Increased mercury bioaccumulation following water quality improvement.

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ABSTRACT

Changes in physical and chemical characteristics of aquatic habitats made to reduce or eliminate ecological risks can sometimes have unforeseen consequences. Environmental management activities on the U.S. Dept. of Energy reservation in Oak Ridge, Tennessee, have succeeded in improving water quality in streams impacted by discharges from industrial facilities and waste disposal sites. The diversity and abundance of pollution-

improved after new waste treatment systems or remedial actions reduced inputs of various toxic chemicals. Two of the streams were known to be mercury-contaminated from historical spills and waste disposal practices. Waterborne mercury concentrations in the third were typical of uncontaminated systems. In each case, concentrations of mercury in fish, or the apparent biological availability of mercury increased over the period during which ecological metrics indicated improved water quality. In the system where waterborne mercury concentrations were at background levels, increased mercury bioaccumulation was probably a result of reduced aqueous selenium concentrations; however, the mechanisms for increased mercury accumulation in the other two streams remain under investigation. In each of the three systems, reduced inputs of metals and inorganic anions was followed by improvements in the health of aquatic invertebrate communities. However, this reduction in risk to aquatic invertebrates was accompanied by increased risk to humans and piscivorous wildlife related to increased mercury concentrations in fish.

INTRODUCTION

Changes in physical and chemical characteristics of aquatic habitats made to reduce or eliminate ecological risks can sometimes have unforeseen consequences. In some cases, reduction of one ecological risk may be accompanied by increases in another. Environmental management activities on the U.S. Dept. of Energy reservation in Oak Ridge, Tennessee, have succeeded in improving water quality and ecological

effects on the bioaccumulation of mercury in aquatic ecosystems.

METHODS

Ecological conditions in streams receiving National Pollution Discharge Elimination System (NPDES)-regulated discharges from U.S. Dept. of Energy facilities in Oak Ridge, TN have been monitored regularly since the mid 1980's as a requirement of the NPDES permits for those facilities. That monitoring includes measurements of contaminant accumulation in fish and other aquatic life, as well as measures of the health of the fish and benthic invertebrate communities. Detailed methods of those investigations are presented in references (1-4)). Mercury was measured in muscle tissue of individual redbreast sunfish (*Lepomis auritus*), rock bass (*Ambloplites rupestris*) and largemouth bass (*Micropterus salmoides*) at regular intervals (yearly or twice yearly) in collections of six or eight fish per site, using acid digestion and cold vapor atomic absorption spectrophotometry. Structural indices of the integrity of the benthic invertebrate fauna were used to infer temporal trends in general water quality at each site. Multiple quantitative benthic samples were taken from riffle habitat at each site using a 0.09 m^2 Surber sampler. Three samples were taken at each site, twice yearly. Invertebrates were sorted from each sample, then counted and identified to the lowest practical taxonomic level (usually genus). Similar samples were taken from a wide array of reference sites. These represented similar habitats in local streams assumed to be relatively unimpacted by chemical discharges. Taxonomic richness of the total invertebrate fauna and the pollution sensitive components of the fauna at sites affected by the industrial facilities were compared with the range of those metrics observed in the reference sites.

CASE HISTORIES

Rogers Quarry

An abandoned quarry in the McCoy Branch watershed was used for disposal of slurried fly ash until 1989. Elevated concentrations of selenium, arsenic, and suspended solids characterized water quality in McCoy Branch during that time (5), and the aquatic fauna of the stream was severely impacted. After fly ash discharge to the stream and quarry stopped, the decimated aquatic invertebrate community recovered rapidly (Figure 1). Malformed bass, common in the quarry in 1990 and 1991, disappeared by 1993 and were replaced by a robust population of healthy individuals with growth rates typical of bass from lakes in this region. The bony tissue malformations observed in bass from this site were typical of malformations observed in fish from other selenium-contaminated waters (6,7).

Selenium concentrations in largemouth bass from Rogers Quarry decreased in response to lower concentrations in water, but mercury concentrations in bass have increased steadily since 1990. In 1990, mercury averaged (± SE) 0.014 ± 0.002 μg/g wet weight in bass, but by 1998 the mean concentration was 0.73 ± 0.07 μg/g wet weight, a fifty-fold increase.

The mercury concentration in Rogers Quarry water is typical of uncontaminated waters in east Tennessee. Mercury concentrations in bass from the quarry in 1990 were much lower than is typical of this species in streams and reservoirs in this region. Increased mercury bioaccumulation probably was a response to reduced selenium inputs. Selenium is well known to inhibit the toxicity and bioaccumulation of mercury in fish (8) and the increasing trend in mercury in fish may represent a return to 'normal' for an unexploited population in an oligotrophic quarry.

East Fork Poplar Creek

East Fork Poplar Creek originates within the storm drain network of a U.S Department of Energy industrial facility and is contaminated with mercury as a result of losses and spills that occurred more than thirty years ago. Aqueous mercury concentrations are typically around 500 ng/L in the upper third of the stream, and mercury accumulation in fish is a concern throughout its 25 km length (9). New waste treatment facilities, dechlorination of process water discharges, and the addition of water from a nearby reservoir to maintain stable baseflow have improved general water quality in East Fork Poplar Creek. Releases of mercury have also been curtailed by the remediation of sources within the facility.

The invertebrate communities in East Fork Poplar Creek provide clear evidence of improved water quality over time (Figure 2, but remain in poor condition relative to reference sites. The numbers of taxa of all benthic invertebrates have nearly tripled in response to those actions, but are less than 50 % of the value typical of reference streams. Pollution sensitive taxa (mayflies, stoneflies, and caddisflies), which were virtually absent in this system prior to 1989, have increased in numbers but remain at a small fraction of the value (15 to 25 taxa per sample) typical of unpolluted streams in this region. Possible causes of the continued impacts to the aquatic community include nutrient enrichment, metals, and elevated temperatures.

Although water quality has improved, the biological availability of mercury in East Fork Poplar Creek water, indexed by bioaccumulation factor, has increased over this period. (Bioaccumulation factor is the ratio of the concentration of a chemical or element, in this case mercury , in fish to the concentration of the same substance in the water of its habitat. It is a field-measured parameter, and incorporates the pathways of direct uptake [illegible] bioaccumulation factor, the greater the biological availability of the chemical in that ecosystem.

Bioaccumulation factors for mercury in redbreast sunfish in East Fork Poplar Creek near the industrial facility have increased approximately three-fold over the past ten years (Figure 3) as water quality at the site has improved. Most of this change has been a result of decreasing aqueous total mercury concentrations while mercury concentrations in fish have declined only slightly (4). The current bioaccumulation factor, 1200, is much lower than values typical for redbreast sunfish in either uncontaminated streams (~30,000) or

other streams (5,000 to 60,000) contaminated by industrial sources (10). Thus, bioavailability of mercury in East Fork Poplar Creek is low in comparison to other mercury-contaminated sites as well as to uncontaminated sites. If improved water quality is responsible for the increase in bioavailability of mercury in East Fork Poplar Creek since 1989, further improvements in water quality may exacerbate the mercury bioaccumulation problem or render mercury source control efforts ineffective.

Bear Creek

The headwaters of Bear Creek are contaminated by a groundwater plume high in dissolved salts that originated from the disposal of acid wastes in unlined ponds. Aqueous mercury concentrations in Bear Creek headwaters (15 - 35 ng/L) are 5 - 10 fold higher than uncontaminated streams in this region, but dilution reduces mercury concentrations to within background ranges in the lower reaches of the creek, 12 km downstream. Closure and remediation of the pond site in the mid 1980's was followed by a gradual decrease in dissolved metal concentrations and improvement in the taxonomic richness of the stream invertebrate community (Figure 4). Improvement was most noticeable in the middle reaches of the stream, where numbers of pollution-sensitive taxa increased nearly [illegible] the headwater site, while adverse ecological impacts were not readily discerned at the lowermost site at any point over this period.

The lower reaches of Bear Creek contained a large population of rock bass (*Ambliploites rupestris*) throughout the study period. In the mid-1980's, mercury contamination was evident in fish from this site, which averaged two to three times background concentrations. Mean mercury concentrations in this species exhibited a gradual increase over the ensuing years, with a regular cycle of decreases over the winter/spring period and increases over the summer/fall period (Figure 5). By 1996, the average mercury in rock bass at the site had nearly doubled, with no known increase in inputs of aqueous mercury.

CONCLUSIONS

Although in these cases improvements in water quality were associated with increased bioavailability of mercury, causality has not been clearly established. Mercury bioaccumulation in fish occurs primarily through food chain amplification of methylmercury concentrations and, thus, is sensitive to alterations in community food web structure (11,12). However, aqueous methylmercury concentrations in East Fork Poplar Creek were similar to those in contaminated streams where waterborne total mercury concentrations were much lower (10), indicating that the differences in bioavailability center on the production dynamics of waterborne methylmercury rather than on differences in food chain structure.

Mercury bioaccumulation has been found to be sensitive to a number of site-specific environmental parameters, including pH and buffering capacity, trophic status, thermal regime, and suspended solids loads (13 - 15). Discharges from industrial facilities have

the potential to alter characteristics of receiving waters in ways that would tend to reduce mercury bioavailability, such as raising pH and dissolved salts, increasing suspended solids, and adding nutrients or organic enrichment. In such cases, improving water quality in receiving streams by reducing or modifying discharge characteristics could result in enhanced mercury bioaccumulation even at relatively lower concentrations of waterborne mercury.

Except for selenium in Rogers Quarry, this study did not identify probable causal agents. However, the empirical findings suggest that in watersheds containing multiple and varied sources of possible contaminants, actions that affect one facet of water quality can have unintended and unanticipated effects on other facets of environmental quality. Evaluating the effects of specific actions on a watershed wide basis will yield a greater likelihood of identifying potential adverse effects of efforts to improve water quality at an early stage.

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Figure 1. Increase in mean number of pollution-sensitive taxa in McCoy Branch following the elimination of fly ash discharges to the stream.

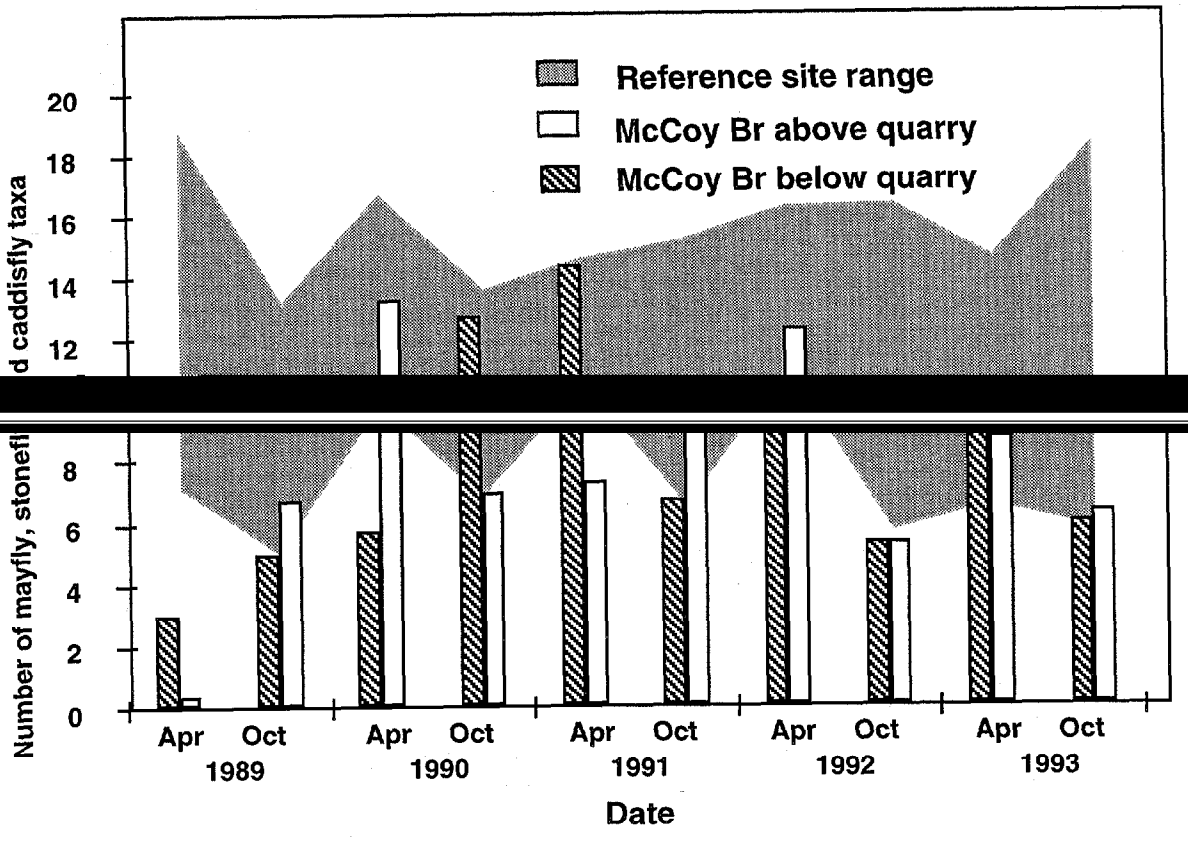


Figure 2. Increase in mean number of all benthic invertebrate taxa and pollution-sensitive taxa over time, upper East Fork Poplar Creek.

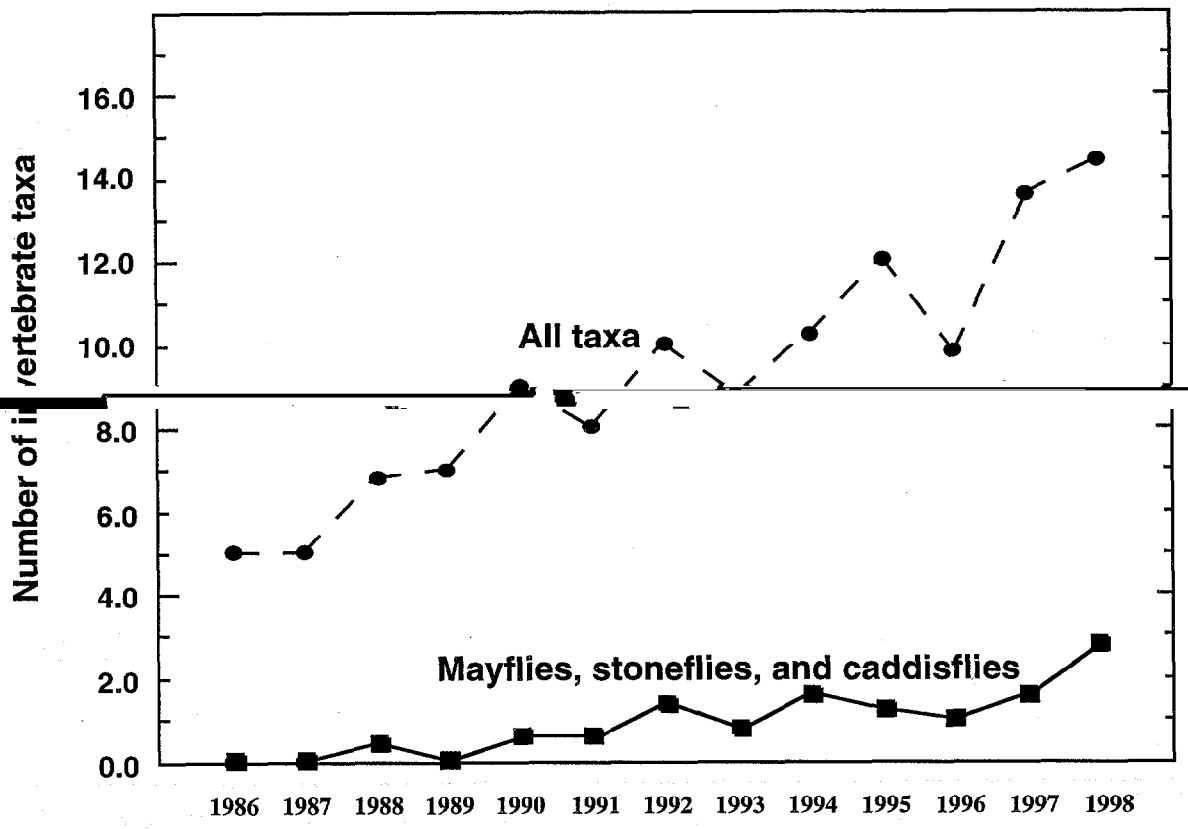
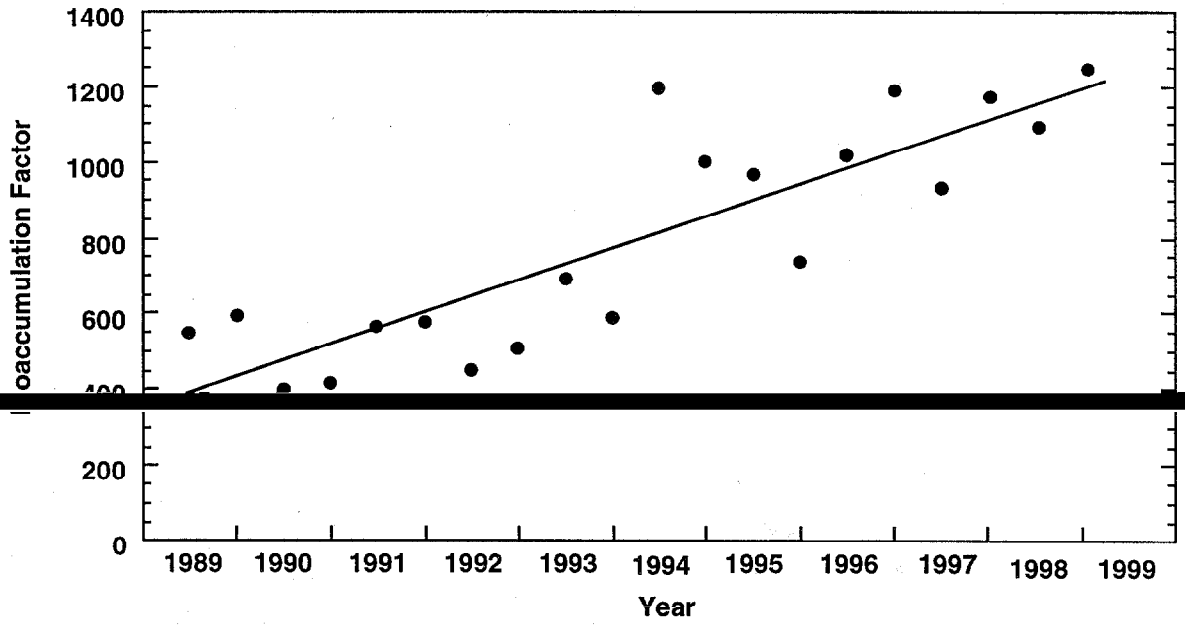


Figure 3. Increase in bioaccumulation factor (ratio of concentration of mercury in fish (μg/kg) to mercury in water (μg/L) for redbreast sunfish (*Lepomis auritus*) in upper East Fork Poplar Creek, 1989 - 1999.



caddisflies) per sample over time at sites in Bear Creek

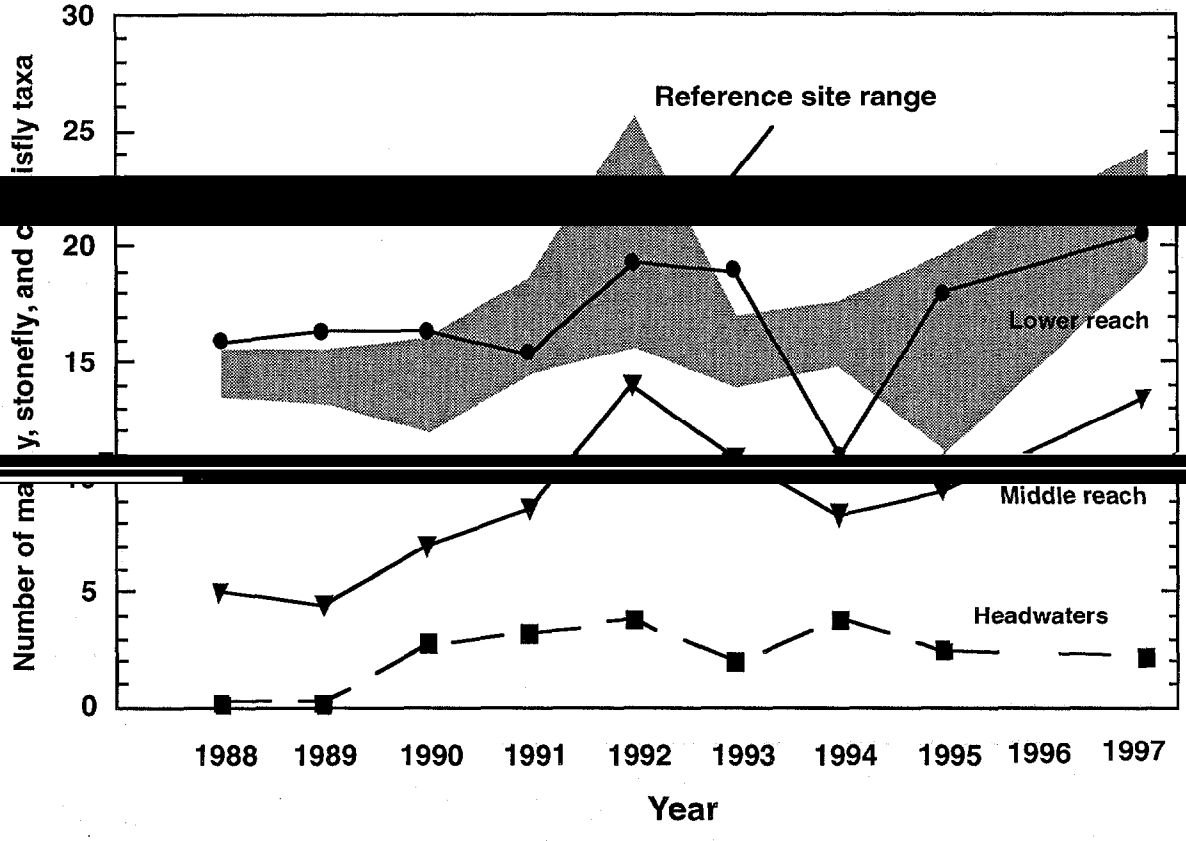
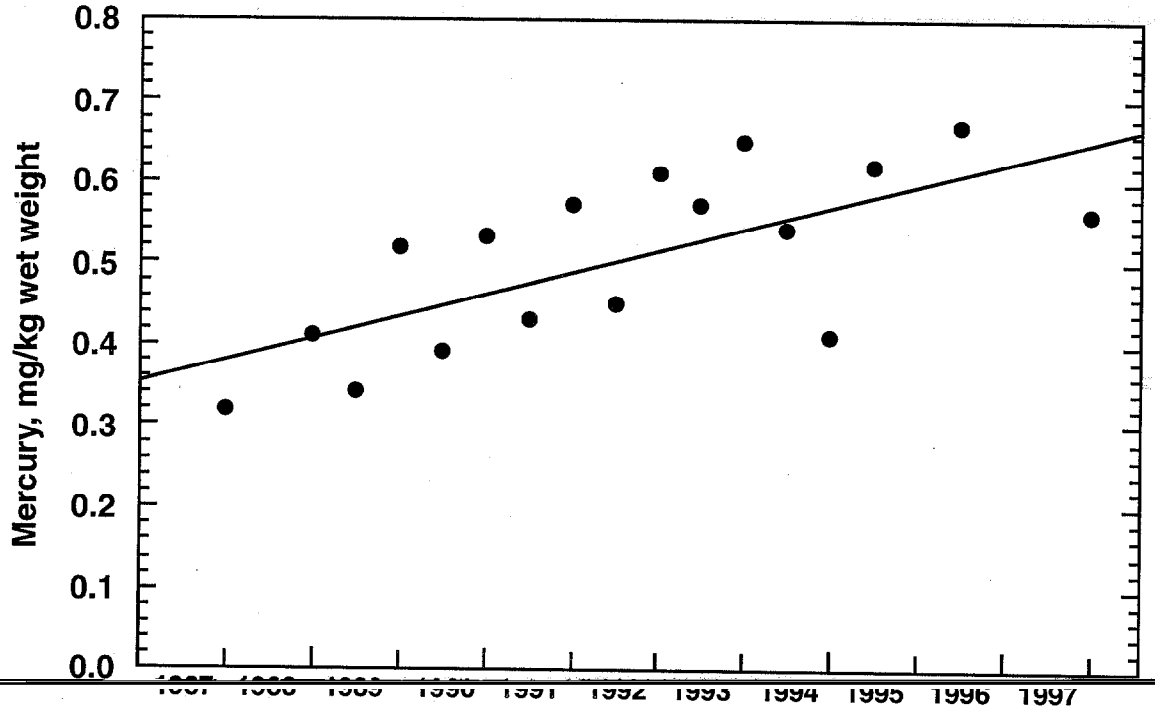



Figure 5. Mean concentrations of mercury in rock bass (*Ambloplites rupestris*) from lower Bear Creek, n = 8. Means are adjusted for covariance of mercury with fish weight.