

ABSTRACT

LAUREN ELIZABETH ELMORE. An Evaluation of Mercury in the Fish Communities of Abbotts Creek, Davidson County North Carolina. (Under the direction of Edward J. Kuenzler)

A fish tissue contamination data set, collected by the North Carolina Division of Environmental Management, was examined to determine the mechanisms behind mercury accumulation in Abbotts Creek fish. Mercury concentrations, undetectable in the water column, bioaccumulate to measurable levels in Abbotts Creek fishes. Piscivorous species bioconcentrate mercury; there is a significant relationship between largemouth bass size and mercury contamination levels. Trophic position, as determined by dietary preferences, affects fish mercury concentrations. Locational differences were observed in the contamination of each species, with highest concentrations observed most consistently at North Carolina Highway 47. Mercury levels in Abbotts Creek fish appear to be changing at different rates. These rates appear to be affected by sampling location. Mercury contamination levels for largemouth bass in 1990 are significantly lower than in 1981 for all Abbotts Creek sites. The largemouth bass appears to be a species which can be used to monitor environmental effects of Hg concentrations that are unmeasurable in industrial and municipal effluents.

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OLD COUNCIL TREE
BENT

100% COTTON, 1988

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INTRODUCTION

Mercury (Hg) is an environmental contaminant, and is found in industrial effluents. The atmosphere, and some rocks and soils also contribute Hg to the environment. Current regulations involving mercury discharges are limited by analytical detection capabilities in water. Fish Hg levels may be used to assess the environmental impact of low levels of Hg contamination. The purpose of this investigation was to determine whether fish may be used as indicators of mercury contamination when Hg concentrations in water are below the limits of detection.

Elevated mercury concentrations in fishes have been well documented for decades. The highest levels of Hg are most consistently found in large, and particularly predaceous, fishes. Researchers disagree over the mechanisms behind the accumulation of Hg in fishes; bioaccumulation, biomagnification, bioconcentration, or combinations of these processes have been suggested. The contributions of bioaccumulation, biomagnification, and bioconcentration can lead to mercury concentrations in top predators that may present a threat to human health. There also appear to be considerable regional differences in Hg accumulation patterns. For example, fish tissue from top predators in contaminated areas has been found to bioaccumulate 10,000-100,000 times the amount of Hg found in the surrounding water (EPA 1984).

Bioaccumulation is the accumulation of Hg above background levels in the water. Biomagnification occurs when mercury is concentrated by the food

chain, causing predaceous fishes to have higher contamination levels than planktivorous fishes. Bioconcentration occurs when more of a contaminant is contained in larger fish than smaller fish. Environmental factors which effect the bioavailability of Hg can influence the rates of mercury accumulation, concentration, and magnification. Dietary Hg levels, fish age (or the length of exposure to mercury), fish size, and chemical and biotic (prey availability) conditions at the location where the fish lives all influence Hg contamination and are intercorrelated with each other. Richman et al. (1988) suggested that the bioconcentration and bioaccumulation of mercury is well known but that there is less evidence for biomagnification. Meili (1991) suggested that fish size, growth rates, and duration of Hg exposure exert a smaller influence on Hg contamination than does the fish's dietary Hg content.

Piscine Exposure to Mercury

Mercury may enter fish through skin, gills, or food, but the diet is generally considered to be the primary source of mercury in fish (Jernelöv and Lann 1971; Tsubaki and Irukayama 1977; Rodgers et al. 1987; Richman et al. 1988). Dietary methylmercury is reported to be absorbed at a 67-87% uptake efficiency (Hannerz 1968; Stillings and Lagally 1974; Suzuki and Hatanka 1975; Norstrom et al. 1976), while in contrast only about 10% of the methylmercury in water passing over the gills is absorbed by fish (Phillips and Buhler 1978; Norstrom et al. 1976).

Trophic Position and Mercury Contamination

In their recent review, Richman et al. (1988) noted that predatory fishes typically contain higher concentrations of Hg than do prey species of

comparable age and body mass, indicating significant biomagnification. In addition, shifts in trophic status with age are frequently mirrored by changes in Hg body burdens (Grieb et al. 1990) which may reflect biomagnification. A Division of Environmental Management study (1983) of mercury levels in Jordan Lake fishes found fish tissue mercury levels to be related both to trophic position and dietary choices; top predators had the highest levels of mercury, as ug/g wet weight, and omnivores the least.

Body Size Relationship with Mercury Contamination

The evidence for increasing tissue mercury content with increasing fish size (bioconcentration) is equivocal. Mercury contamination in sunfish and yellow perch have been found by some researchers to be strongly related to body size (Wren and MacCrimmon 1983; Grieb et al. 1990). However, Suns et al. (1980) found the correlation between yellow perch (perca flavescens) size and Hg content to be positive in only two lakes out of the sixteen investigated. Furthermore, when Cope et al. (1990) investigated the relationship between Hg content and body size in yellow perch, they found no significant correlation between either mean body weight or total length and Hg content (ug/g). Meili (1991) found a general pattern of increased tissue mercury concentrations with increased body size in adult pike, a piscivore, but found that among different lakes the relationship between mercury content and body size changed. Planktivorous fish and species less piscivorous than pike appeared to accumulate mercury less consistently than pike (Meili 1991). The phenomenon of increasing tissue mercury burden with increased fish size (most likely due to length of exposure and volume of food consumption) thus appears to be highly

variable, and may be linked with both locational differences in prey Hg content and the availability of mercury (Meili 1991).

The Bioavailability of Mercury to Fish

Mercury's toxicity to aquatic organisms and its behavior in the aquatic environment is affected by its chemical speciation. Mercury (Hg) has three main oxidation states: Hg^{+2} (mercuric), Hg_2^{+2} (mercurous), and Hg^0 (metallic), but methylmercury, $(\text{CH}_3)_2\text{Hg}^+$, is the predominant form found in fish (Noren and Westö 1967; Buhler et al. 1973; and Phillips and Buhler 1978; Grieb et al. 1990) (See Figure 1.1). Most forms of mercury can be readily methylated within the sediments, and evidence for both biotic (Jensen and Jernelöv 1969) and abiotic (Brigham and Brezonik 1989) mechanisms for methylation have been presented. Methylated mercury bioaccumulates to a greater extent than other forms of mercury and is particularly toxic because of its ability to be transported across membranes and bind with the sulfhydryl groups of proteins.

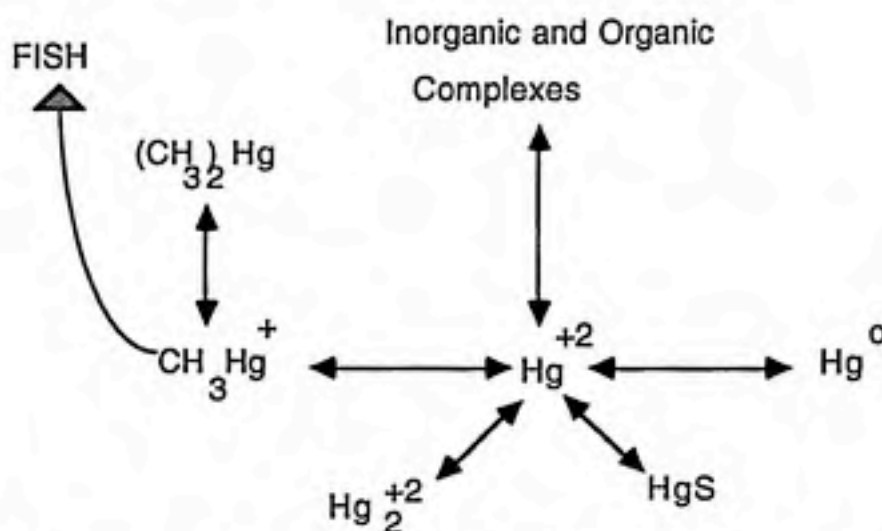


Figure 1.1 Common transformations of mercury within the watercolumn and sediments.

The availability of mercury to fish is affected by a number of physical and chemical factors including: the distance from a mercury source (Håkanson et al. 1988); the size of the drainage basin (Grieb et al. 1990); the concentration of dissolved and particulate organic matter in the water column (Grieb et al. 1990) and in the sediments (Håkanson et al. 1988); pH (Cope et al. 1990; Håkanson 1980; Björklund et al. 1984); sulfide concentrations in sediments (Björnberg et al. 1988); and oxygen concentrations (Weis et al. 1986). Mercury adsorbs rapidly onto organic particles (Rudd and Turner 1983), and the sedimentation rate of suspended particles strongly affects the spatial transport of mercury. In addition, the organic content of suspended material will affect the chemistry of specific locations. Spatial differences in chemical conditions directly affect the speciation of mercury and indirectly influence the level of contamination of the fish.

The Effects of Sediment Chemistry on Hg Bioavailability

Water and sediment chemistry determine the potential for biotic uptake of mercury by affecting the mobility of mercury within the sediments. Sediments containing high concentrations of organic material tend to have high bacterial decomposition rates which lead to low oxygen concentrations and indirectly to lower pH and redox potentials in the sediments (Wetzel 1983). Sulfide produced by sulfate reducers under these anaerobic conditions reacts readily with Hg^{+2} thereby reducing its bioavailability; the solubility constant for HgS(s) , ($K_s=10^{-52}$), is so low that when sulfide is present, most of the Hg will precipitate as HgS (Björnberg et al. 1988). Mercuric mercury, Hg^{+2} , also binds with other anions such as selenium (Björnberg et al 1988). Many authors have also found

that decreases in pH are associated with increased mercury in fish (Björnberg et al. 1988; Wren and MacCrimmon 1983; et al. 1984; 1980). Low pH conditions appear to increase mercury accumulation by organisms at the base of the food chain (Wiener 1987 and Xun et al. 1987).

An important factor linked with mercury accumulation in fish is the humic content of the water and the sediments. High humic contents are positively correlated with high mercury content in fish (Mannio et al. 1986). Björnberg et al. (1988) proposed that mercury transported with humic substances from the watershed is biotransformed into methylmercury within the sediments, thus increasing the bioavailability of mercury to fish.

Potential Effects of Mercury In Sediments

The availability of mercury to the lower trophic levels of food webs provides the foundation upon which the mercury burden of top predators is based (Meili 1990 and Meili 1991). Mercury in the sediments is one of the most important factors influencing the availability of mercury to low trophic level organisms. Aquatic invertebrates (especially insects) can accumulate very high concentrations of mercury (World Health Organization 1990). Benthic feeders can significantly bioaccumulate Hg (Jernelöv and Lann 1971), and food webs with strong benthic components may contain fish with high mercury contamination levels. Contact with the sediments can potentially have a greater affect on fish Hg concentrations than its trophic position (Wren et al. 1983). A recent review of twenty years of fish mercury data from Swedish lakes (Håkanson et al. 1988) found that the amount of mercury in surface sediments (sediments 0-1 cm deep) was positively correlated with fish (pike) Hg concentrations. However, it has been found that Hg accumulation in fish (white

sucker and northern pike) is not directly associated with Hg concentrations in lake sediments (Harrison and Klaverkamp 1990). It was also suggested by Harrison and Klaverkamp (1990) that long-term mercury contamination in an aquatic system is more likely to affect sediment Hg levels than water column Hg concentrations.

The concentration of mercury in fish appears to be affected by the activity of the microbes in the sediments (Jackson 1991). Sediment methylmercury concentrations are a result of a combination of simultaneous and demethylation reactions. The predominance of methylating or demethylating bacterial populations appears to be affected by the amount of organic material present in the sediment (Jackson 1991). Increasing the organic content within the sediments has often led to higher methylation rates, but the further addition of organic matter to sediments already high in organic matter appears to stimulate the bacteria responsible for demethylation (Jackson 1991). Increases in methylmercury production can be related to increased activity in the methylating bacteria and decreased methylmercury production can be related to increasing activity in the demethylating bacteria and bacteria producing sulfides. Sulfate reducing bacteria produce sulfide which binds with inorganic mercury, and reduces its availability to fish. (Björnberg et al. 1988)

Effects of Time on Mercury Accumulation

Two temporal aspects need to be considered when examining patterns of mercury accumulation by fish. First, sediment deposition over time may bury past Hg accumulation and remove it as a potentially bioavailable Hg source. How this will affect the availability of the Hg within the sediments is unknown, but Rudd et al. (1983) found that only the mercury in surface sediments (0-1 cm) in lakes was biologically available. Stream sediments are subject to periodic

disturbances, (e.g., flooding events, carp feeding, etc.) which may be responsible for redistributing the sediments and resuspending the Hg. Despite potentially lowered bioavailability of Hg deep in the sediments, the accumulation of Hg in sediments may provide the potential for long-term effects on biota even after Hg sources to the system are curtailed.

In addition, Phillips and Buhler (1978) noted that seasonal differences in methylmercury availability needed to be taken into account when predicting the accumulation of methylmercury in fishes. Seasonal changes in temperature and humic loading affect methylation rates, and seasonal variations occur in the methylmercury content of the food organisms themselves (Phillips and Buhler 1978). Moreover, fish feeding rates change seasonally in response to fluctuations in dissolved oxygen content and temperature (Peters 1983), and fish food availability which also follows seasonal trends; benthic organisms have yearly patterns of emergence and growth.

Goals

The purpose of this study was to investigate mercury contamination of fishes in Abbotts Creek using available monitoring information. Fish tissue data collected by the Division of Environmental Management were analyzed for patterns and trends in fish mercury contamination in relation to; fish trophic status, fish size, location, and time. This evaluation may lend support to other research concerning the behavior of mercury in fish communities. The following questions were addressed in this evaluation:

1. Does Hg bioaccumulate in Abbotts Creek fish?
2. Does the bioaccumulation of Hg differ among fish species?
3. Are there locational differences in the Hg content of the fish?

4. Does the degree of mercury bioconcentration vary with fish weight or length?
5. Are mercury levels in Abbotts Creek fishes changing with time?

Data Source

The evaluation presented here focused on the mechanisms behind the mercury contamination of fishes in a North Carolina stream, Abbotts Creek as could be determined by analyzing a decade of fish tissue data collected by the Division of Environmental Management. Mercury has been a known pollutant in Abbotts Creek fishes for over ten years. The North Carolina Division of Environmental Management closely monitors the quality of water and fish tissue in Abbotts Creek. Abbotts Creek is located below the town of Lexington and flows into a downstream multi-purpose reservoir, High Rock Lake (Figure 1.1). At the the time of this evaluation, warnings were posted along Abbotts Creek cautioning individuals to limit fish consumption to less than one half pound of fish per week from Abbotts Creek. Women of childbearing age were advised not to eat any fish from this system.

Mercury Sources

Various industrial and municipal Hg sources have been identified but the total amount of mercury that has entered this system is currently unknown. A mercury-cell battery factory was responsible for some of the non-point sources of Hg to Abbotts Creek and sent Hg-containing waste to Lexington's wastewater treatment plant. Lexington opened a new wastewater treatment plant in the summer of 1986 to provide additional wastewater treatment and mercury in the treatment plant's discharge now satisfies both State and Federal wastewater permitting regulations.

Site Description

Three Abbotts Creek sampling sites were chosen for investigating the behavior of Hg in the stream's fish community. All three sites are located downstream of Lexington. The first site, Center Street (Center St.), crosses Abbotts Creek below the battery facility but above both of the wastewater treatment outflows; Abbotts Creek is narrower at Center Street than at any other location. The second site is located where State highway 47 (NC47) crosses Abbotts Creek about one mile below the outfall of the new wastewater treatment plant. Abbotts Creek widens substantially around the area of NC47 and considerable deposition of sediments occurs in this area. The NC47 location is about five miles below Center Street and almost eight miles above where highway 8 crosses Abbotts Creek. The third site is located at State highway 8 (NC8) where Abbotts Creek enters the main body of the reservoir.

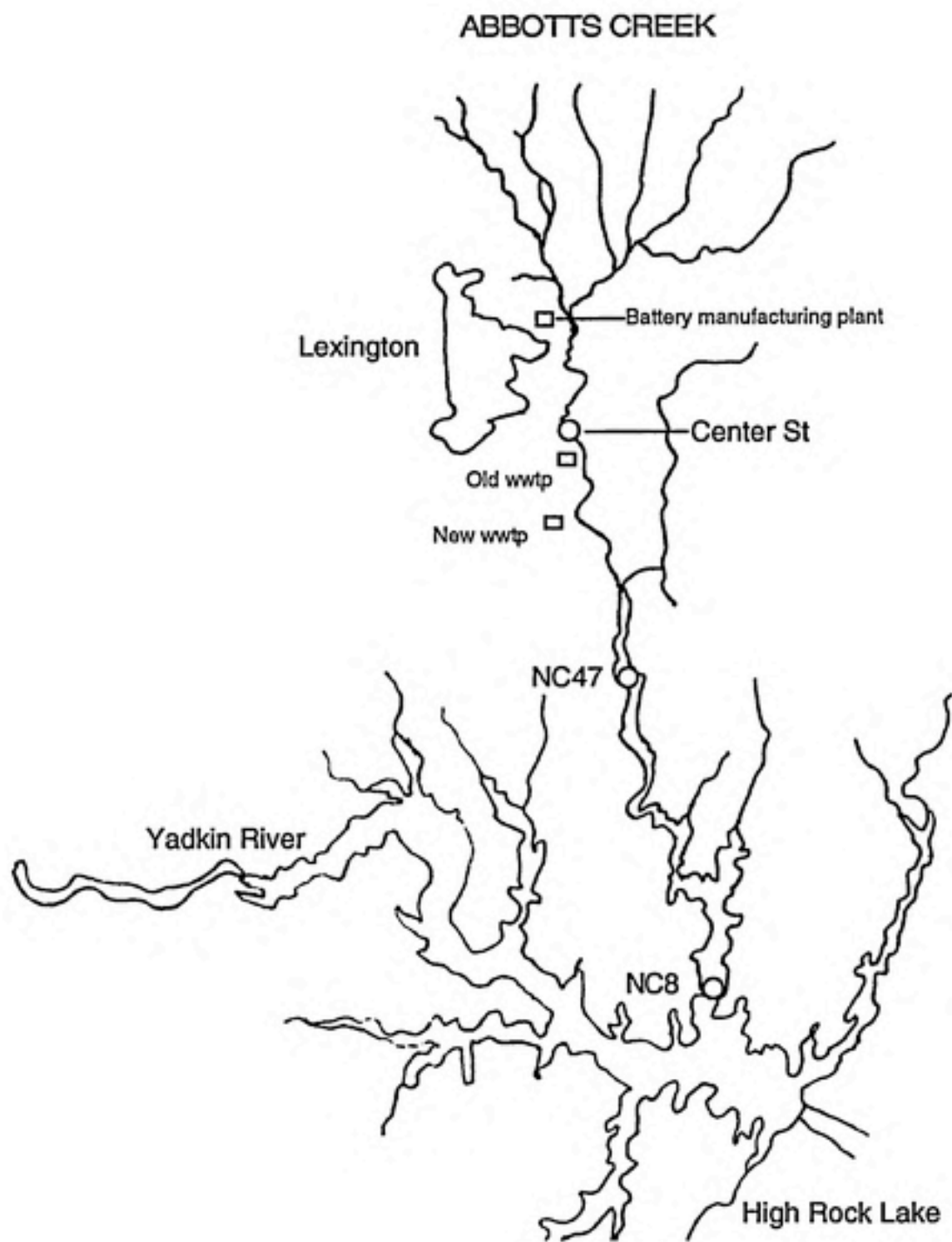


Figure 1.2 Map of Abbots Creek.

The section of Abbotts Creek surrounding NC8 is an upper arm of the High Rock Lake reservoir.

Lake Tom-A-Lex (LTAL) is a reservoir on Abbotts Creek located above both the town of Lexington and the battery production facility. Lake Tom-A-Lex served as a reference location and is representative of water bodies in the area. Lake Tom-A-Lex has had no known sources of mercury contamination other than atmospheric.

METHODS

Sampling Methods as practiced by the Division of Environmental Management

From 1980 to 1986, fish were sampled by electro-shocking in the spring and fall, but only in fall since 1986. The sampling effort emphasized shoreline as available habitat. Fish collections focused on largemouth bass, with an attempt to catch at least 30 largemouth bass per sampling event (Vince Schneider, personal communication).

Mercury sediment testing was not done routinely: a few initial samples were collected in 1990, and sporadic sediment information was collected from 1981-1986 (Jaynes, 1991).

Analysis of Fish Tissue for Mercury

Total mercury concentrations were determined using flameless Atomic Absorption Spectrophotometry by the Division of Environmental Management's laboratory in Raleigh, North Carolina (from Roy Byrd, Metals Unit Supervisor, personal communication). The technique is based on EPA procedures for the screening of fish for priority pollutants (USEPA, 1977), and fish mercury concentrations were reported as ug/g fresh weight. Some fish were analyzed whole (w) and others as fillets (f).

Quality Control

The accuracy and calibration of the Atomic Absorption unit was checked before and during each sampling run. Each analysis run used an EPA Hg

standard to test precision. The procedure maintained an accuracy of at least 75-125% of spike recovery. Standards and duplicates were run every tenth sample to evaluate calibration, and the information from the duplicates was used to evaluate test quality control.

Analytical Reporting Limits for Hg in Fish Tissue

Detection limits for the fish tissue testing over the eleven year period 1980-1990 were reduced from 0.05 ug/g to 0.02 ug/g when the state switched from a model 403 AA to a model 5000 AA in 1982 to get better optics and electronics as well as less background instrument noise. Less than three percent of the samples in the entire data set (1580 observations) were below detection limit. For tissue concentrations below the detection limit, one half of the detection limit has been used in the statistical analyses (Wren et al., 1991). This value is conservative but does not assign a false value of zero to concentrations below the limit of detection.

Statistical Methods

The data were analyzed using SYSTAT version 5.0 (Wilkinson, 1990). Multiple linear regression models were formulated using the MGLH module for analysis of variance testing. Very similar F-values and significance of variables were found when data was analyzed using Statview® and SAS® packages. An ANOVA would have been performed but adequate sample sizes were not available.

The fish Hg data were not normally distributed. Normally distributed data is a requirement for using multiple linear regression, and logarithmic (base 10) transformation was used to improve the normality of the distribution

(Peters, 1983; Grieb et al., 1990; Wren et al., 1991). The normality of the transformed data was evaluated by plotting the logarithmically transformed mercury values against a normal probability distribution; the resulting plot was approximately a straight diagonal line, which indicated that the transformed data were normally distributed (Figure 3.1). When using multiple linear regression, model errors should also be normally distributed. The model errors (Student residuals) were plotted against the predicted Hg values and the distribution appeared to be randomly distributed in a band within two or three units around zero (Figure 3.2). Cooks residuals were plotted against the estimated Hg values to test whether the data met the assumption that one linear model can describe the data (Figure 3.3). The data appeared to generally adhere to this assumption by forming a line at the base of the graph. All models used in the analyses were tested for adherence to regression assumptions.

Medians were compared using Systat notch box-plots. The ends of the boxes are the upper (75%) and lower (25%) percentiles around the median of each group (Hspread). If the ranges between the notches, the widest parts of the boxes, do not overlap then the medians can be assumed, to be statistically different at approximately the 95% confidence level. Lines coming out of the ends of the boxes extend to the ends of the inner fence ($1.5 \cdot \text{Hspread}$). Asterisks represent outliers ($>1.5 \cdot \text{Hspread}$) and circles designate extreme values ($>3.0 \cdot \text{Hspread}$) beyond the inner quartile range (Hspread) (SYSTAT 5.0, Wilkinson 1990 from McGill, Tukey and Larsen 1978).

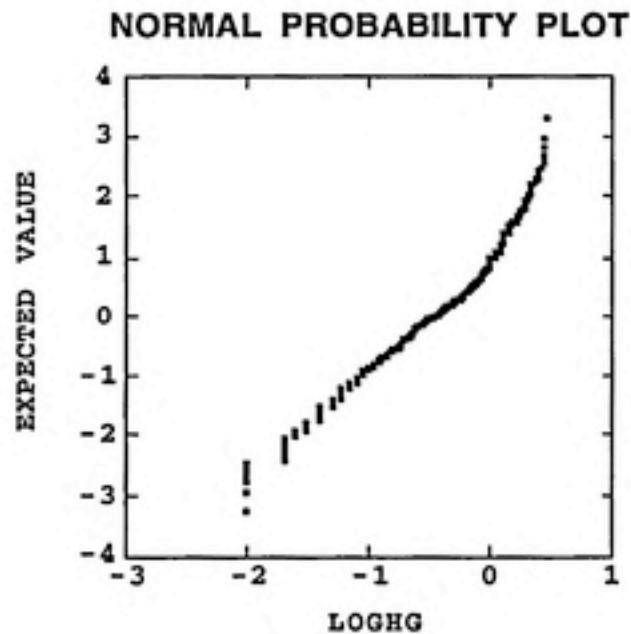


Figure 3.1 Evaluating the normality of the transformed data .

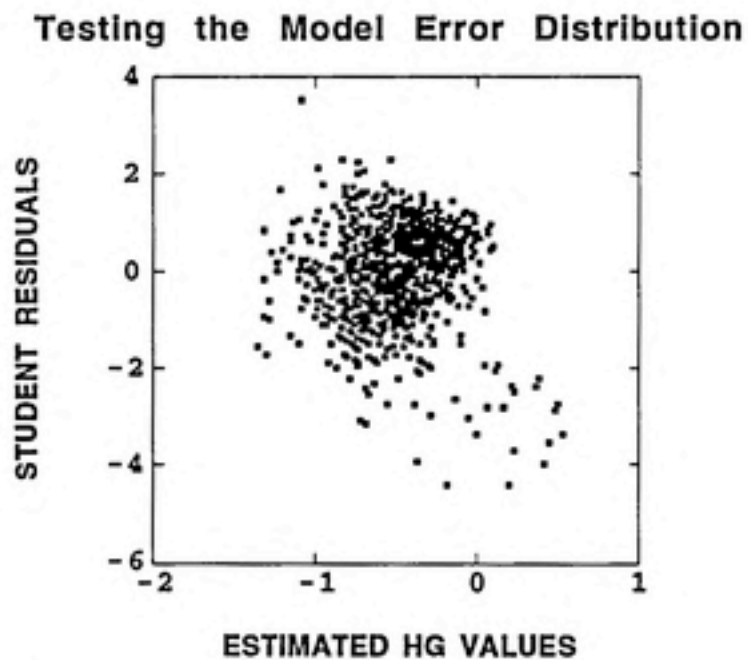


Figure 3.2 Examining the variance of the model residuals for uniformity.

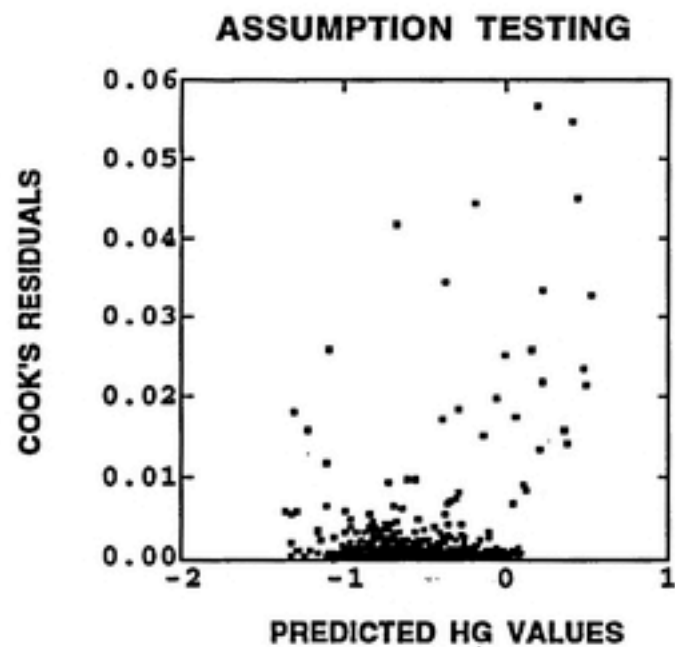


Figure 3.3 Evaluating the applicability of one linear model.

RESULTS

Regression Information

Multiple linear regression analysis was used to examine the effect of fish size, sampling location, trophic position, time, and season on fish tissue Hg concentrations. Individual fish species were chosen to represent three different trophic groupings in the model. Group 2 and group 3 represent the same trophic level but the species feed in different locations. Group membership was based upon major food preferences (Table 4.1). For more extensive diet information see Appendix 1. Type III sums of squares were used to determine the effect of particular variables on Hg concentrations.

Table 4.1 Species selected and diets for each grouping.

Dietary Group	Species	Diet
Group One	Largemouth Bass (<u>Micropterus salmoides</u>)	Piscivore
Group Two	Bluegill (<u>Lepomis macrochirus</u>)	Omnivore
Group Three	Common Carp (<u>Cyprinus carpio</u>)	Benthic Omnivore
Group Four	Gizzard Shad (<u>Dorosoma cepedianum</u>)	Planktivore

When type III sums of squares are calculated, the variance in the dependent variable (LogHg) contributed by each independent variable is calculated last after the variance due to all other variables has been accounted for. The order of variable entry into the model is unimportant. Location, trophic position (as dietary grouping), year, and season were analyzed in the model as categorical variables. Fish size as represented by log-transformed fish length or weight was considered a continuous variable. Fish weight and length were used separately due to collinearity problems if used in the same model. Transformed fish length explained very similar amounts of the variance in Hg levels when substituted in the model for weight (F-Values of 250.05 for weight and 250.08 for length). Weight was chosen to be representative of fish size because better associations between LogHg and fish weight were found than between LogHg and fish length.

Regression analysis indicated that trophic position, sampling location, fish weight, and sampling year significantly ($p < 0.001$) influenced the amount of Hg in Abbotts Creek fish (Table 4.2). Fish length was also related ($p < 0.001$) to mercury concentration. The season of sampling did not appear to contribute significantly to the variance seen in fish mercury concentrations ($p = 0.08$). Close to 76% of the variance in Hg concentrations was explained by sample location, trophic group, fish weight and year. The location at which the samples were taken accounted for most of the variance in Hg; location has the largest F value (477.80). The effect of fish weight on the mercury concentrations observed was the second most important factor affecting Hg levels ($F = 250.05$), and the species of fish followed weight in its effect on mercury concentrations ($F = 73.71$). Sampling year appeared to exert less of an influence on the mercury

concentrations observed ($F=10.74$) than fish weight, the species considered, or the sampling location. (See Table 4.2)

Table 4.2 Evaluation of influence of independent variables on transformed Hg measurements. Type III sums of squares.

ANALYSIS OF VARIANCE					
Dependent Variable =logHg N=725			Squared Multiple R=0.760		
Independent Variables:	DF	Sum-of-Squares	Mean-Square	F-Ratio	P
Log(10) of Fish Weight	1	15.48	15.48	250.05	<0.001
Sampling Location	3	88.73	29.58	477.8	<0.001
Trophic Group	3	13.69	4.56	73.71	<0.001
Year	10	6.55	0.66	10.58	<0.001
Season	1	0.19	0.19	3.14	0.077
Error	706	43.7	0.06		

Biomagnification of Mercury in Fish

Mean Hg concentrations for the eleven-year period differed significantly among trophic levels (Figure 4.1). Biomagnification of mercury, the increasing accumulation of a contaminant as it moves up the food chain, appears to have occurred in Abbots Creek. The piscivore exhibited the highest mean Hg concentration, the benthic omnivore had the next highest Hg level, the omnivore less strongly associated with the sediments had the third highest Hg contamination, and the planktivore had the lowest mean Hg content. The regression analysis suggested that trophic position significantly influenced Hg contamination.

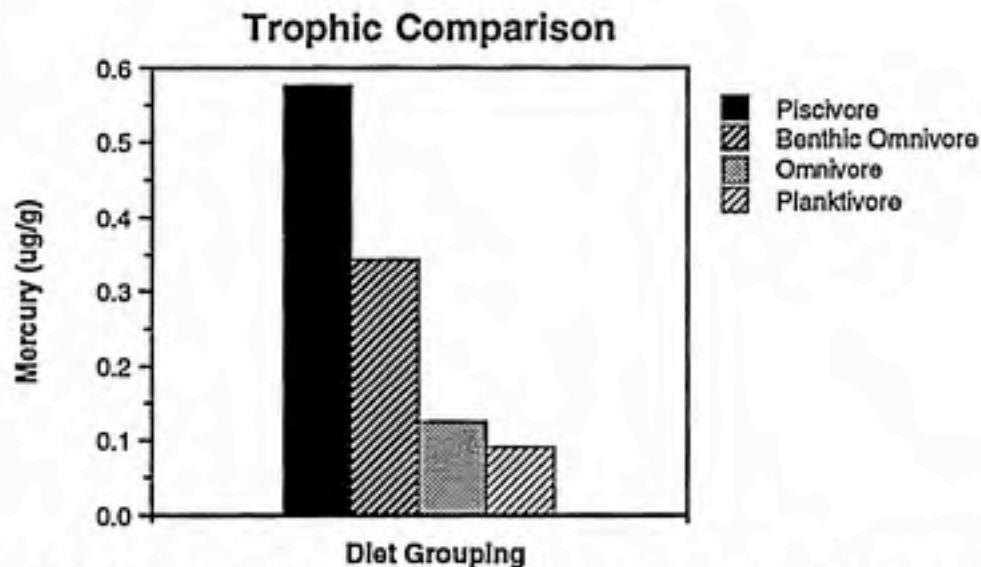


Figure 4.1 Median (from transformed data) ten-year mercury concentration for each trophic group.

When median Hg concentrations for five individual species were compared, species at different trophic levels tended to have medians that were significantly different (Figure 4.2). The largemouth bass's median Hg concentration was significantly higher (at a 95% confidence level) than all other species except for the white catfish. Largemouth and catfish are in the same trophic level. The median Hg level in catfish was not significantly larger than the carp's. The median Hg concentration in carp was significantly different than all other species except the catfish. The mercury content of the gizzard shad was significantly lower (at a 95% confidence level) than all species except for the bluegill and both species had lower Hg concentrations than the other three. The shad are feeding on organisms at the base of the food chain, there was no time for biomagnification to occur. These comparisons suggest that Hg is biomagnifying in this system. Locational differences and fish size may also

have affected the pattern of biomagnification observed in Abbotts Creek (Figure 4.2).

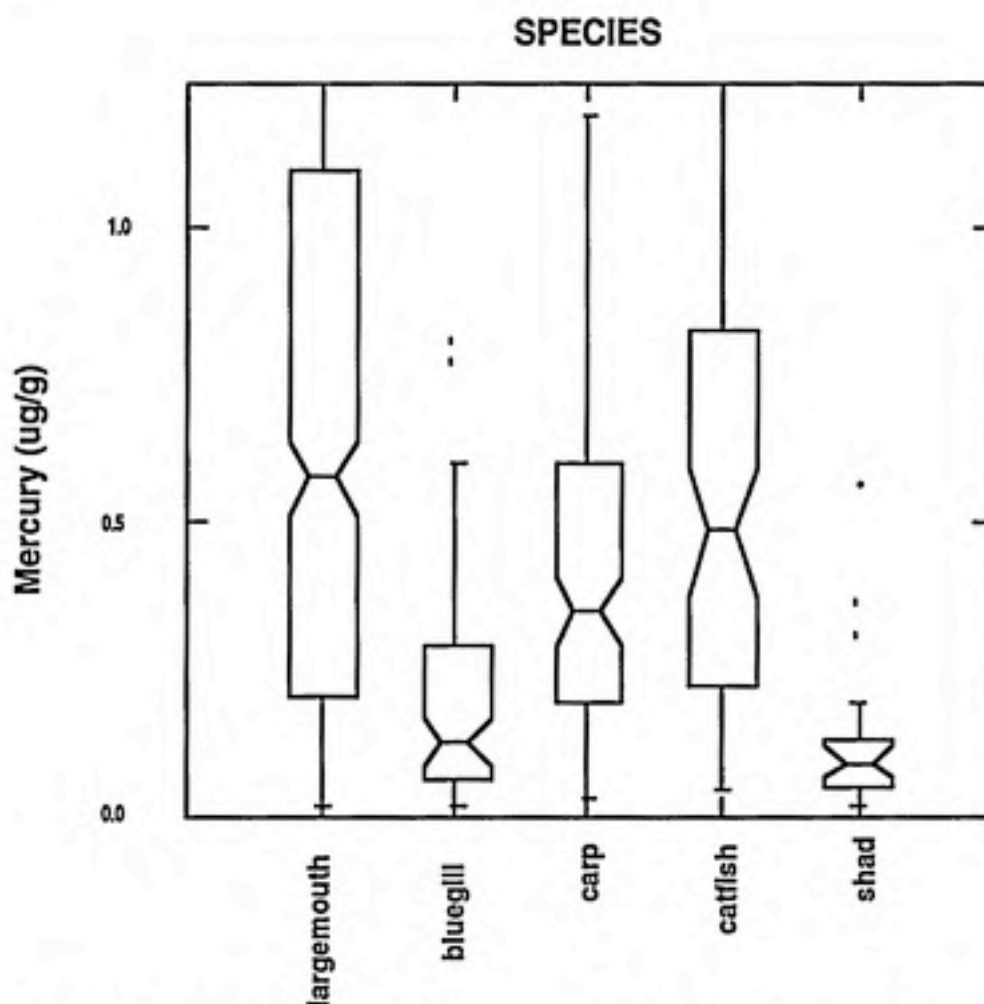


Figure 4.2 Notch box-plot showing median mercury concentration for each species.

Locational Influence on Mercury Accumulation in Fish

When trophic groups are compared within each location, the classic pattern of biomagnification is interrupted at Center Street (Figure 4.3). Piscivores had the highest Hg concentrations at all locations except Center Street where benthic feeders contained more Hg.

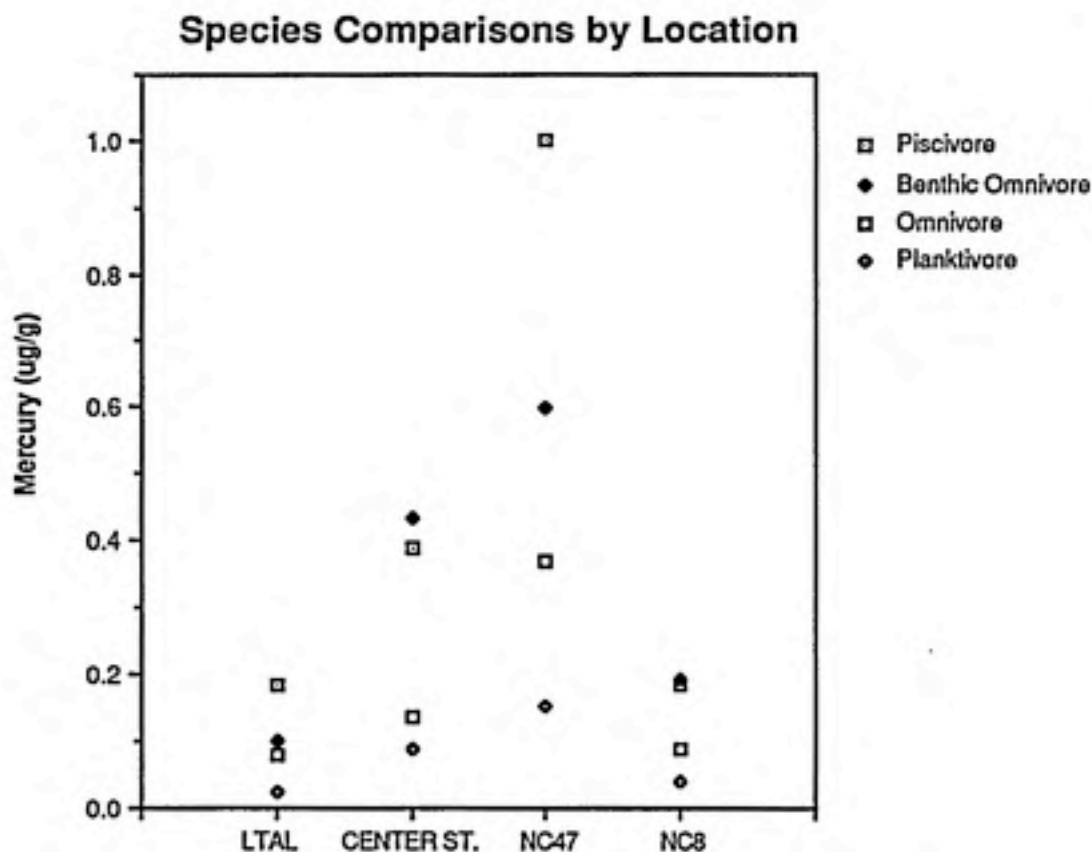


Figure 4.3 Median mercury concentration in four trophic levels at each sampling location.

When all trophic levels were combined (Figure 4.4), and when only largemouth data were used (Figure 4.5), the median Hg values were different (with 95% confidence) at each location. Median Hg concentrations are highest for each trophic group at NC47 (Figure 4.4 and Figure 4.3). Center Street had median Hg levels higher than at NC8 or LTAL but lower than at NC47. The control location, Lake Tom-a-Lex reservoir, consistently had the lowest median Hg level for any location or trophic group.

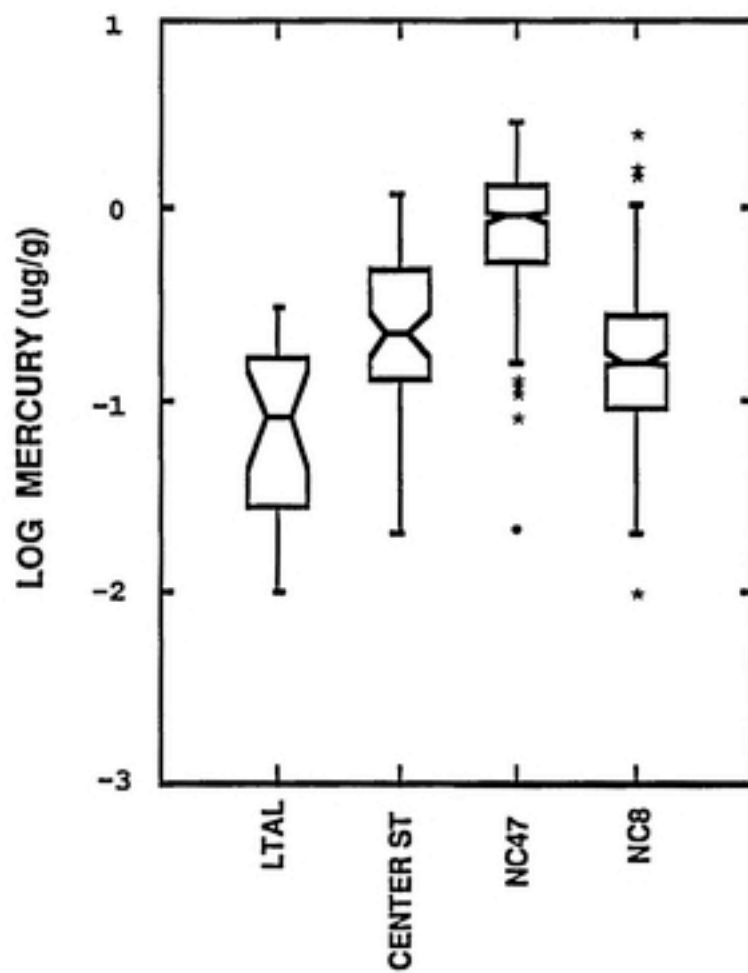


Figure 4.4 Median logHg concentrations using all trophic levels.

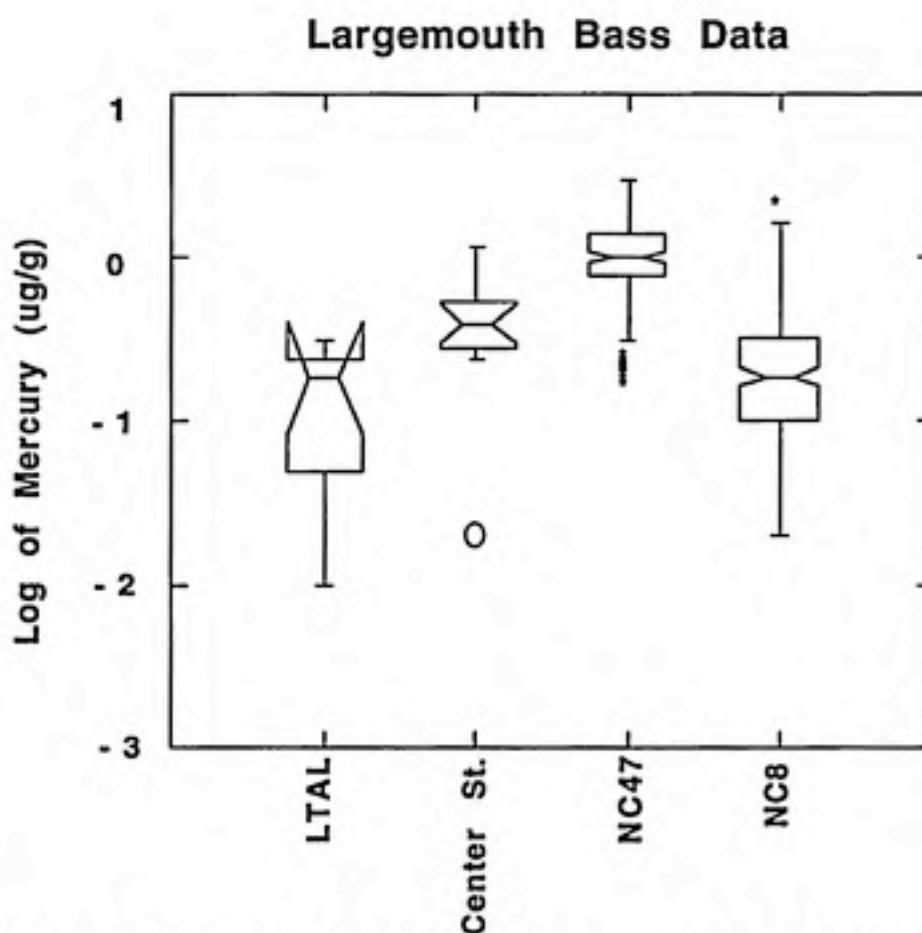


Figure 4.5 Notch box-plot of median logHg concentration for largemouth bass.

Distance from the mercury sources did not always appear to affect fish contamination levels (See Figure 1.1 and Figure 4.4). Center Street fish had higher median mercury concentrations than NC8 although Center street is upstream of the wastewater treatment plant Hg sources.

Sediment Mercury Concentrations

Site NC47 sediments appear to have contained higher amounts of mercury than sediments at Center Street except in 1983 (Figure 4.6). Sediment Hg concentrations appeared to decrease at both locations between 1980 and

1990. Sample site and year did not significantly effect sediment Hg measurements (Table 4.3).

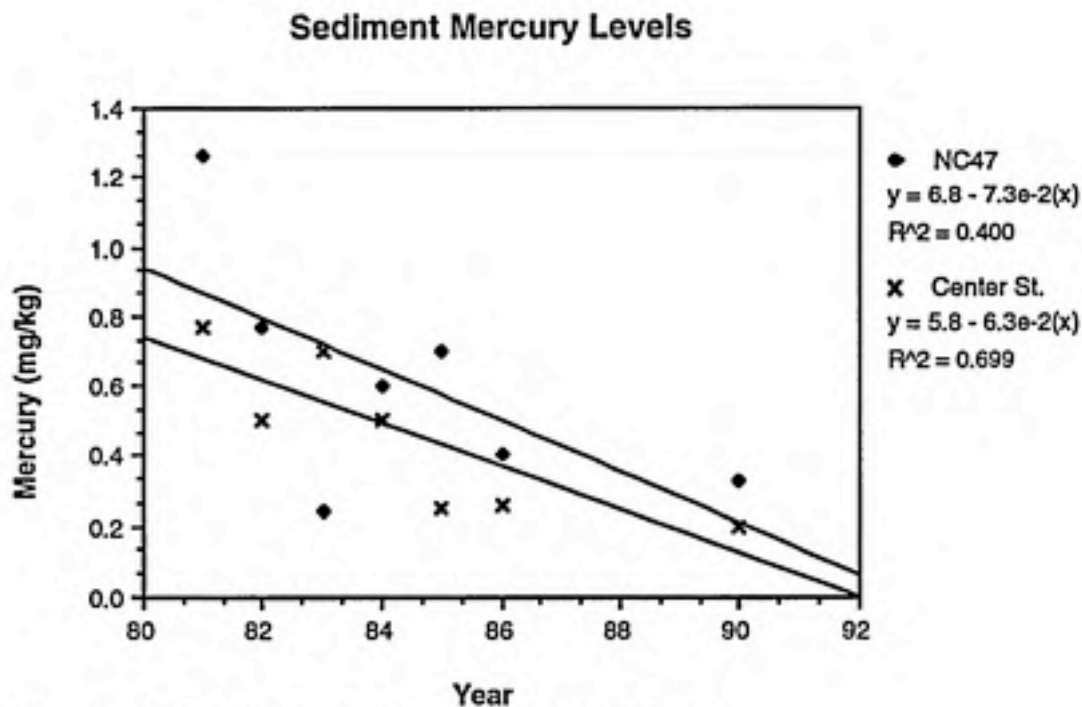


Figure 4.6 Sediment mean mercury concentrations.

Table 4.3 Multiple linear regression model of sediment data.

ANALYSIS OF VARIANCE					
Dependent Variable=LogHG		N=14	Squared Multiple R=0.677		
	DF	SUM-OF-SQUARES	MEAN-SQUARE	F-RATIO	P
Independent Variable:					
YEAR	6	0.447	0.074	1.868	0.23
LOCATION	1	0.054	0.054	1.347	0.29
ERROR	6	0.239	0.04		

Effects Of Fish Weight On Mercury Concentrations

The relationship between mercury concentration and fish weight varied among species. The association between mercury concentration and fish weight was generally positive in the piscivorous species, largemouth bass, but appeared more variable in the non-piscivorous carp and shad. A similar relationship was observed between fish length and Hg concentration. Plotting log-transformed data did not usually help to clarify the patterns observed.

The largemouth bass was the only species with sufficient data collected in a given year for regression analysis. In largemouth bass there was a significant positive association between mercury contamination and fish weight at NC47 and NC8 (Figures 4.7 and 4.8). The slopes of the relationship between Hg and largemouth body weight at NC47 and NC8 were very similar although the intercept at NC8 was lower. Tissue mercury levels predicted from fish weights using these equations would have broad confidence limits due to the relatively modest R^2 values of 0.42 and 0.60 for NC47 and NC8.

A largemouth's diet changes as its size increases. Larger fish consume larger prey with correspondingly higher mercury content initiating an increase in mean mercury content as size increases. The mean weight of largemouth bass at Center Street for all years was lower than at any other site (Figure 4.9). This may be related to the smaller size of Abbotts Creek at Center Street. All the other locations resemble lake systems at least part of the year. NC47 is flooded when the High Rock Lake reservoir level rises.

Highway NC47 1990 Data

$$y = -0.5 + 4.0(10^{-4})(x)$$

$$R^2 = 0.47$$

$$p < 0.001$$

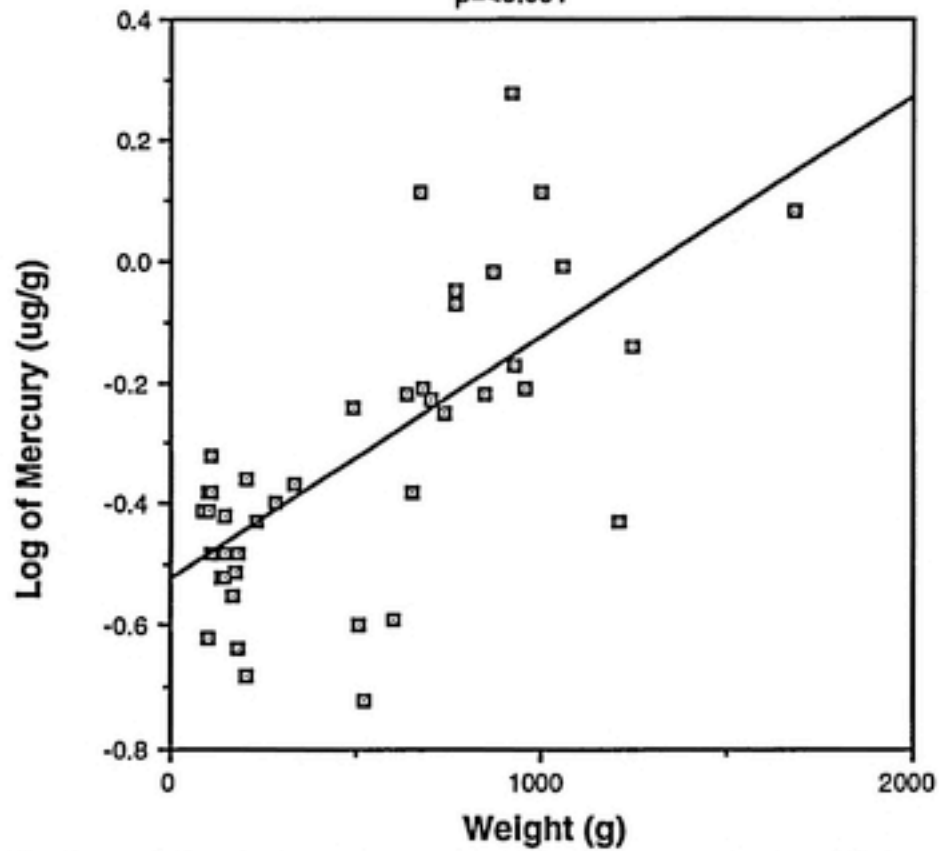


Figure 4.7 Association between largemouth mercury content and fish weight.

Highway NC8 1990 Data

$$y = -1.22 + 5.5(10^{-4})(x)$$

$$^2R = 0.60$$

$$p < 0.001$$

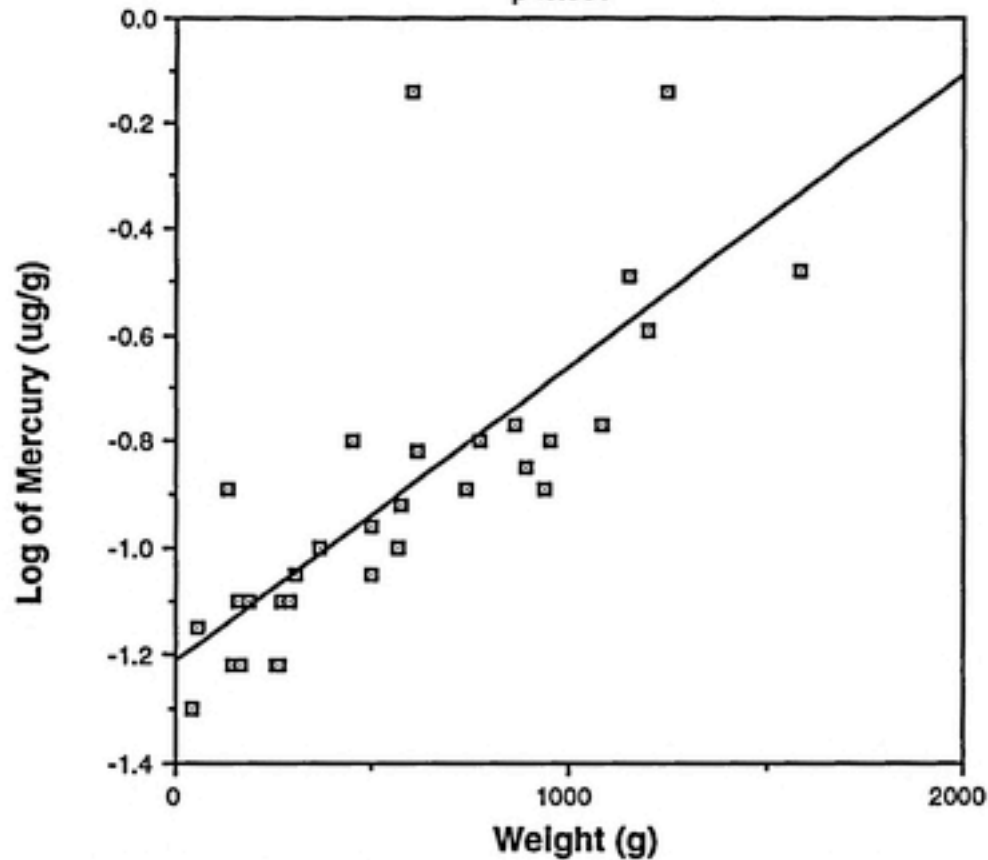


Figure 4.8 The association between largemouth Hg content and weight.

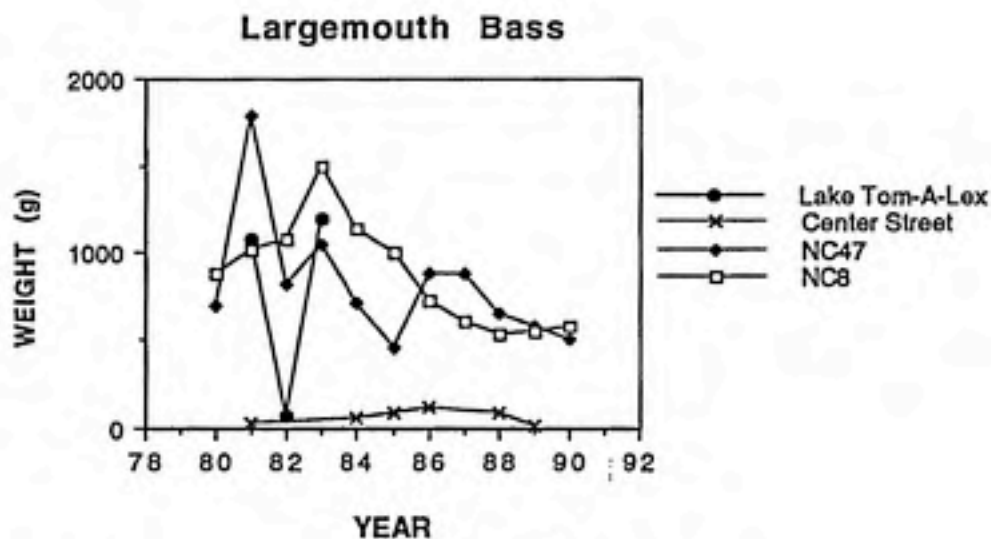


Figure 4.9 Largemouth mean weight at all locations.

Effects Of Sample Type On Mercury Concentration

Under the Division of Environmental Management's sampling protocol, fish fillets were obtained whenever possible and fish were analyzed whole only when individuals were too small to obtain a fillet sample. Only about 3% of the fish in the data set were ground up and analyzed whole. A comparison of the Hg content of both sample types revealed that whole fish had significantly higher ($p < 0.05$) mercury content than fillets (Figure 4.10). These findings were expected since fish are known to accumulate some forms of mercury within their kidneys and livers. However, sample type did not have a large effect on Hg levels; only about 3 percent of the Hg variance was explained by type differences.

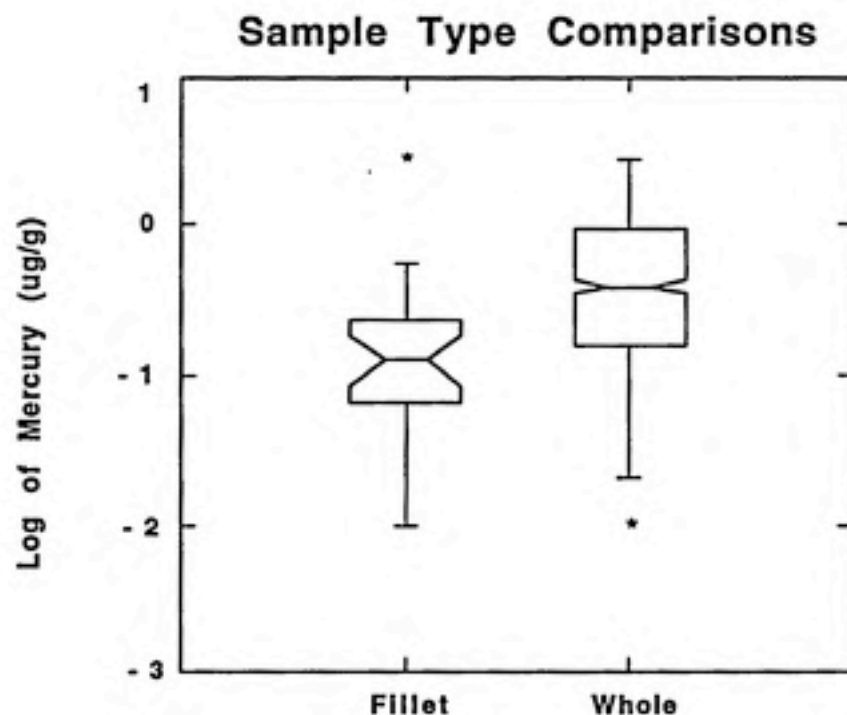


Figure 4.10 Notch box- plot of median Hg level for fillets and whole fish.

Time Patterns In Mercury Accumulation

When data from all locations were combined, trends in Hg contamination over time were very slight (Figure 4.11). Few significant trends occurred in median Hg levels between years although linear regression found that the sampling year appeared to significantly influence mercury concentrations. Significant year to year variations presumably are due in part to annual fluctuations in Hg loading or availability.

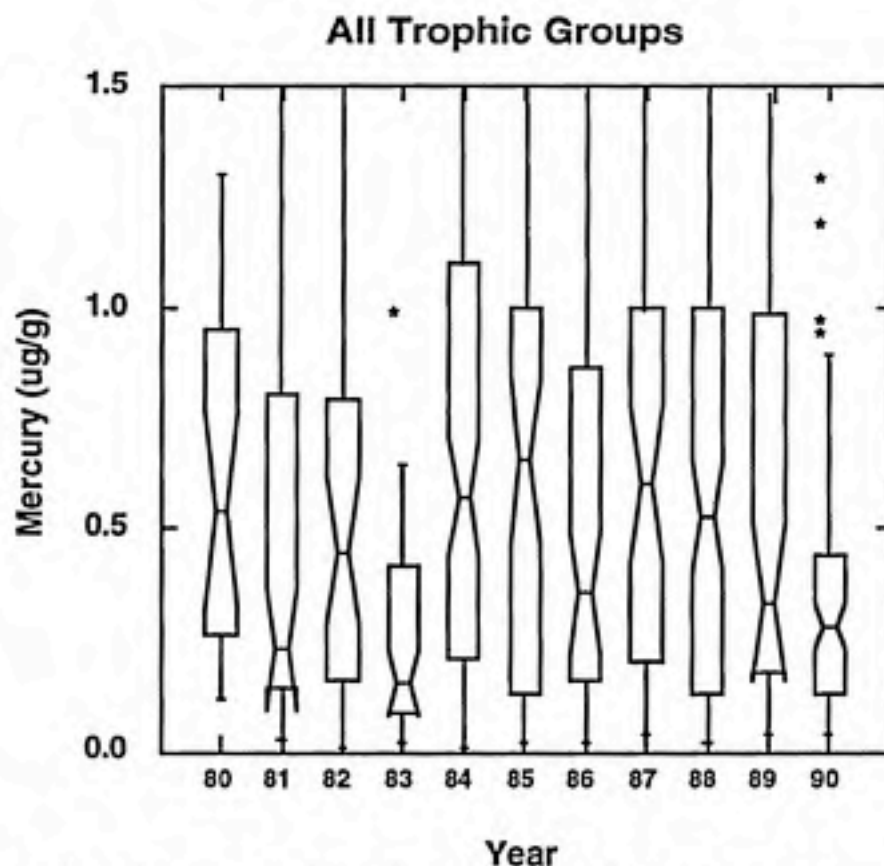


Figure 4.11 Notch box-plot of median Hg concentrations for all four species at all locations.

Largemouth Bass

There appears to be no consistent trend in the Hg content of largemouth bass at all sites over the ten year period (Figure 4.12-4.15). There was no apparent correlation between fish Hg concentrations and year at LTAL (Figure 4.12). Fewer largemouth bass were caught at Center Street than at the other Abbots Creek sites, sample sizes did not provide enough information with which to determine trends in Hg concentration at this location (Figure 4.13). There were not enough data to form ranges around the median in 1981, 1984, 1985, or 1989. Median Hg concentrations at NC47 from 1985 to 1990 were usually lower than from 1981 to 1984 (Figure 4.14). The mercury content in

bass at NC8 increased from 1980-82 then declined fairly steadily until 1990 (Fig. 4.15). After 1985, the contamination of bass at NC8 was below the 1983 level for the control reservoir. Mercury contamination in NC8 largemouth bass may therefore be approaching background levels. The final few years of data at NC47 and NC8 suggested that the mercury concentrations in fish may be decreasing, but continuing data collection will be necessary to determine whether this trend will continue.

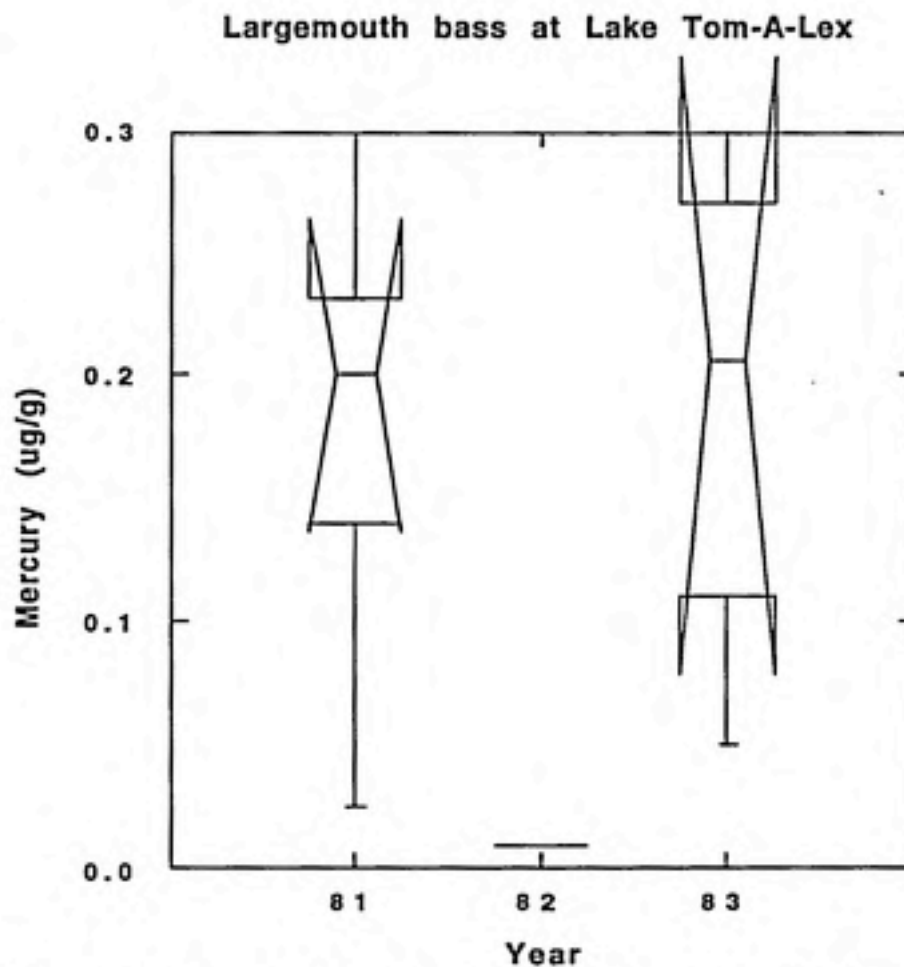


Figure 4.12 Notch box-plot of largemouth contamination at lake Tom-A-Lex.

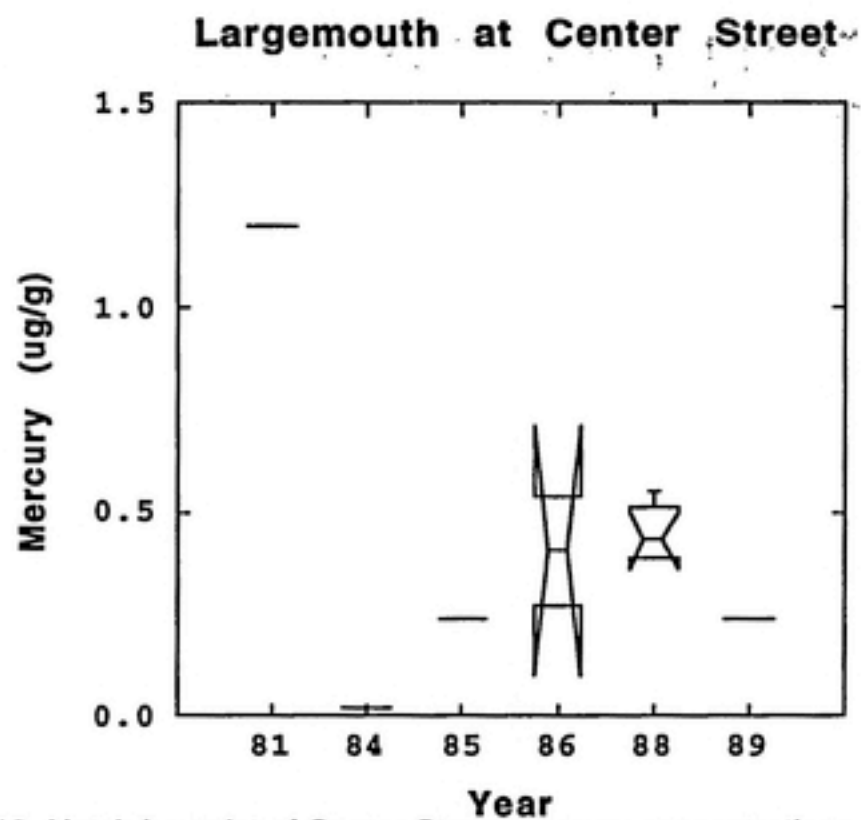


Figure 4.13 Notch box-plot of Center Street mercury concentrations.

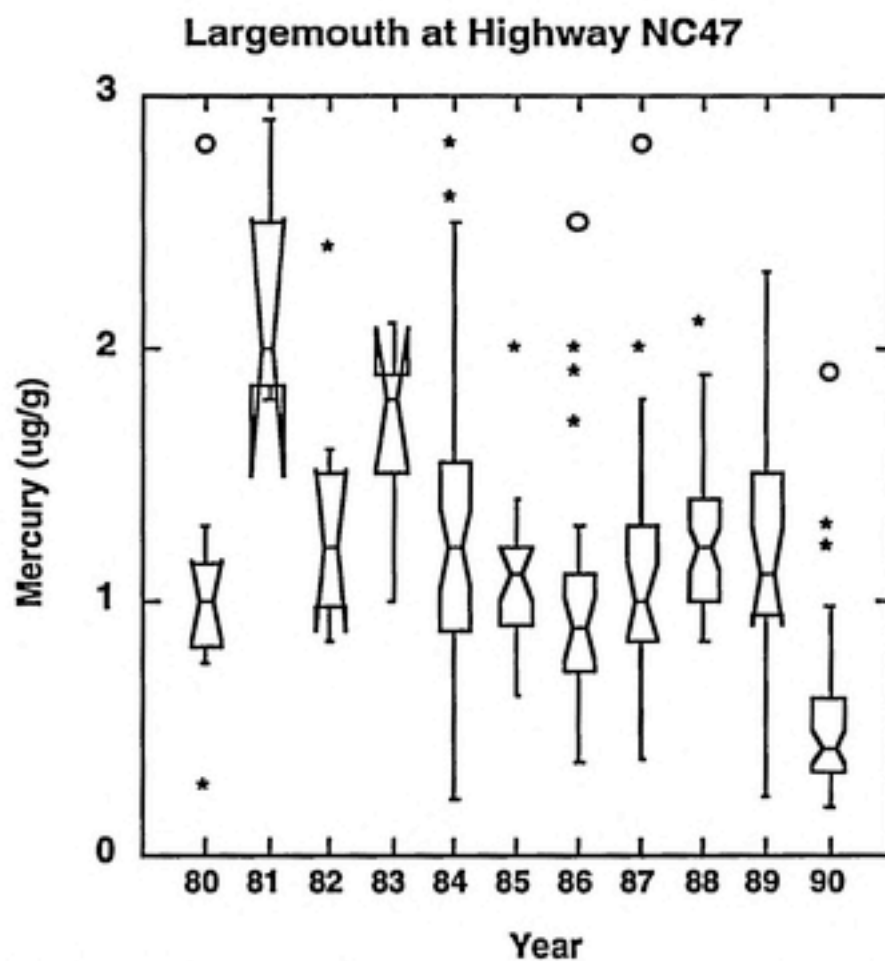


Figure 4.14 Notch box-plots of mercury concentrations over time at NC47.

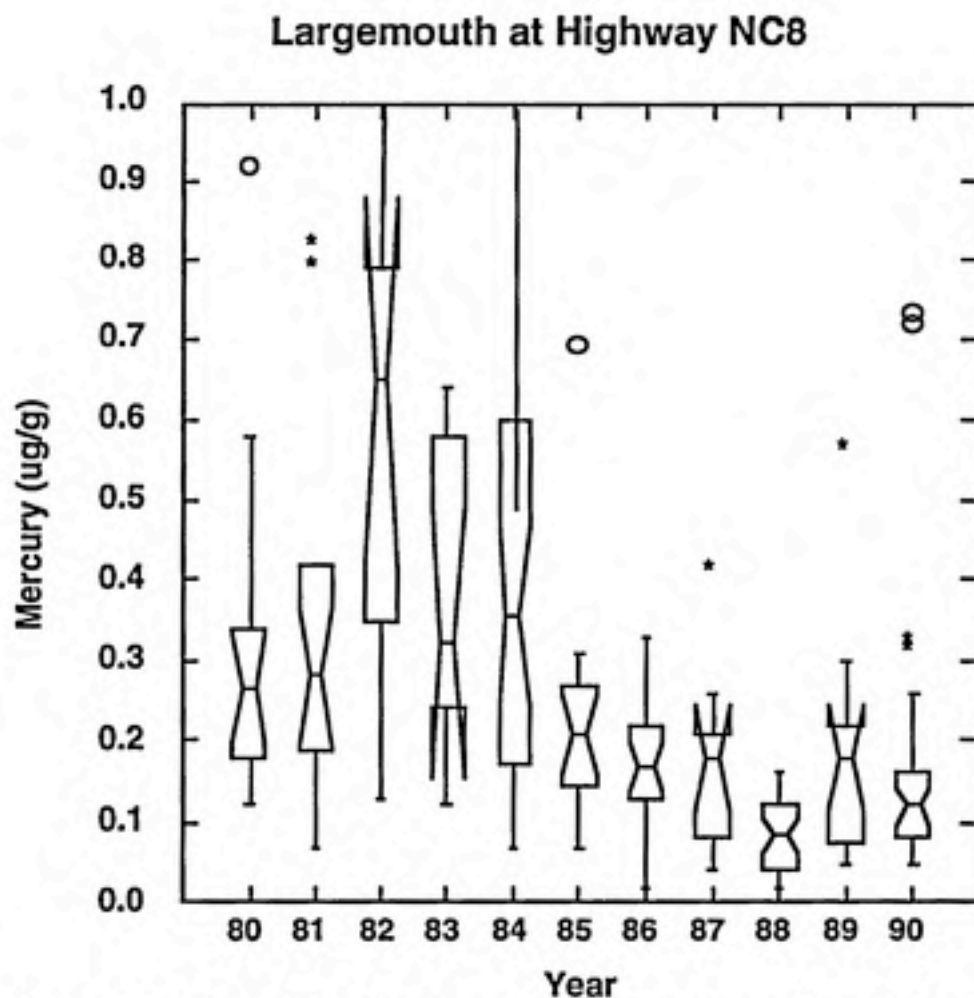


Figure 4.15 Notch box-plots of largemouth mercury levels from 1980-1990 at NC8.

Seasonal Patterns In Mercury Accumulation

The data suggest that season of collection did not have a profound effect on fish Hg burdens in this system. Season did not significantly influence the mercury concentrations either for all species (Table 4.4) or for the largemouth bass alone (Figure 4.16).

Table 4.4 Evaluation of seasonal impact on mercury content in all trophic levels.

Dependent Variable=LogHg	N=963		Squared Multiple R=0.004		
Independent Variable:	Sum-Of-Squares	DF	Mean-Square	F-Ratio	P
Season	1.1	2	1.1	4.22	0.04
Error	250.63	961	0.26		

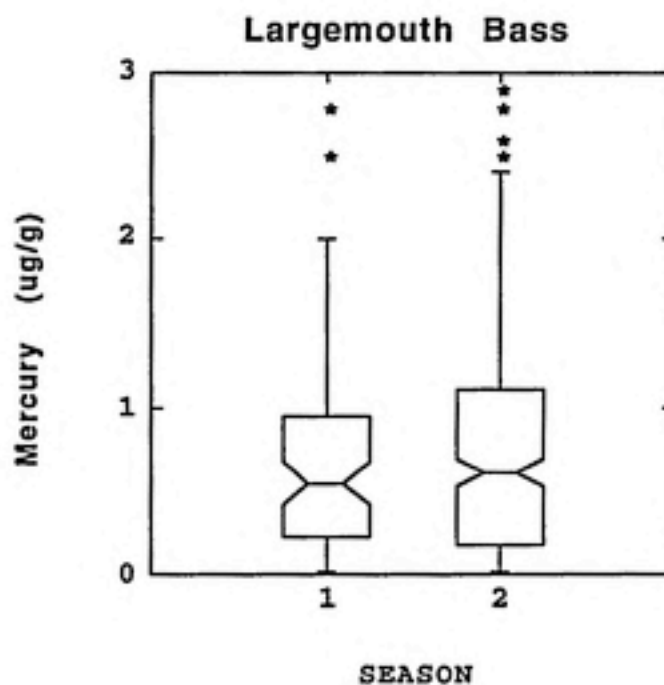


Figure 4.16 Median values for largemouth bass. 1=Spring 2=Fall

DISCUSSION

When all the data were analyzed as a group, trends in mercury contamination over fish size and time were not always apparent. Examining the behavior of Hg accumulation within an individual species, the largemouth bass highlighted relationships that otherwise might have been overlooked. The sampling location appeared to influence much of the variance in fish mercury concentrations in Abbotts Creek, and the size of the fish and its trophic position also effected fish contamination levels. The accumulation of Hg in fish over time varied among sampling locations which may have been due to distance from mercury sources, possible reductions in mercury discharges, or sedimentation patterns.

Ninety to ninety-five percent of the water column mercury levels from 1980 to 1990 fell below analytical detection capabilities (Jay Sauber, personal communication), suggesting either that mercury was removed quickly from the water column or that very low concentrations of Hg are capable of accumulation in fish. Bioaccumulation of Hg was occurring in Abbotts Creek which led to measurable Hg levels in the fish community. Mercury is known to sorb quickly to organic particles. High concentrations of suspended organic matter are common in stream systems. In Abbotts Creek, exposure to mercury in the watercolumn may or may not directly affect fish contamination levels.

Fish, especially largemouth bass, appear to be suitable organisms for use in monitoring the environmental impacts of very low concentrations of mercury. Largemouth bass are large fish at the top of the food chain. There were enough largemouth data to begin to understand some of the mechanisms

behind the accumulation of mercury in fish. Small sample sizes limited the interpretation of trends in other species. Fish bioaccumulate Hg from undetectable levels in water to detectable levels in their tissues. The amount of Hg that was accumulated differed among species (Figure 4.2). The different levels of Hg accumulation appeared to be related to dietary and trophic differences, size differences, length of exposure time (fish age), and possibly feeding location. Metabolism and age differences among species will affect uptake of Hg from the water column and mercury concentrations in fish tissues (deFreitas et al. 1975). The data indicated that diet as reflected by trophic position, (Figure 4.1), was a reasonable predictor of inter-species contamination differences when water column Hg concentrations were below test detection limits.

Impact of Dietary Hg on Fish Contamination

The contribution of diet to Hg contamination varied among fish species but it appeared to be the major Hg source in this system (Figure 4.2). Dietary Hg content may have contributed to both biomagnification and bioconcentration patterns in Abbotts Creek fish. Piscivorous fish and fish such as carp whose diet is more closely associated with sediments, appeared to attain higher Hg burdens than zooplanktivores (Figure 4.3). This conclusion is consistent with Jernelöv and Lann's (1971) conclusion that mercury in benthic feeders can be high. The high mercury concentrations in benthic fish were probably due to a variety of factors, including fish size, physical interaction with the sediments, and the ability of benthic macro-invertebrates to accumulate higher concentrations of Hg than fish (UN-WHO, 1989).

Biomagnification

Biomagnification of mercury appeared to occur in Abbotts Creek. Predaceous fish contained higher concentrations of Hg than did planktivorous fish, as found previously by Grieb et al. (1990) and Lindqvist (1991). The planktivorous shad consistently had the lowest amount of Hg contamination (Figure 4.3). Plankton and zooplankton are at the base of the food chain and obtain Hg directly from the water column, and do not accumulate high mercury levels. Largemouth bass, the top predator in the system, generally has the highest Hg concentrations of all species considered here. However, at Center Street, the carp had more mercury than the bass (Figure 4.3). This suggested that trophic magnification was not the sole process affecting Hg accumulation. The common carp often had Hg levels second only to, or greater than, those in the largemouth bass. The carp feeds in close proximity to the sediments and actually takes sediment into its mouth (Scott and Crossman, 1973). The location and manner of feeding that the carp practices may have been responsible for the high Hg concentrations in this species. Fish size and feeding location, or possibly the Hg in sediments or benthic fauna, may also be contributing to the elevated Hg levels in Abbotts Creek fish.

Bioconcentration

Fish size had two main effects on tissue Hg content of individual fish. Large, older fish had been accumulating mercury for a longer time than younger fish and the diets of large fish consisted of larger prey items with correspondingly higher mercury burdens. When weight was considered within a trophic grouping it affected the average Hg concentration (Figures 4.7 and 4.8). Weight differences may have created differences in Hg concentration

between trophic levels if the average size of individuals in the separate trophic groups was quite different.

Mercury appeared to be bioconcentrated by largemouth bass in this system, but ultimately the amount of mercury accumulated was affected by sampling location. The slopes of the relationship between largemouth Hg concentration and fish weight were very similar at NC47 and NC8, for 1990 data, (Figure 4.7 and 4.8) but the intercept of the line was higher at NC47 where consistently the highest Hg levels were seen in all the species investigated (Figure 4.3). Carp Hg concentrations appeared to stay fairly constant in relation to body weight. The carp's diet changes little between age or size classes. An adult largemouth bass's dietary content does not change as it grows but it will consume increasingly larger fish with more Hg ingested per fish. For the gizzard shad, mercury contamination did not appear to be as closely related to the fish's weight. Unlike other species, a shad continues to feed on the same foods as its weight increases (Ewers and Boesel 1935; Lee et al. 1980). Consistency in Hg concentration within a particular location, despite fish size, was the usual pattern for the shad.

Carp were larger than bass on average but only contained slightly higher median mercury levels at Center Street (Figure 4.3). The mean size of largemouths at this location was smaller than at other locations indicating that bioconcentration differences may have effected fish Hg concentrations more than trophic level at this location (Figure 4.9).

In general, bioconcentration appears to be greater in the piscivores than in other species of Abbots Creek, lending further support to the findings of Wren et al. (1983) that Hg bioconcentrates in piscivorous fish. Variations in the pattern of Hg accumulation with fish size at different locations were observed in

Abbotts Creek fish and also among different Swedish and Canadian lakes (Lindqvist 1991, and Suns and Hitchin 1990). In agreement with the Abbotts Creek evaluation, Meili (1991) found that the relationship between fish size and Hg content was not always positive or linear in non-piscivorous fish species. Zooplanktivores and insectivores appeared to accumulate Hg with increased size in a more random manner than did piscivores. Small sample sizes in the Abbotts Creek data may have contributed to the variable patterns of Hg concentration observed in species other than the largemouth bass. The bioconcentration of Hg in fish did not occur independently from the effects of location and trophic level.

Sample Type

The type of sample, fillet or whole, did significantly affect fish Hg contamination (Figure 4.6). Only three percent of all the samples were analyzed as whole fish. Monitoring programs in Sweden (Meili 1991) are based on the analysis of Hg concentrations in fillets of one kg pike (the top predator). EPA and FDA fish consumption advisories are typically based on fish-fillet Hg concentrations. It is not efficient to spend time and money analyzing samples that do not provide useful information.

Locational Effects

Locational differences significantly affected the mean mercury content of the species considered (Table 4.2), but when Hg levels within a single species were compared by location, a complex picture presented itself. Center Street probably received most of its mercury contamination from battery plant sources (Jay Sauber personal communication). As expected, highway NC47 has higher

median mercury concentrations than any sampling site since it is located directly below all of the known mercury sources (See Figures 4.4 and 4.5). At NC47, stream flow dynamics are such that sediment deposition occurs here. Lower mercury concentrations at highway NC8 may be due to the removal of some of the mercury from the water column by sedimentation in the NC47 area. Straightforward biomagnification appeared to be occurring at all locations except at Center Street (Figure 4.3). The implications are that trophic level was important but that locational differences also needed to be considered.

All species evaluated appeared to have their highest contamination levels at NC47 (Figures 4.3; 4.4; 4.5). At most locations there appeared to be an increase in average mercury with an increase in fish weight, but the intercepts of the lines differed among locations. Increased mercury concentration with increased weight, was greatest at NC8 (Figure 4.7 and 4.8). The intercept is higher at NC47. Whether there was more Hg at this site or its bioavailability was greater is unknown. High mercury levels in fish at NC47 may have been related to the large amount of sedimentation that occurred at this location. If mercury was accumulating in the sediments, then benthic fauna may have accumulated higher Hg burdens at NC47 than at other locations. The mercury content of benthic organisms would have affected the mercury contamination in benthic feeders (carp) and possibly have increased mercury levels in the food chain. There was not enough data to support the findings of Håkanson et al. (1988) that sediment mercury concentrations are highly correlated with fish Hg levels, but the preliminary analysis suggested that areas with higher levels of Hg in sediments also had high Hg concentrations in fish (Figure 4.6). Different rates of sedimentation and rates of exchange of mercury between the sediments and the biota at different locations may explain the

patterns of mercury accumulation observed within certain species. Methyl Hg formation has been shown to increase when organic material is added to sediment (Jackson 1991). Areas experiencing organic deposition may be associated with more rapid accumulation of mercury by the biota as is suggested by the findings at NC47 (Figure 4.6).

Center Street largemouth bass had mean contamination levels higher than at NC8 (Figure 4.5) even though Center Street is located above two potential Hg sources and the bass at this location were smaller than at the other locations. The smallest fish of each species were obtained at the Center Street sampling site. A smaller range of fish sizes was also caught at the Center Street location and can possibly be related to the size of the stream. Proximity to the main source of mercury to Abbots Creek may be an important factor effecting Hg concentrations at this location.

Time

Time patterns in Hg contamination were not clear (Figure 4.11). Temporal patterns were difficult to associate with particular mercury releases because the extent and timing of Hg inputs to Abbots Creek were unknown. The mercury content of individual species did not show any clear trends in Hg contamination, but there appeared to be an overall decrease in all fishes at all locations during the last few years of data collection (Figures 4.12-15). Median Hg values in largemouth bass at NC8 from 1985 to 1990 were equal to or lower than the median Hg concentrations in the control reservoir (LTAL) in 1981 and 1983. Further data collection will be needed to determine if the decreases observed will persist in the future.

Seasonality

The effect of seasonality was investigated to determine if changes in Hg concentrations due to season may have biased the interpretation of the results. Unlike Phillips and Buhler (1978) there appeared to be no significant effect of season on fish Hg concentrations (Figure 4.16). Potential seasonal changes in the mercury content of fish are no longer a problem for data interpretation because fish are now sampled only in the fall.

CONCLUSION

Mercury appears to accumulate significantly in the fish community even when Hg concentrations in water meet current regulatory standards and are below analytical detection capabilities. The analytical limitations on Hg measurement restrict the ability of regulatory agencies to lower instream mercury standards.

Further monitoring in Abbotts Creek should include the sampling of fish foods and sediments for Hg analysis to understand better the pathways through which mercury moves into the fish community. Benthic insects could be analyzed for their mercury content to increase understanding of potential routes of mercury cycling from sediments into the food chain. Knowledge of dietary Hg concentrations would help with the quantification of contamination obtained by fish from different environmental sources. Remedial action could then focus upon areas from which fish obtained much of their contaminant load.

Further sediment sampling should help elucidate whether there is a relationship between fish and sediment Hg contamination at the sampling location. Sediment-bound mercury may or may not be an important source of mercury contamination for biota in the years to come. Further data collection may possibly lead to answers to specific questions concerning the behavior of Hg in Abbotts Creek and improve understanding of the trends in Hg contamination over time. An overall decrease in fish mercury levels may be occurring but more data will be needed to reach a more definite conclusion.

This study's findings may help with prediction of contaminant levels and help improve future monitoring and remedial strategies. Without Hg loading information and data on the effects of Hg within the sediments on overlying biota, it is not possible to accurately predict future fish concentrations accurately. Management plans may not need to focus on an individual species, but information can be lost through an interpretation scheme which is too broad. Future questions that could be addressed are:

1. Are the monitoring techniques providing enough useful information?
2. How much of the current fish contamination is being contributed by new Hg sources?
3. How much of the current fish contamination is ten-year old mercury being recycled through the system?
4. At what rate is biomagnification occurring in this system?
5. What can be done to reduce the mercury within the system to a level at which fish are safely edible?

Currently these questions cannot be answered. New methods need to be developed for lowering the analytical detection of mercury so that lower standards of Hg contamination can be developed to protect ecosystem health. Until new techniques exist, measuring mercury in fish is one way to assess the effects of mercury concentrations unmeasurable in wastewaters on aquatic environments.

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APPENDIX 1

Diet by Species

Largemouth Bass (Micropterus salmoides)

Largemouth bass divided into three size groups with corresponding diets (Ewers and Boesel 1935):

21-50 mm: 70% crustaceans, 27% insects and 1.4% fish
51-80.5 mm: 29% crustaceans, 66% insects, and 4.8% fish
81-112 mm: no crustaceans, 11.5% insects, and 88.5% fish

As a largemouth grows, the size of prey fish consumed increases. Fish appear to enter the largemouth diet at about 20mm (Carlander 1969).

Table 8.1 Abbots Creek largemouth length information.

Largemouth Length Information		
Lake Tom-A-Lex		
Mean Length (cm)	Range	Sample Size
36	17.4 to 46.5	10
Center Street		
Mean Length (cm)	Range	Sample Size
17.7	8.3 to 24.5	14
Highway NC47		
Mean Length (cm)	Range	Sample Size
32	10.0 to 50.5	260
Highway NC8		
Mean Length (cm)	Range	Sample Size
34.8	16.2 to 57.9	212

White Catfish (Ictalurus catus)

White catfish eat vegetation and insects, but predominantly fish (Carlander 1969).

Common Carp (Cyprinus carpio)

Carlander (1969) found the basic food of carp to be bottom fauna; primarily chironomids, zooplankton, phytoplankton, and plant remains. Ewers and Boesel (1935) listed the carp's food consumption to be: 51.5% crustaceans, chiefly cladocera; and 36.5% insects. A DEM 1988 State of North Carolina report by Vince Schneider noted that carp consume many different foods including aquatic insects, crustaceans, annelids, mollusks, weeds, seeds, aquatic plants, and algae and that a carp's feeding strategy includes sucking up mouthfuls of bottom sediments then spitting them out and selecting food items from the suspended matter (from Scott and Crossman 1973).

Bluegill (Lepomis macrochirus)

Seaburg and Moyle (1964) found insects and plant material to be the two most important food items and noted that bluegills were rarely piscivorous. Fish in the size range of 60-170mm were found by Etnier (1971) to consume a variety of "small aquatic organisms" most frequently diptera and trichoptera larvae. In streams, terrestrial arthropods were a significant portion of the food. (Carlander 1969).

Gizzard Shad (*Dorosoma cepedianum*)

Shad feed on zooplankton, microcrustaceans, phytoplankton and detritus

(Lee et al. 1980)

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APPENDIX 2

Environmental Monitoring

The purpose of this section is to identify the main components of a successful monitoring program. A monitoring program is most successful when it is tailored to fit the specific conditions. Success can be measured by how well the information gathered addresses the questions being asked. In order to attempt to obtain information that will help solve particular questions, the questions must first be identified. Monitoring for a specific pollutant is affected by a number of factors, including the sources of the chemical, the chemistry of the contaminant and the environment, and the potential movement of the chemical through the environment. A chemical's motility is affected by a number of factors, including its chemistry, bioavailability, persistence, and transformation reactions. During the planning stage of a monitoring program, consideration of the expected behavior of a contaminant can improve the ability of the monitoring program to evaluate the chemical's effect on the environment.

The development of a successful monitoring program begins with a planning stage. This stage should be used to assess the particular situation and to identify data needs. State clearly the purpose of the monitoring program at the start of the planning phase. Identifying the questions that are being asked will provide the base on which to establish monitoring efforts. The type and number of samples needed for statistical or other analyses can be determined by identifying how the data will be used and analyzed. Methods for accurately measuring the contaminant in environmental samples should be established.

Analytical considerations affect how samples are obtained, stored, and transported.

When a monitoring program is initiated in response to a particular problem it is important to consider the contamination sources and the amounts released. Identifying the sources will enable the program to set sampling boundaries and map out specific sampling locations. Information on how much contamination was released may make possible the use of mass balance calculations to predict the fate and movement of the chemicals. Establishing a control or comparison site not exposed to the contaminant ^{is important for} will aid data interpretation. The ability to interpret trends in data is improved by having monitoring information from a reference site that has been exposed to lower contamination levels than the study area. During the planning stages an attempt should be made to predict the behavior of the chemical in the environment based on known chemical properties, and predicted transformation reactions, ^{and results from other field studies.}

When focusing on a particular contaminant, consideration of its chemical behavior will provide information that can be used to identify which substrates to sample. ^{redundant} ~~Knowledge of the chemical's typical behavior increases the ability of~~ researchers to predict where the chemical will be found. ^{strongly adsorbs} ~~If it can be predicted that the chemical will have an affinity for sorption onto surfaces of suspended~~ particles ~~in the water column~~, then sediments as well as the water column should be monitored. Knowledge of the chemical transformations and common reactions ^{also permit} may ~~make possible~~ predictions of the chemical's behavior within the environment over time. ^{the location, the mechanism,}

^{and so} The behavior of a contaminant over time determines ~~how and to what~~ extent ^{is critical} organisms will be exposed. ~~Where and how a chemical moves through~~

the behavior in
the environment ^{determine} affects which species are affected and the concentrations ^{to which} they are exposed ^{of}. Any planning effort should attempt to predict the behavior of the contaminant in the ecosystem so that the monitoring program can obtain information on the areas and organisms most affected by the chemical. The organisms most likely to be affected can be monitored for adverse affects. Sampling a range of different biota may uncover information on unexpected pathways in the environment.

Ideally, a monitoring program should be designed so that it is flexible enough to incorporate new information and can adapt to changes in environmental conditions. Results obtained from initial monitoring efforts can be reviewed to determine ways to improve future methods. Monitoring information may indicate the need to sample different or additional substrates and organisms if the current program is not providing the needed information. Ongoing reassessment of the monitoring program's needs and goals will provide the framework for a successful monitoring effort.

*But one also must
with () internal
considering in data base*

*Changes in methods??
should be made only if
then will improve significance,
with due regard to problems
arising in statistical treatment
of data.*