mercury concentrations in similar-size blacknose dace (62 - 82 mm) and slimy sculpins (47 - 85 mm), and one-year-old brook trout from the Neversink Reservoir watershed, 2003.

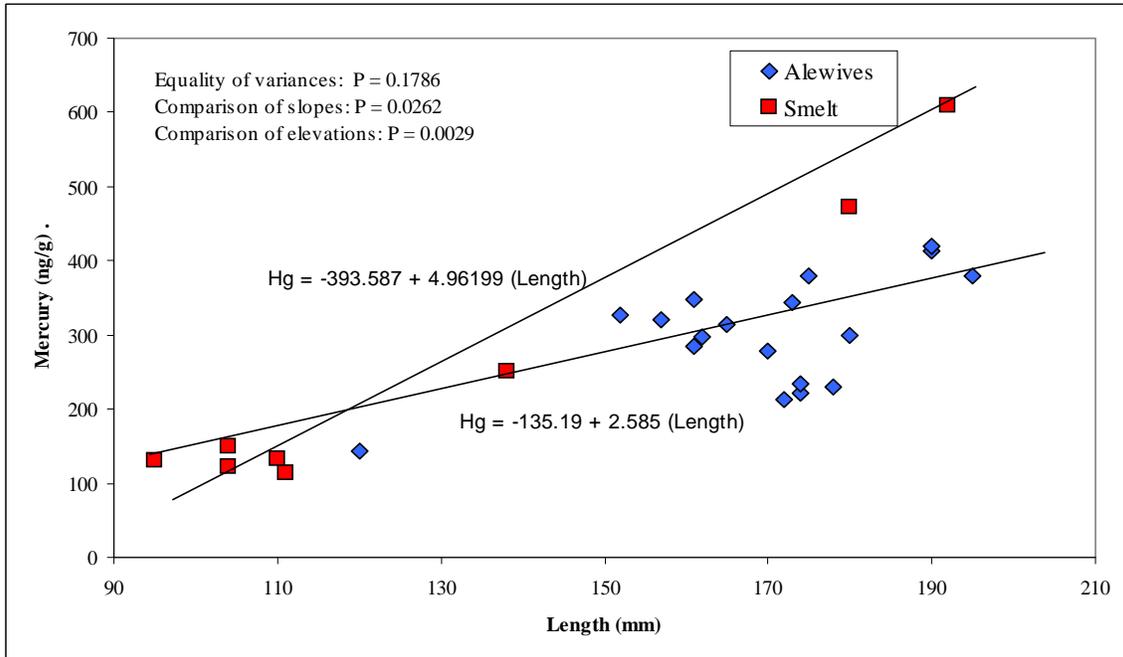


Figure 13. Total mercury concentration - fish length relationships for alewives (n = 18) and smelt (n = 8) from the Neversink Reservoir, 2003.

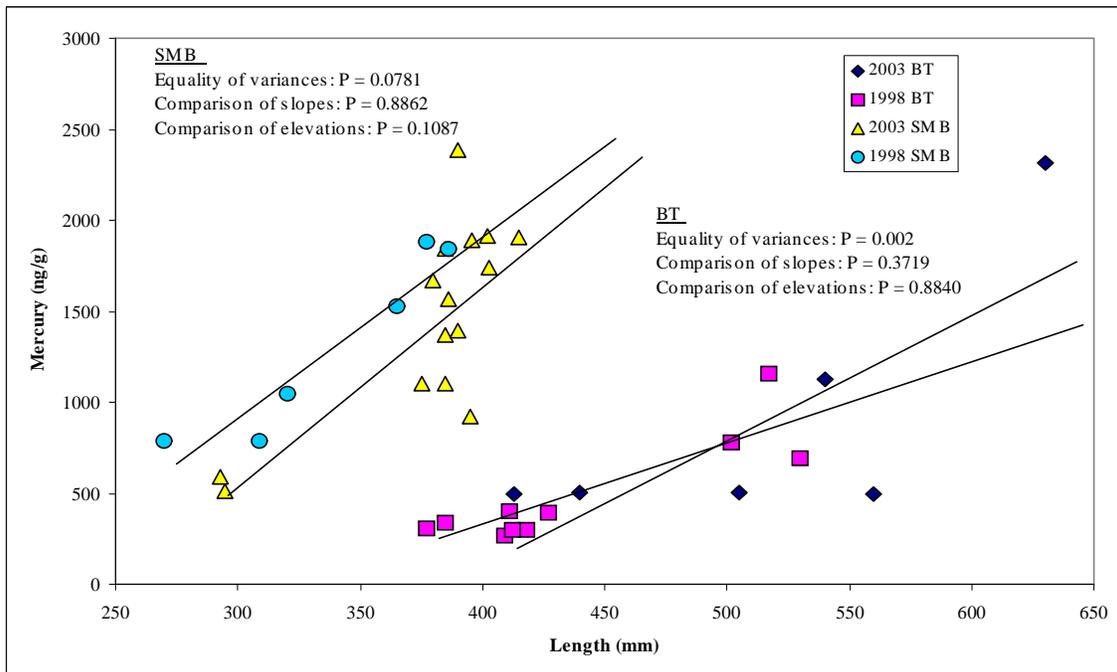


Figure 14. Total mercury concentration-fish length relationships for 1998 and 2003 smallmouth bass (SMB) and brown trout (BT) collections from the Neversink Reservoir.

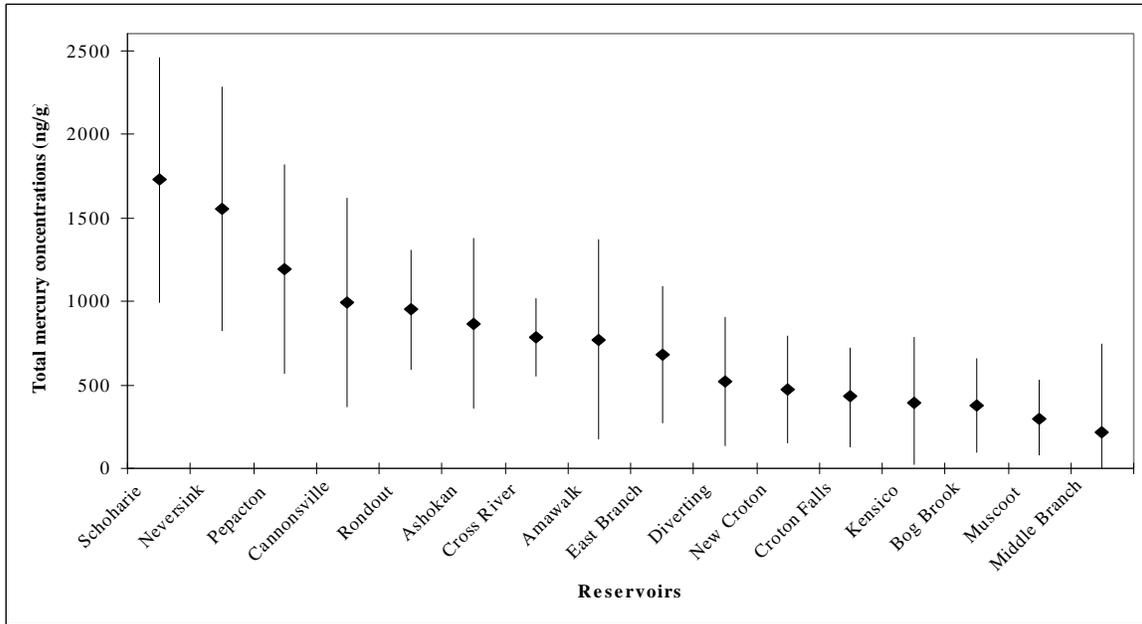


Figure 15. Predicted total mercury concentrations and 95% prediction intervals for 381 mm smallmouth bass throughout the NYC Reservoir system.

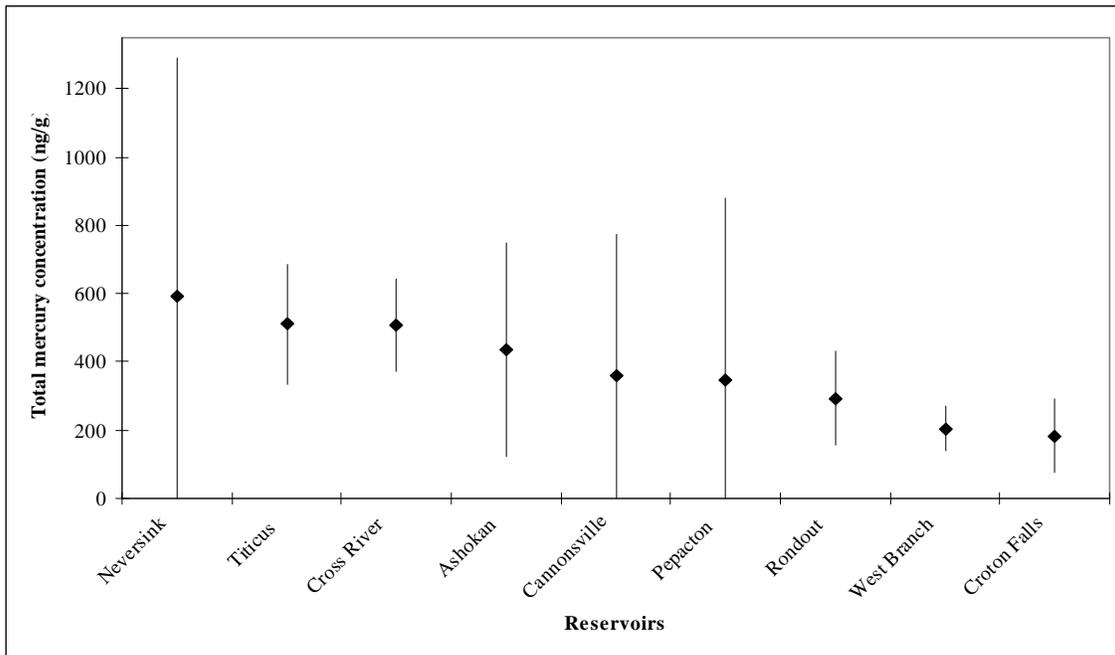


Figure 16. Predicted total mercury concentrations and 95% prediction intervals for 457 mm brown trout throughout the NYC Reservoir system.

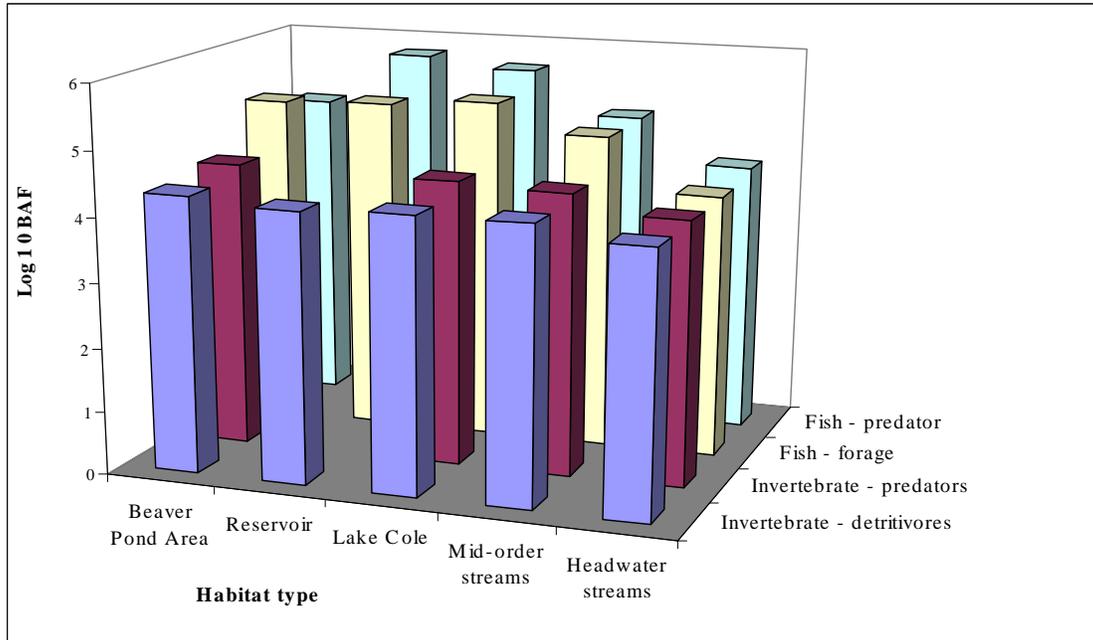


Figure 17. Bioaccumulation factors (log₁₀) between total mercury concentrations in water and biota in five aquatic habitat types in the Neversink Reservoir watershed.

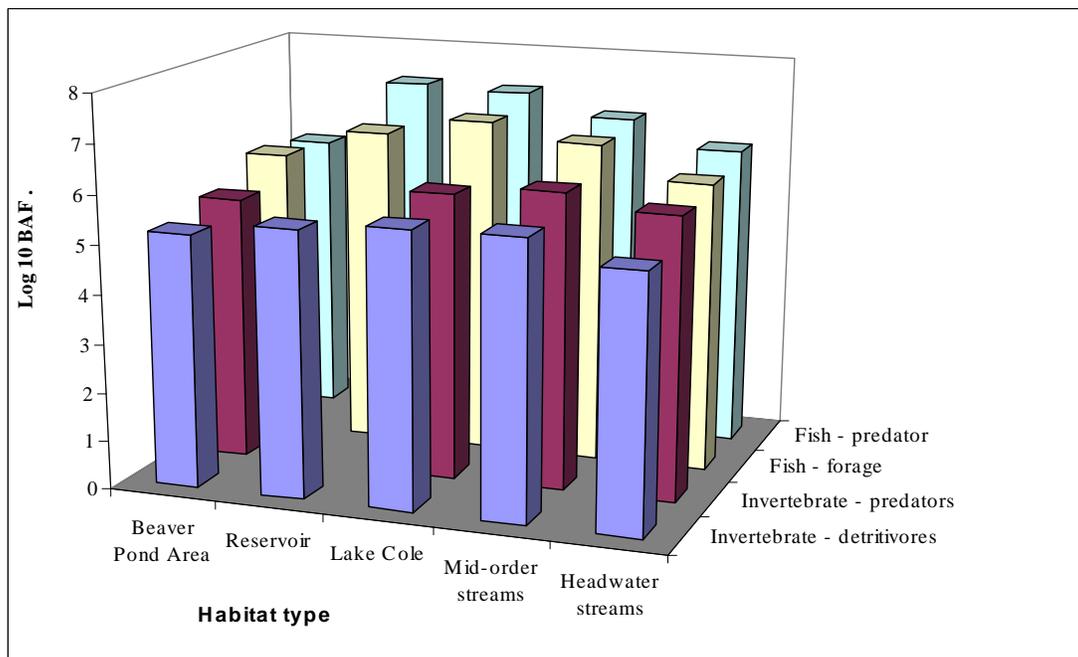


Figure 18. Bioaccumulation factors (log₁₀) between methyl mercury concentrations in water and biota in five aquatic habitat types in the Neversink Reservoir watershed.

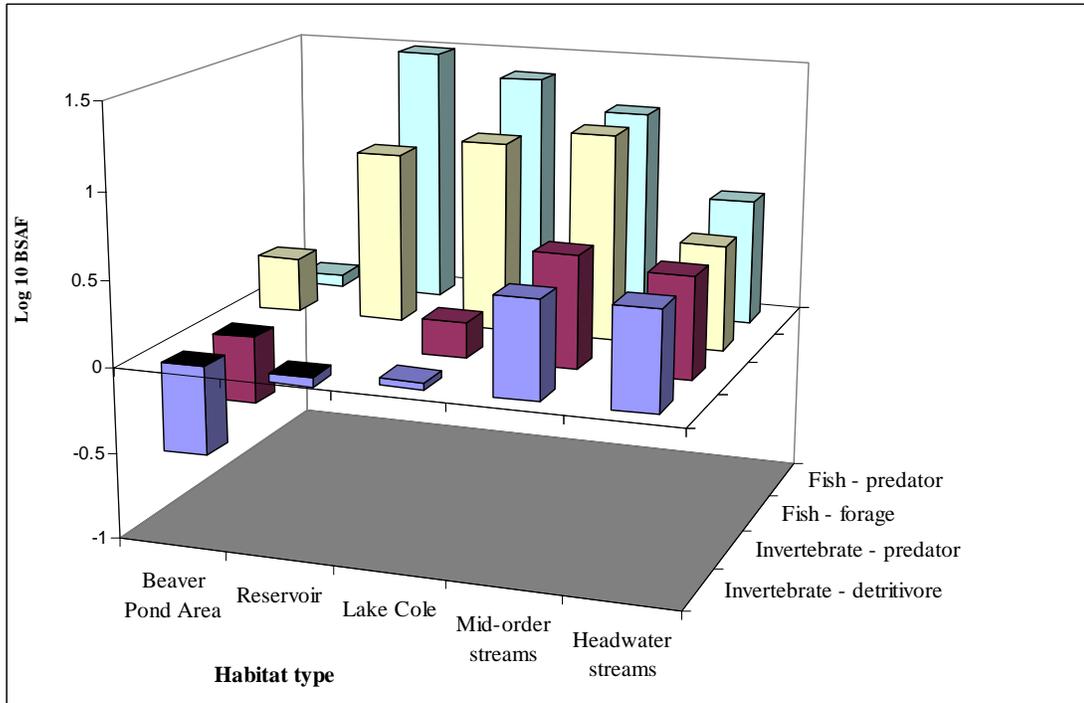


Figure 19. Bioaccumulation factors (log₁₀) between total mercury concentrations in sediment and biota in five aquatic habitat types in the Neversink Reservoir watershed.

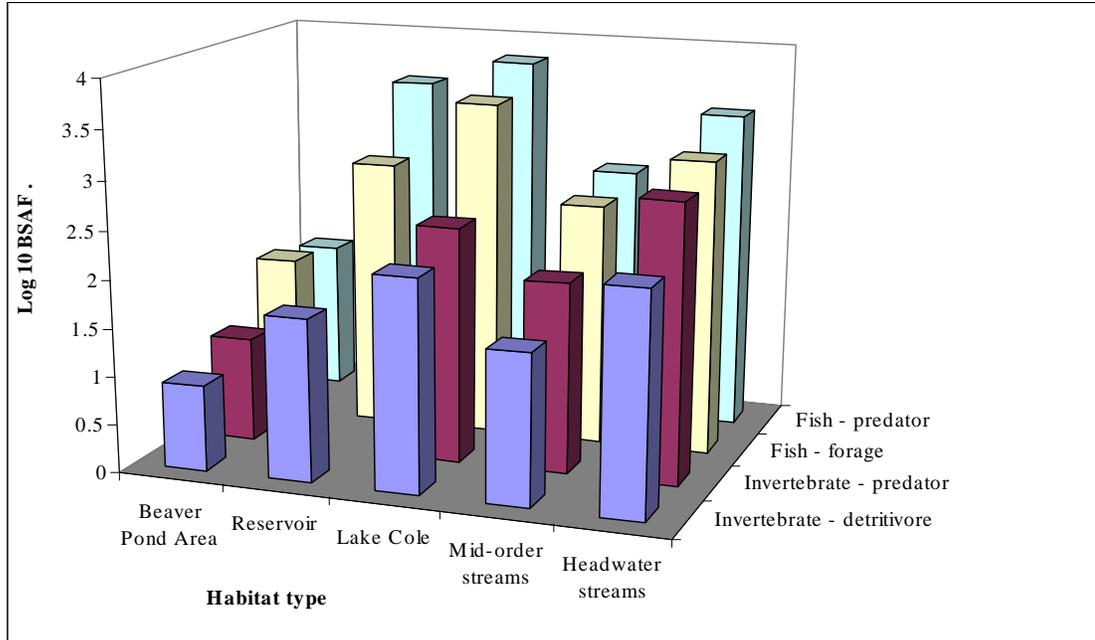


Figure 20. Bioaccumulation factors (log₁₀) between methyl mercury concentrations in sediment and biota in five aquatic habitat types in the Neversink Reservoir watershed.

APPENDICES

APPENDIX A. Standard NYSDEC fish handling and processing forms

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

GENERAL FISH COLLECTION PROCEDURES

- A. Following data are to be taken on each fish collected:
1. Date collected
 2. Species identification (please be explicit enough to enable assigning genus and species)
 3. Total length (nearest mm or smallest sub-unit on measuring instrument) and weight (nearest g or smallest sub-unit of weight on weighing instrument). Take all measures as soon as possible with calibrated, protected instruments (e.g. from wind and upsets) and prior to freezing.
 4. Method of collection (gill net, hook and line, etc.)
 5. Sample location (Waterway and nearest prominent identifiable landmark).
 6. Sex - fish may be cut enough to allow sexing, but do not eviscerate.
 7. Tag number (each specimen to be individually tagged, immediately upon collection, with jaw tag). Must be a unique number, NYSDEC can supply bags and tags, if necessary. For composites of small fish, double bag with tag inside bag. If compositing small fish, try to group similar species together.

Record length and weight as soon as possible after collection and before freezing. Other data are recorded in the field upon collection. An age determination of each fish is optional, but if done, it is recorded in the appropriate "Age" column.

The original of all collection record and continuity of evidence forms shall accompany delivery of fish to the lab. A copy shall be directed to Larry Skinner or Ron Sloan. All necessary forms will be supplied by the Bureau of Habitat.

Please submit photocopies of topographic maps or good-quality navigation charts indicating sampling locations. These records are of immense help to us (and hopefully you) in providing documented location records which are not dependent on memory and/or the same collection crew. In addition, they may be helpful for contaminant source trackdown and control efforts of the Department.

- B. Each fish to be wrapped in a plastic bag. The Bureau of Habitat will supply the bags.
- C. Groups of fish, by species, to be placed in one large plastic bag per sampling location. The Bureau of Habitat will supply the larger bags.
- D. Do not eviscerate.

- E. All fish must be kept at a temperature below 45 (degrees)F immediately following data processing AS soon as possible, freeze at 0 (degrees)F + 10 F. Due to occasional freezer failures, daily freezer temperature logs are required.
- F. Prior to any delivery of fish, coordinate delivery with, and send copies of the collection records, continuity of evidence forms, and freezer temperature logs, to:

Larry Skinner or Ron Sloan
Bureau of Habitat
625 Broadway
Albany, New-York 12233-4756

Samples will then be directed to:

The analytical facility and personnel noted on specific project descriptions.

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

I, _____, of _____ have collected the following
 (Print Name) (Print Address)
 on _____, 20____ from _____ in the vicinity of
 _____ Town of _____, _____ County.

Item(s): _____

said sample(s) were in my possession and handled according to standard procedures provided to me prior to collection. The sample(s) were placed in the custody of a representative of the New York State Department of Environmental Conservation on _____, 20____.

I, _____, have received the above mentioned same(s) on the date specified and have assigned identification number(s) _____ to the sample(s). I have recorded pertinent data for the sample(s) on the attached collection records. The sample(s) remained in my custody until subsequently transferred, prepared or shipped at times and data as attested to below.

Signature Date

<u>SECOND RECIPIENT (Print Name)</u>	<u>TIME & DATE</u>	<u>PURPOSE OF TRANSFER</u>
<u>SIGNATURE</u>	<u>UNIT</u>	
<u>THIRD RECIPIENT (Print Name)</u>	<u>TIME & DATE</u>	<u>PURPOSE OF TRANSFER</u>
<u>SIGNATURE</u>	<u>UNIT</u>	
<u>FOURTH RECIPIENT (Print Name)</u>	<u>TIME & DATE</u>	<u>PURPOSE OF TRANSFER</u>
<u>SIGNATURE</u>	<u>UNIT</u>	
<u>RECEIVED IN LABORATORY BY (Print Name)</u>		<u>TIME & DATE</u>
<u>SIGNATURE</u>	<u>UNIT</u>	
<u>LOGGED IN BY (Print Name)</u>	<u>TIME & DATE</u>	<u>ACCESSION NUMBERS</u>
<u>SIGNATURE</u>	<u>UNIT</u>	

NOTICE OF WARRANTY

By signature to the chain of custody (reverse) , the signator warrants that the information provided is truthful and accurate to the best of his/her* ability. The signator affirms that he/she is willing to testify to those facts provided and the circumstances surrounding same. Nothing in this warranty or chain of custody negates responsibility nor liability of the signators for the truthfulness and accuracy of the statements provided.

HANDLING INSTRUCTIONS

On day of collection, collector(s) name(s), address(es), date, geographic location of capture (attach a copy of topographic map or navigation chart), species, number kept of each species, and description of capture vicinity (proper noun, if possible) along with name of Town and County must be indicated on reverse.

Retain organisms in manila tagged plastic bags to avoid mixing capture locations. Note appropriate information on each bag tag.

Keep samples as cool as possible. Put on ice if fish cannot be frozen within 12 hours. If fish are held more than 24 hours without freezing, they will not be retained or analyzed.

Initial recipient (either DEC or designated agent) of samples from collector(s) is responsible for obtaining and recording information on the collection record forms which will accompany the chain of custody. This person will seal the container using packing tape and writing his signature, time and date across the tape onto the container with indelible marker. Any time a seal is broken, for whatever purpose, the incident must be recorded on the Chain of Custody (reason, time and date) in the purpose of transfer block container then is resealed using new tape and rewriting signature, with time and date.

**NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION
BUREAU OF HABITAT**

FISH PREPARATION PROCEDURES FOR CONTAMINANT ANALYSIS

Background

New York State Department of Environmental Conservation (DEC) conducts studies requiring chemical analysis on fish tissues. Routine monitoring and surveillance studies develop data on contaminants in fish for several reasons:

1. To identify sources of environmental contamination;
2. To identify the geographic extent of environmental contamination;
3. To identify temporal trends of contaminants in fish and wildlife; and
4. To provide information regarding human consumption advisories.

Chemical analyses of edible-fish flesh have been determined to be the most appropriate analyses for satisfying all of these objectives. The following methodology has been developed in order to standardize the tissues under analysis and to adequately represent the contaminant levels of fish flesh. The methodology is slightly modified from the U.S. Food and Drug Administration procedures. The portion of edible flesh analyzed will be referred to as the standard fillet unless otherwise noted. For some species, the procedure is modified as indicated below.

Procedures for Standard Filleting

1. Remove scales from fish. Do not remove the skin.
2. Make a cut along the ventral midline of the fish from the vent to the base of the jaw.
3. Make diagonal cut from base of cranium following just behind gill to the ventral side just behind pectoral fin.
4. Remove the flesh and ribcage from one-half of the fish by cutting from the cranium along the spine and dorsal rays to the caudal fin. The ribs should remain on the fillet.
5. Score the skin and homogenize the entire fillet.

Modifications to Standard Fillet

Four modifications of the standard fillet procedure are designed to account for variations in fish size or known preferred preparation-methods of the fish for human consumption.

1. Some fish are too small to fillet by the above procedure. Fish less than approximately 6 inches long and rainbow smelt are prepared by cutting the head off from behind the pectoral fin and eviscerating the fish. Ensure that the belly flap is retained on the carcass to be analyzed. When this modification is used, it should be noted when reporting analytical results.
2. Some species are generally eaten by skinning the fish. The skin from these species is also relatively difficult to homogenize in the sample. Hence, for the following list of species, the fish is first skinned prior to filleting:

Brown bullhead	White catfish
Yellow bullhead	Channel catfish
Atlantic sturgeon	Lake sturgeon
Black bullhead	
3. American eel are analyzed by removing the head, skin, and viscera; filleting is not attempted.
4. Forage fish and young-of-year fish are analyzed whole. This category is considered to be less than 150mm (6 inches).

APPENDIX B. Quality assurance/Quality Control Results

Appendix B-1. Summary of quality control results for analysis of total mercury in biota from the Neversink Reservoir watershed, 2003.

QC sample type	Units	n	Mean ± SD	Range
Method blanks	ng/g	13	< 0.5	<0.5
Calibration standards	% recovery	11	97.7 ± 5.9	88.8 - 107.5
Check standards	% recovery	10	96.4 ± 6.1	85.7 - 104.5
Reference materials	% recovery	7	94.3 ± 3.6	89.5 - 99.3
Sample Duplicates	RPD	18	4.9 ± 5.1	0.3 - 18.7

Appendix B-2. Summary of quality control results for analysis of methyl mercury in biota from the Neversink Reservoir watershed, 2003.

QC sample type	Units	n	Mean ± SD	Range
Method blanks	ng/g	8	< 0.1	<0.1
Calibration standards	% recovery	8	97.4 ± 10.2	86.0 - 114.3
Check standards	% recovery	8	96.8 ± 9.2	83.6 - 108.8
Reference materials	% recovery	4	100.0 ± 1.4	98.2 - 101.5
Sample Duplicates	RPD	12	14.5 ± 16.0	0.5 - 51.5

Appendix B-3. Summary of quality control results for analysis of total and methyl mercury in sediments from the Neversink Reservoir watershed, 2003.

QC sample type	Units	n	Mean \pm SD	Range
Calibration standards	% recovery	2	100.1	94.8 - 105.4
Check standards	% recovery	4	94.3 \pm 3.3	89.7 - 97.2
Reference materials	% recovery	4	99.3 \pm 7.2	90.3 - 107.8
Sample Duplicates	RPD	3	3.4 \pm 3.2	1.2 - 7.1

Appendix B-4. Summary of quality control results for analysis of total and methyl mercury in water from the Neversink Reservoir watershed, 2003.

QC sample type	Units	n	Mean \pm SD	Range
Calibration standards	% recovery	8	99.2 \pm 5.6	91.4 - 108.4
Check standards	% recovery	12	101.8 \pm 8.8	89.4 - 113.0
Reference materials	% recovery	8	101.5 \pm 4.5	94.2 - 108.5
Sample Duplicates	RPD	7	4.9 \pm 3.0	0.0 - 8.1

APPENDIX C. Data Summaries

Appendix C-1. Total and methyl mercury concentrations (ng/L) in water samples from the Neversink Reservoir watershed, 2003.

Site	June	August	September	November
Reservoir (site 1: 0.5 m ¹)	-	-	-	1.05 (0.027)
Reservoir (site 1: 5 m)	-	1.10 (0.063)	1.29 (0.108)	-
Reservoir (site 1: 30 m)	-	1.39 (<0.025)	0.77 (0.061)	-
Reservoir (site 2: 5m)	4.50 (<0.025)	1.02 (0.058)	1.15 (0.091)	-
Reservoir (site 2: 15 m)	-	-	-	1.87 (0.050)
Reservoir (site 2: 40 m)	3.07 (<0.025)	1.47 (<0.025)	1.36 (0.032)	1.18 (0.044)
Reservoir (site 3: 0.5 m)	2.31 (<0.025)	-	-	1.19 (<0.025)
Reservoir (site 3: 5 m)	-	1.45 (0.080)	1.60 (0.070)	-
Reservoir (site 3: 32 m)	-	1.20 (0.048)	1.04 (0.044)	-
Reservoir (site 4: 0.5 m)	-	-	-	1.37 (0.035)
Reservoir (site 4: 5 m)	-	2.00 (0.111)	0.91 (0.067)	-
Lake Cole	1.17 (<0.025)	-	-	1.65 (0.061)
Beaver Pond	2.73 (0.35)	-	-	-
Beaver Pond Outlet	3.35 (0.28)	-	-	1.53 (0.118)
Claryville ²	1.17 (<0.025)	-	-	1.14 (<0.025)
Aden Brook ²	0.70 (<0.025)	-	-	0.80 (<0.025)
Main Branch ²	1.00 (<0.025)	-	-	0.89 (<0.025)
Biscuit Brook ³	1.16 (<0.025)	-	-	1.47 (<0.025)
Winnisook ³	1.51 (<0.025)	-	-	1.23 (<0.025)
Tison ³	1.74 (<0.025)	-	-	1.34 (<0.025)

¹ Sampling depth

² Mid-order stream

³ Headwater stream

Appendix C-2. Total and methyl mercury results from Neversink Reservoir watershed sediment samples (ng/g, dry weight), 2003.

Location	Total Mercury	Methyl Mercury	Total Solids (%)
Reservoir (site 1)	17.5	0.2	66.6
Reservoir (site 2)	62.2	0.3	40.1
Reservoir (site 3)	21.2	0.2	64.5
Reservoir (site 4)	42.7	0.8	43.7
Reservoir (site 5)	17.9	0.3	72.5
Reservoir (site 6)	6.6	0.1	73.4
Lake Cole	24.4	0.1	56.6
Beaver Pond	187	5.5	9.3
Aden Brook ¹	6	0.3	71.2
Main Branch ¹	2.4	0.1	87.7
West Branch ¹	10.3	0.3	63.8
East Branch ¹	3.7	<0.02	74.2
Claryville ¹	3.4	0.1	76
Biscuit Brook ²	3.5	<0.02	76.1
Winisook ²	8	<0.02	81.2
Tison ²	2.3	<0.02	77.3

¹ Mid-order stream

² Headwater stream

Appendix C-3. Total and methyl mercury concentrations (ng/g) in macroinvertebrates from the Neversink Reservoir watershed, June 2003.

Site	Family	Common name	Trophic level	MeHg	THg
Reservoir	Siphonuridae	primitive minnow mayflies	detritivore	32.8	47.5
	Limnephilidae	n. case maker caddisflies	detritivore	6.5	24.2
	Siphonuridae	primitive minnow mayflies	detritivore	10.1	19.4
	Asellidae	aquatic sow bugs	detritivore	8.9	13.6
Lake Cole	Cambaridae	crayfish	detritivore	34.6	72.9
	Cambaridae	crayfish	detritivore	16.3	26.6
	Gomphidae	clubtail dragonflies	predator	31.8	43.2
	Macrимиidae	cruiser dragonflies	predator	24.3	36.5
Beaver Pond Area	Aeshnidae	darner dragonflies	predator	62.2	68.3
	Gomphidae	clubtail dragonflies	predator	36.8	42.3
	Coenagrionidae	narrowwinged damselflies	predator	30.3	39
	Aeshnidae	darner dragonflies	predator	111.6	119.3
	Tipulidae	crane flies	detritivore	16.3	27.2
	Corydalidae	dobsonflies	predator	65.7	82.2
	Asellidae	aquatic sow bugs	detritivore	12.3	18.7
	Cambaridae	crayfish	detritivore	76.3	83.6
	Limnephilidae	n. case maker caddisflies	detritivore	61.4	74.1
	Hydropsychidae	netspinner caddisflies	detritivore	44	56.4
Aden Brook ¹	Hydropsychidae	netspinner caddisflies	detritivore	4.1	17.5
	Limnephilidae	n. casemaker caddisflies	detritivore	1.1	10.9
	Heptageniidae	flatheaded mayflies	detritivore	2.6	20.3
	Perlidae	common stoneflies	predator	10	16.8
	Cambaridae	crayfish	detritivore	16.1	21.9
	Tipulidae	crane flies	detritivore	13.4	21.7
	Tipulidae	crane flies	detritivore	1.1	9
Main Branch ¹	Limnephilidae	n. casemaker caddisflies	detritivore	3.2	16.5
	Aeshnidae	darner dragonflies	predator	16.4	24.7

Appendix C-3. Continued.

Site	Family	Common name	Trophic level	MeHg	THg
Claryville ¹	Tipulidae	crane flies	detritivore	20.9	30.7
	Cambaridae	crayfish	detritivore	18.1	22.3
	Heptageniidae	flatheaded mayflies	detritivore	3.8	30
	Limnephilidae	n. casemaker caddisflies	detritivore	3.2	19.7
Biscuit Brook ²	Heptageniidae	flatheaded mayflies	detritivore	1.6	19.1
	Ephemerellidae	spiny crawler mayflies	detritivore	2.1	17.9
	Gomphidae	clubtail dragonflies	predator	14.8	29.7
	Tipulidae	crane flies	predator	10.1	367.6
	Limnephilidae	n. casemaker caddisflies	detritivore	2.4	17.1
Winnisook ²	Perlodidae	perlodid stoneflies	predator	2.8	10.3
	Heptageniidae	flatheaded mayflies	detritivore	2	16.8
Tison ²	Perlodidae	perlodid stoneflies	predator	7.3	14.9
	Rhyacophilidae	freeliving caddisflies	predator	5.9	18.4
	Heptageniidae	flatheaded mayflies	detritivore	2.1	12.9

¹ Mid-order stream

² Headwater stream

³ Sample considered an outlier and removed from analyses

Appendix C-4. Summary Hg data (ng/g) for macroinvertebrates and amphibians from the upper Neversink Reservoir Watershed, 2003.

Group	Variable	N	Mean	SD	Minimum	Maximum
Odonata (Dragonflies)	MeHg	8	41	32	15	112
	THg		50	31	25	119
	%MeHg		76	15	50	93
Ephemeroptera (Mayflies)	MeHg	8	7	11	2	33
	THg		23	11	13	47
	%MeHg		24	23	9	69
Diptera (True Flies)	MeHg	5	12	7	1	21
	THg		91	154	9	368
	%MeHg		41	31	3	68
Trichoptera (Caddisflies)	MeHg	9	15	22	1	61
	THg		28	22	11	74
	%MeHg		34	27	10	83
Decapoda (Crayfish)	MeHg	4	32	30	16	76
	THg		39	30	22	84
	%MeHg		77	13	61	91
Megaloptera (Dobsonflies)	MeHg	1	66			
	THg		82			
	%MeHg		80			
Isopoda (Aquatic sowbugs)	MeHg	2	11	2	9	12
	THg		16	4	14	19
	%MeHg		66	1	65	66
Plecoptera (Stoneflies)	MeHg	3	7	4	3	10
	THg		14	3	10	17
	%MeHg		45	16	28	60
Northern two-lined salamander	MeHg	8	21	18	5	56
	THg		35	24	13	71
	%MeHg		56	22	22	83
Red-spotted newt	MeHg	3	34	20	12	49
	THg		45	24	18	63
	%MeHg		59	34	22	88
Green frog tadpole	MeHg	2	9	2	8	11
	THg		26	13	17	36
	%MeHg		39	12	30	47

Appendix C-5. Mercury concentrations (ng/g) in amphibians in the Neversink Reservoir Watershed, 2003.

Site	Species	N	MeHg	THg	%MeHg
Lake Cole	Red-spotted newt	2 ¹	26.2	40.1	65.7
Beaver Pond	Green frog tadpole	1	8	17	47.3
	Red-spotted newt	1	48.8	55.1	88.5
Aden Brook ²	Northern two-lined salamander	2 ¹	23.6	30.4	70.3
Claryville ²	Northern two-lined salamander	2 ¹	16.2	45.8	30.9
Main Branch ²	Northern two-lined salamander	1	55.6	70.9	78.4
	Green frog tadpole	1	10.9	35.8	30.4
Tison ³	Northern two-lined salamander	2 ¹	8.9	19.3	45.8
Winnisook ³	Northern two-lined salamander	1	13.6	18.1	75.4

¹ Mean concentrations

² Mid-order stream

³ Headwater stream

Appendix C-6. Mercury concentrations (ng/g) in fish from the Neversink Reservoir watershed, 2003.

Site	Species	N ¹	Length (mm) ²	Weight (g) ²	Total Mercury ²
Reservoir	Alewife	18	169 ± 17 120 - 195	36 ± 10 14 - 61	303 ± 74 143 - 420
	Smelt	8	129 ± 37 95 - 192	13 ± 12 5 - 32	248 ± 189 114 - 608
	Brown trout	6	515 ± 80 413 - 630	1672 ± 818 634 - 2800	910 ± 734 498 - 2318
	Smallmouth bass	15	378 ± 36 293 - 415	652 ± 209 220 - 920	1460 ± 531 514 - 2386
Lake Cole	Pumpkinseed	5	153 ± 38 94 - 186	77 ± 49 13 - 126	325 ± 140 161 - 510
	Smallmouth bass	5	278 ± 46 218 - 335	235 ± 105 105 - 355	591 ± 285 315 - 939
Beaver Pond Area	Blacknose dace	5	75 ± 8 65 - 86	4 ± 2 2 - 6	572 ± 100 428 - 705
	Golden shiner	5	112 ± 19 82 - 130	14 ± 7 5 - 24	253 ± 68 161 - 348
	Brown trout	2	162 155 - 168	40 33 - 46	146 87 - 206
	Brook trout	3	310 ± 14 295 - 322	312 ± 22 291 - 335	315 ± 28 286 - 342
Aden Brook ³	Blacknose dace	5	67 ± 4 62 - 73	2 ± 1 2 - 4	58 ± 16 44 - 82
	Slimy sculpin	5	68 ± 8 58 - 75	3 ± 1 2 - 4	33 ± 5 27 - 36
	Brook trout	5	183 ± 66 125 - 285	78 ± 85 18 - 221	115 ± 93 32 - 232
Main Branch ³	Blacknose dace	5	77 ± 3 75 - 82	4 ± 1 4 - 5	149 ± 18 137 - 178
	Slimy sculpin	5	72 ± 15 50 - 85	4 ± 2 1 - 6	80 ± 59 29 - 179
	Brook trout	5	146 ± 18 120 - 170	29 ± 10 14 - 43	45 ± 6 39 - 54
Claryville ³	Slimy sculpin	5	72 ± 10 60 - 83	4 ± 2 2 - 6	85 ± 37 48 - 127
	Brook trout	5	136 ± 30 97 - 170	25 ± 16 8 - 46	64 ± 17 45 - 87
Biscuit Brook ⁴	Slimy sculpin	5	59 ± 13 47 - 75	2 ± 2 1 - 5	19 ± 7 11 - 18

Appendix C-6. Continued.

Site	Species	N ¹	Length (mm) ²	Weight (g) ²	Total Mercury ²
Biscuit Brook ⁴	Brook trout	5	117 ± 12 105 - 132	16 ± 5 11 - 21	25 ± 3 23 - 29
Tison ⁴	Brook trout	2	101 96 - 105	10 8 - 11	25 23 - 27

¹ N = Number of fish analyzed as individual samples.

² Values given are the mean ± standard deviation; minimum and maximum values are reported on the second line.

³ Mid-order stream

⁴ Headwater stream