Effects of stream water chemistry on mercury concentrations in brook trout (*Salvelinus fontinalis*) in Shenandoah National Park

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BACKGROUND AND JUSTIFICATION

Mercury (Hg) is a toxic element that naturally occurs in aquatic systems in very low concentrations. Past human use of the metal for industrial and agricultural purposes has resulted in serious contamination of many surface waters. Even in remote, relatively pristine areas where direct anthropogenic inputs are lacking, long-range atmospheric transport of Hg from fossil fuel combustion and other sources has led to increased concentrations in freshwater systems and biota (Downs et al. 1998, Fitzgerald et al. 1998). Concentrations of Hg sufficient to prompt fish consumption advisories (i.e., > 0.5 ug/g) have been reported for predatory fish from relatively remote areas with no on-site anthropogenic or geologic sources of Hg (e.g., Abernathy and Cumbie 1977, Bodaly et al. 1984).

The chemistry of Hg is complex and consequently its behavior is difficult to predict in nature. Total mercury concentrations in the environment have not been found to be effective predictors of bioaccumulation in fish. Depending on physical, chemical, and biological conditions at a site, Hg can remain largely tied up in sediments, released from sediments to the water column, be lost to the atmosphere, be transported with sediment particulate matter to other locations, or be taken up by aquatic biota where it may concentrate and become a threat to humans and other fish-eating animals (reviewed in Ullrich et al. 2001). Although the precise factors controlling the accumulation of Hg in aquatic biota are not fully understood, it is clear that fish and other aquatic species are much more efficient in accumulating methylmercury (MMHg) than the inorganic forms that predominate in the abiotic component of the environment (Mason et al. 1995). Thus, factors that influence the rate in which in inorganic Hg is transformed to MMHg also influence bioaccumulation as well.

Although the process of Hg methylation is complex, the results of numerous studies on contaminated lakes indicate that enhanced Hg methylation rates and bioaccumulation have been consistently linked to low pH, low salinity, and the presence of organic matter in low oxygen environments (reviewed in Ullrich et al. 2001). The relationship between water chemistry and Hg methylation has not been fully investigated in stream ecosystems.

Streams in SNP vary considerably in terms of pH and other important water chemistry parameters due to variation in dominant bedrock class underlying individual catchments. All the streams in SNP are characterized by low salinity or ionic strength. Streams underlain by siliciclastic bedrock have low acid neutralizing capacities (ANC) and consequently very low pH. As a result of their low pH, these streams may be the most vulnerable to mercury contamination. Streams underlain by basaltic bedrock have higher ANC and pH. Streams underlain by granitic bedrock have intermediate ANC and pH. We thus expect that bedrock distribution in SNP may reflect a gradient in watershed response to atmospheric deposition of mercury.

In addition to variation in water chemistry, there is variation in landscape setting that may be important. In particular, elevation has been shown to affect Hg deposition in some areas though results have been contradictory. For example, total Hg deposition has been shown to be greater in watersheds at higher elevations due to cloud deposition (i.e., wet Hg deposition associated with mist and fog) (Shanley et al. 2005). However, methylmercury in sediments and biota have been shown to be higher in lower elevation sites, presumably because the greater watershed areas support a larger number of wetlands and other sites where Hg methylation occurs (Kamman et al. 2005).

The objectives of this study were to 1) evaluate the potential threat of mercury to humans that consume fish caught in the park, and 2) determine the extent to which variation in bedrock geology and water chemistry influence mercury accumulation in brook trout, the primary game fish in the park.

METHODS

General Design and Site Selection

We conducted a comparative watershed study to determine Hg concentrations in brook trout and other fish species in SNP streams. Sampling occurred in three distinct stream types that were defined by the major bedrock type underlying the watershed. Previous research has established a strong association between bedrock distribution and stream water chemistry, physical habitat, and the richness and productivity of fish assemblages (Bulger et al. 1999a, Galloway et al. 1999). Major bedrock strata for the study included the low acid-neutralizing capacity (ANC) siliciclastic bedrock, medium ANC granitic bedrock, and the high ANC basaltic bedrock type. We also stratified sites by elevation. Specifically, we selected sites in upper (high elevation) and lower (low elevation) portions of selected catchments.

Sampling occurred during the summer (July-August) of 2004 and coincided with fish monitoring conducted as part of the park's Fisheries Monitoring Program (Atkinson 2002). Fish and stream water chemistry data were collected from a total of 32 sites representing 18 catchments (seven catchments underlain by mostly siliciclastic bedrock, six catchments by granitic bedrock, and five catchments by basaltic) (Fig. 1). In most catchments we sampled fish at two sites, one further up in the watershed at higher elevation, and a more downstream site that was lower in elevation. The main focus of the study was on brook trout (*Salvelinus fontinalis*). However, we also collected individuals of six other species at some sites. Other species included American eel (*Anguilla rostrata*), blacknose dace (*Rhinichthys atratulus*), brown trout (*Salmo trutta*), rock bass (*Ambloplites rupestris*), smallmouth bass (*Micropterus dolomieui*), and white suckers (*Catostomus commersoni*). Only total Hg in fish was assessed. However, it has been repeatedly shown that nearly all Hg mercury in fish is in the more toxic methylmercury form (Bloom 1992).

Field sampling

We collected approximately 15 brook trout at each site using electrofishing gear and techniques as prescribed in the park's Fisheries Monitoring Protocol (Atkinson 2002). In addition, at some sites we collected several fish of other species. Because of the overwhelming influence of age or size on Hg concentrations in fish (Mason et al. 2000), we made special efforts to collect fish that represented all life stages. The sampling goal at each site was five young-of-the-year or age zero trout, five age one/age two trout and five age two/age three trout. Fish Samples were placed into zip-lock bags and placed on ice and frozen upon returning to the lab (within 24 h).

Subsequently, frozen fish samples were shipped to the Patuxent Analytical Control Facility (PACF) for analysis.
Immediately prior to fish sampling, we obtained *insitu* measurements of stream water temperature and pH, and stream water samples were collected for laboratory analysis of pH, ANC, conductance, and major ions.

Laboratory analysis

Total Hg concentrations in fish were assessed at the Patuxent Analytical Control facility using atomic absorption spectrometry (USEPA 1991). Fish were measured, weighed, and the moisture content determined prior to digestion and analysis. Digestion and mercury analyses included quality control procedures as described in Stafford and Haines (1997). Water chemistry samples collected in the field were analyzed at the SWAS program laboratory at the University of Virginia. Protocols for analyses, and quality assurance were performed by methods appropriate for low-ionic strength waters, as documented in the SWAS Standard Operating Procedure. All water quality data obtained through the project will be maintained in the SWAS data base. Analysis of pH and sample collection and handling were conducted in accordance with the SWAS Standard Operating Procedure (http://wsrv.clas.virginia.edu/~swasftp/docs/9509_sop/cover.html). Major ion analysis included sulfate, nitrate, chloride, calcium, magnesium, potassium, and sodium.

Data Analyses

To assess health risks of Hg ingestion by humans from eating contaminated fish caught in the park, we evaluated the levels of total mercury found in fishes in SNP streams relative to "Fish Consumption Limits" developed by the EPA (USEPA 2001). These guidelines report the number of allowable fish meals per month based on the ranges of methylmercury in the consumed fish tissue, and are based on the following assumptions:

1) Consumer adult body weight of 70 kg (154 pounds)
2) Average fish meal size of 0.225 kg (8 oz).
3) Time-averaging period of 1 mo
4) Reference dose of 1x10-4 mg/kg/d

We used Principal Components Analysis (PCA) to determine the predominant gradients in overall water chemistry within SNP streams. Subsequently, we used PCA scores as the dependent variable in ANOVA to determine the amount of variation in water chemistry explained by underlying geology.

We used general linear modeling (GLM) to test the effects of bedrock type (and thus water chemistry correlates) on mercury accumulation rate in brook trout. Specifically, we regressed total mercury concentration in individual brook trout (ppm wet weight) by fish size (grams wet weight), and evaluated the significance of the interaction between bedrock type and fish size. The interaction term specifies whether the rate of mercury accumulation with size (i.e., the regression slope) is dependent on bedrock type. Subsequently, we used two-sample t-tests to the statistical significance of differences in Hg accumulation rates between each pair of bedrock types (i.e., siliciclastic versus basaltic, siliciclastic versus granitic, granitic versus basaltic). We used the same approach to test for the influence of elevation (upper versus lower sites) on Hg accumulation.

RESULTS

Potential human effects

One of the primary objectives of the study was to determine whether Hg concentrations in fish in SNP streams were of a level that poses a threat to humans who consume fish for food. Our focus for this study was on brook trout. However, we collected individuals of six other species for Hg analyses, though sampling was much more limited for these species with relatively few individuals collected from only one or two sites. Thus, we do not attempt to imply with these data that the ranges observed for these other species represent the range found in SNP streams. Rather, these data can only be used to infer the lower bounds on maximum concentrations. That is, it is possible that some of these species have higher mercury concentrations in other SNP streams.

Total Hg concentrations in fish in SNP streams varied substantially among species (Fig. 2). Hg concentrations were highest in American eel and brown trout. This is not surprising as both of these species are at the top of the food web, consuming mainly other fish. It is well known that Hg concentrations magnify up the food chain (Wiener et al. 2002) with top predators having several orders of magnitude more Hg than species near the bottom of the food web. Moreover, American eel is by far the longest lived fish in these small streams, and the age of fish has also been shown to be a strong predictor of Hg concentrations (Huckabee et al. 1979). Based on their large size, it is likely that a large fraction of the 13 eels collected were 10+ years old. Likewise, the 15 brown trout collected were mostly of larger age classes.

Rock bass and smallmouth bass were intermediate in terms of Hg concentrations (Fig. 2). This pattern is also not surprising because, relative to the other species sampled, these species are intermediate in terms of both their position on the food web and longevity.

However, blacknose dace also had relatively high mercury concentrations, typically lower than both American eel and brown trout, but higher on average than both rock bass and smallmouth bass (Fig. 2). This is surprising in light of their relatively low position on the food web and their fairly short life spans and small sizes. All blacknose dace were collected from Lewis Run, a stream that is underlain by siliciclastic bedrock and consequently possibly more vulnerable to Hg accumulation (see below). However, all the smallmouth bass and rock bass assessed were also collected only from streams underlain by siliciclastic bedrock. Thus, it is unclear why Hg concentrations in blacknose dace are so high relative to some of the other species.

Also somewhat surprising was our observations that brook trout had the lowest Hg concentrations measured (Fig. 2). Based on their position on the food web, size and longevity, we would have predicted Hg concentrations comparable to those found in rock bass and smallmouth bass. Our results suggest that Hg accumulation patterns in both blacknose dace and brook trout are different than what one would expect given current paradigms regarding biomagnification of mercury.

The United States Environmental Protection Agency (EPA) has estimated human risk associated with eating mercury contaminated fish. Short-term, acute toxicity (e.g., impaired central nervous system function, kidney failure, cardiovascular collapse, and death) has only been demonstrated in areas severely polluted with industrial wastes and where humans consume very high quantities of fish (USEPA 2000). Acute mercury toxicity is clearly not an issue in Shenandoah National Park.

However, there has been considerable debate within the scientific community regarding the level of exposure to methylmercury that is likely to produce no appreciable risk of deleterious effects during a human lifetime (i.e., chronic effects). Of particular concern are effects of dietary exposure of mercury on children, the elderly and infirm, and pregnant women and their fetuses. Although considerable uncertainty remains, the EPA has developed a set of recommendations regarding consumption of contaminated fish based on available data and factors built in for uncertainty (USEPA 2000).

Table 1 shows the recommended fish consumption limits for various fish tissue concentrations. Clearly, mercury concentrations measured for many of the species collected in SNP streams exceed levels that can be safely consumed in large amounts. For example, based on the observed median Hg concentrations in some species, and the consumption limit recommendations of the EPA, humans should consume fewer than three 8-ounce meals per month of American eel, and fewer than four 8-ounce meals per month of brown trout. Also, median Hg concentrations observed in smallmouth bass and rock bass indicate that fewer than eight 8-ounce meals can safely be consumed per month (Table 1). However, as stated above, many of the animals collected of these species were probably older and of larger than average size, and therefore observed concentrations probably reflect the upper end of Hg concentrations for these species park-wide. Nevertheless, because, with the exception of American eels, these species are frequently taken for food by fishermen, park management may want to consider management actions to minimize human risks.

Table 1. Monthly fish consumption limits for methylmercury (USEPA 2000). Table shows the number of meals (8 oz wet weight portions) that can be safely consumed for various levels of tissue contamination. Table also shows the proportion and number (in parentheses) of brook trout we caught in each tissue contamination range.

Fish meals per month	Fish tissue concentrations (ppm, wet weight)	Proportion of brook trout
NA	<0.03	0.467 (196)
16	>0.03 – 0.06	0.421 (177)
12	>0.06 – 0.08	0.074 (31)
8	>0.08 – 0.12	0.036 (15)
4	>0.12 – 0.24	0.002 (1)
3	>0.24 – 0.32	0
2	>0.32 – 0.48	0
1	>0.48 – 0.97	0
0.5	>0.97 – 1.9	0
0	> 1.9	0
	Total	1.000 (420)

The main focus of this study was on brook trout because of their high abundance in SNP streams relative to other game species. However, in contrast to other species assessed, Hg concentrations in brook trout were low, and consequently they are not likely to pose a significant risk to humans. For example, we found that nearly half (46.7%) of the brook trout we caught had Hg tissue concentrations below which EPA consumption limit recommendations apply (i.e., <0.03 ppm) (Table 1). Moreover, another 42% of brook trout we collected had tissue concentrations of 0.03 to 0.06 ppm, the lowest level for which consumption limit recommendations apply. At this level of contamination, recommendations call for eating no more than 16 fish meals per month (Table 1). This is a relatively high consumption rate. Only about 11% of brook trout had Hg concentrations higher than 0.06 where stricter consumption limit recommendations apply. One cautionary note, fish taken for food tend to be the larger fish, and larger fish typically contain higher mercury concentrations. However, because of our sampling design, approximately one third of all the brook trout collected (approx. 140 fish) were larger fish (>2 yrs). Because only 47 fish had Hg concentrations above 0.06 ppm, it is clear that even most large fish had Hg concentrations of less than 0.06 ppm. Thus, the odds of taking a brook trout with Hg concentrations above 0.06 ppm is fairly low (approx. 1 in 9), and the consumption limit recommendations for brook trout with relatively high Hg concentrations (i.e., between 0.06 and 0.12) are fairly liberal (8-12 8 oz fish meals per month), it seems fairly unlikely that Hg exposure to humans from consumption of SNP brook trout poses a serious health threat to humans.

Spatial Variation in Hg Concentrations

Water Chemistry Patterns

Though mercury concentrations in brook trout in streams in SNP are not likely to pose a risk to human health, there were clear differences in the range of mercury concentrations in brook trout among streams in SNP (Fig. 3). The second objective of this study was to assess spatial variation in mercury concentrations in an effort to identify important environmental factors that affect mercury accumulation in fish.

Prior to assessing Hg accumulation patterns in fish, we examined water chemistry patterns to determine if stratifying sampling by bedrock geology was effective in representing major gradients in water chemistry as we intended. Principal Components Analysis indicated that the 12 water chemistry variables measured at each site could be reduced to three uncorrelated factors that explained 90% of the variability in overall water chemistry. The first factor explained nearly 64% of the total variance and positively correlated with calcium, alkalinity, pH, sodium, specific conductance, silica, and magnesium; and negatively correlated with hydrogen ions and potassium (Table 2). A second uncorrelated factor explained about 14% of the total variance and positively correlated with sulfates. The third factor explained about 13% of the total variance and positively correlated with chlorides and nitrates (Table 2).

Table 2. Results of Principal Components Analysis of 12 water chemistry variables. We report the factor loadings of each of the three gradients (factors) with eigenvalues greater than 1. PCA scores in bold were highly correlated with the indicated factor.

	Factor Loadings		
Parameter	Factor 1	Factor 2	Factor 3
Calcium	**0.959**	0.200	0.132
Alkalinity	**0.953**	0.237	-0.105
pH	**0.949**	-0.226	-0.054
Sodium	**0.919**	0.072	-0.241
Specific Conductance	**0.871**	0.477	0.097
Silica	**0.858**	0.151	-0.371
Magnesium	**0.841**	0.496	0.042
Hydrogen	**-0.773**	0.374	0.111
Potassium	**-0.740**	0.557	0.026
Sulfate	-0.575	**0.721**	0.166
Chloride	0.530	-0.186	**0.718**
Nitrate	0.314	-0.059	**0.844**

Results of ANOVA comparing PCA factor scores among rock types indicated that a large percentage of variability in overall water chemistry is explained by bedrock geology. Specifically, nearly 88% of the variance in PCA-1 scores was explained by bedrock geology (ANOVA, $F=95.72$, $p<0.00000001$). PCA-1 scores were highest in basaltic bedrock, followed by granitic, and then by siliciclastic (Fig. 3). Likewise, a substantial amount of variability in PCA-2 scores (55%) was explained by bedrock geology (ANOVA, $F=16.71$, $p<0.0001$). Specifically, PCA-2 scores in streams draining granitic bedrock were lower than those draining basaltic and siliciclastic bedrock types (Fig. 3). Bedrock geology did not explain a significant amount of variation in PCA-3 scores (ANOVA, $F=0.16$, $p=0.85$) (Fig. 3). Taken together, these results indicate that stratifying our sampling by bedrock geology was effective in representing major gradients in water chemistry with the exception of chloride ions and nitrates (correlated with PCA factor 3) which did not correlate with bedrock geology.

Effect of fish size on Hg concentrations

The age or size of individual fish has repeatedly been shown to have a strong influence on mercury concentrations (Huckabee et al., 1979). Thus, prior to evaluating other factors, it is important to describe and account for the relationship between fish size or age and mercury concentrations. We did not age fish and so we only assessed size (weight) effects.

Overall, the relationship between brook trout Hg concentration and fish weight was linear and relatively strong (Fig. 4). Fish weight alone explained nearly 35% of the total variation in tissue Hg concentrations. Overall in SNP streams, Hg concentrations in brook trout increased, on average, 0.035 ppm with every 0.5 kilogram increase in fish weight.

Effects of bedrock type on Hg accumulation

Although there was substantial within-site variation in Hg concentrations at all sample sites, we found considerable variation in Hg concentrations among streams as well (Fig. 5). Moreover, we found that the interaction between fish size (weight) and bedrock type was a significant predictor of brook trout Hg concentrations ($F = 43.74$; $p < 0.00000001$; df = 2,416), indicating the rate at which Hg accumulated with fish size depended on the dominant surface geology in the watershed. As hypothesized *a priori*, brook trout in streams underlain by Siliciclastic bedrock accumulated mercury at a faster rate than fish in streams underlain by granitic bedrock, and brook trout in streams underlain by granitic bedrock accumulated mercury at a faster rate than fish in streams underlain by basaltic bedrock (Fig. 6). Differences in accumulation rates among bedrock types were statistically significant among all three types (T-test; $p<0.000001$ for all three comparisons). In streams draining predominantly Siliciclastic bedrock, Hg concentrations in brook trout increased on average 0.047 ppm with every 0.5 kilogram (1.1 pound) increase in fish weight. In contrast, in streams draining basaltic bedrock, fish accumulated mercury at about half the rate observed in streams underlain by siliciclastic bedrock (i.e., 0.024 ppm with every 0.5 kilogram increase in fish weight). Hg accumulation rate in streams draining granitic bedrock was intermediate to the other two bedrock types (i.e., 0.033 ppm per 0.5 kilogram increase in fish weight).

However, although we found that bedrock explained a significant amount of variation in Hg accumulation rates in brook trout, there was clearly a substantial amount of unexplained variation. This unexplained variation can clearly be seen in the scatter around the regression lines within all three bedrock types (Fig. 6). The relationship between Hg concentrations and fish size was strongest for the siliciclastic bedrock type with nearly 56% of the variation in Hg concentrations explained by fish size. The relationship between Hg concentration and fish size was substantially weaker for the other two bedrock types with 34% and 27% of the variation in Hg concentrations explained by fish size for basaltic and granitic rock types respectively (Fig. 6).

Effects of elevation on Hg accumulation

In contrast to bedrock type, the other main predictor variable that we used as a sample stratification variable, elevation, did not explain a significant amount of variation in the rate of Hg accumulation with fish size. That is, the effect of the interaction between elevation and fish size was not a significant predictor of Hg concentrations in brook trout ($F = 2.44$; $p = 0.12$; df = 1,402), indicating that Hg accumulation rates were similar between upper and lower sites overall (Fig. 7).

However, when we tested for the effects of elevation *within individual bedrock types*, we found that elevation *did* explain a substantial amount of the variation in Hg concentration within two of the three bedrock types. However, the patterns were not consistent between the two rock types. Specifically, within the basaltic bedrock type, the relationship between fish size and Hg concentration (i.e., Hg accumulation rate) was strong for upper elevation sites but not for lower elevation sites (Fig. 8). This pattern suggests that something else besides bedrock type and fish size was important in terms of Hg accumulation rates in “lower” elevation sites. In contrast, within the granitic bedrock type the exact opposite pattern was observed. Lower elevation sites showed a tight relationship between Hg concentration and fish size; and upper elevation sites did not. In contrast to the other two bedrock types, Hg accumulation rates were not substantially different between upper and lower elevation sites within the siliciclastic bedrock type (Fig. 8).

Effects of sulfates and nitrates
Although bedrock geology explained a significant amount of variation in Hg accumulation rates in brook trout, and site elevation was found to be secondarily important, there remained considerable unexplained variation in Hg accumulation rates. Specifically, there remains substantial variation in low elevation sites in streams underlain by basaltic bedrock, and higher elevation sites underlain by granitic bedrock (Fig. 8).

As noted earlier, a considerable fraction of the variation in water chemistry was explained by bedrock type. However, there was no relationship between bedrock type and some water chemistry variables including nitrate concentrations. In addition, although a significant fraction of variation in sulfate concentrations (correlated with PCA factor 2) was explained by bedrock, a substantial amount of the variation remained even after accounting for bedrock type. Sulfates were of particular interest to us because they have been found to positively stimulate Hg methylation by sulfate reducing bacteria and increase bioaccumulation in fish in field experiments (Harmon et al. 2005). However, in contrast to field experiments, field surveys involving numerous sites in the northeastern US showed sulfate concentrations negatively correlate with methymercury concentrations in fish (Chen et al. 2005). The reasons for these differences are not clear. We conducted additional analyses to determine whether variation in sulfates or nitrates explained additional variation in Hg accumulation patterns in SNP.

For these analyses we took residuals from the linear regression of Hg concentration on fish size, and regressed them against sulfate and nitrate concentrations within each bedrock type. In this way, we are testing for the effects of nitrates and sulfates after accounting for the effects of fish size and bedrock type.

We found that although both sulfates and nitrates explained a significant amount of variation in mercury after accounting for fish size in some bedrock types (i.e., residual variation), the amount of additional variation explained was not particularly large. For example, the relationship between sulfates and residual Hg concentration was statistically significant only within the granitic rock type (LS regression, $T=-2.52$, $p=0.01$). However, even within the granitic rock type, sulfates only explained 4% of the variation in residual Hg concentrations (Fig. 9). The relationship between sulfates and residual Hg concentrations was not significant within the other two rock types (LS regression, $p>0.10$).

The amount of residual Hg concentrations explained by nitrates was only slightly better that observed for sulfates. Specifically, the relationship between nitrates and residual Hg concentrations was statistically significant for granitic and siliciclastic bedrock types (LS regression, $p<0.05$). Nitrates explained about 11% of the variation in residual Hg concentrations at sites underlain by granitic bedrock, and 5.5% at sites underlain by siliciclastic bedrock (Fig. 10).

CONSCLUSIONS

Implications for Human Health

In large measure, we believe that our data suggests Hg does not pose a significant human health threat in SNP. The primary fish species taken for consumption from SNP streams is brook trout, and Hg concentrations in brook trout were very low relative to EPA recommended consumption limits. However, Hg concentrations observed for some other species may suggest some cause for concern. In particular, brown trout, another important game species that is often taken for food were found to have high Hg concentrations relative to EPA recommended consumption limits. American eel also had high mercury concentrations but eels are not frequently taken for food from SNP streams. Two other food species commonly taken in the park, smallmouth bass and rock bass, were also found to have relatively high Hg concentrations, though only about half as high as brown trout. Thus, it may be prudent for park management to consider implementing some management actions, such as posting health advisories, for some of these species.

It should be emphasized that there is considerable uncertainty in our data regarding Hg concentrations in all species collected except for brook trout. In most cases, all individuals of these species came from a single site (American eels samples came from two sites) and the number of individuals examined was small (5-30 animals). Thus, it is possible the Hg concentrations in other streams in the park could be even higher for these species. However, with the exception of brook trout where our sampling was widespread, representative, and relatively intense, we believe it is more likely that observed Hg concentrations for the other six species examined probably represented the higher end of the distribution in terms of Hg concentrations for two reasons. First, we collected mostly larger individuals of these species, and larger animals typically have higher Hg concentrations. Second, all of the animals of these species were collected in streams underlain by siliciclastic bedrock, and fish in these streams accumulated Hg at faster rates than those in other bedrock types (see below).

Factors Affecting Hg Accumulation in Brook Trout

From assessments of spatial patterns of Hg accumulation in brook trout, we conclude that the predominant bedrock type underlying streams was an important predictor of Hg accumulation rates in individual fish. Observed patterns were essentially in accordance with our *a priori* hypothesis. That is, Hg accumulation rates were highest in streams underlain by siliciclastic bedrock, lowest in streams underlain by basaltic bedrock, and intermediate in streams underlain by granitic bedrock. Moreover, these patterns suggest that Hg methylation in streams is sensitive to many of the same water chemistry variables that have been shown to influence Hg accumulation in fish in lake ecosystems. In particular, pH has been found to be indirectly related to Hg methylation and biotic uptake in lakes (Gilmour and Henry 1991, Chen et al. 2005). In this study we found that pH was strongly correlated with bedrock geology, and Hg accumulation rates varied among bedrock types. These patterns suggest that Hg levels in individual fish may be expected to increase if acidic precipitation continues in the region.

In contrast to bedrock type, other factors examined were not particularly informative or patterns were confusing. For example, neither sulfates nor nitrates were particularly informative in terms of explaining variation in fish Hg concentrations. Likewise, although elevation explained a significant amount of variation in Hg accumulation within two of three bedrock types, the effect of elevation was opposite for the two types. This suggests that it was not elevation *per se* that was important but some factor that correlated with elevation within bedrock types but not between bedrock types. One possible explanation that may be consistent with the observed pattern relates to the distribution of wetland habitats. Compared to other aquatic habitats like streams and lakes, wetlands are known to be hotspots of Hg methylation (Wiener et al. 2002). Thus, it could be that wetland habitats may have been distributed differently between the two rock types. That is, in some rock types wetland habitats may tend to be located at higher elevations, perhaps spring seeps in saddle areas where headwaters originate; whereas in streams underlain by other rock types, wetlands habitats may be more prevalent at lower elevations, perhaps in riparian areas. Clearly additional research is needed in this area.

LITERATURE CITED

Abernathy, A. R. and P. M. Cumbie. 1977. Mercury accumulation by largemouth bass (Micropterus salmoides) in recently impounded reservoirs. *Bulletin of Environmental Contamination and Toxicology* 17:595-602.

Atkinson, J. B., 2002. Shenandoah National Park Fisheries Monitoring Protocol. Division of Natural and Cultural Resources, Shenandoah National Park. Unpubl. 68 pp.

Bloom, N. S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian Journal of Fisheries and Aquatic Sciences 49:1010-1017.

Bodaly, R. A., R. E. Hecky, and R. J. P. Fudge. 1984. Increases in fish mercury levels in lakes flooded by the Churchill River Diversion, northern Manitoba. *Canadian Journal of Fisheries and Aquatic Sciences* 41:682-691.

Bulger, A.B., B.J. Cosby, C.A. Dolloff, K.N. Eshleman, J.N. Galloway, and J.R. Webb, 1999a. Shenandoah National Park Fish in Sensitive Habitats (SNP FISH) Project Final Report: Volume I-IV plus interactive computer model. Submitted to National Park Service, Luray, VA. (Available on CD-Rom from John F. Karish, National Park Service, Northeast Field Area, 209B Ferguson Building, University Park, PA 16802-4301, U.S.A.)

Chen, C. Y., R. S. Stemberger, N. C. Kamman, B. M. Mayes, and C. L. Folt. 2005. Patterns of Hg biomagnification and transfer in aquatic food webs across mult-lake studies in the northeast US. Ecotoxicology 14:135-147.

Downs, S. G., C. L. Macleod, and J. N. Lester. 1998. Mercury in precipitation and its relation to bioaccumulation in fish: a literature review. *Water, Air, and Soil Pollution* 108:149-187.

Fitzgerald, W. F., D. R. Engstrom, R. P. Mason and E. A. Nater. 1998. The case for atmospheric mercury contamination in remote areas. *Environmental Science and Technology* 32:1-7.

Galloway, J.N., F.A, Deviney, Jr., and J.R. Webb, 1999. Shenandoah Watershed Study Data Assessment: 1980-1993. Project Final Report, submitted to National Park Service, Luray, VA.

Gilmour, C. C. and E. A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution 71:131-169.

Harmon, S. M., J. K. King, J. B. Gladden, G. T. Chandler, and L. A. Newman. 2005. Mercury body burdents in Gambusia holbrooki and Erimyzon sucetta in a wetland mesocosm amended with sulfate. Chemosphere 59:227-233.

Huckabee, J. W., J. W. Elwood, and S. G. Hildebrand. 1979. Accumulation of mercury in freshwater biota. Pages 277-302 *in* Biogeochemistry of mercury in the environment (J. O. Nriagu, editor). Elsevier Press, New York.

Kamman, N. C., A. Chalmers, T. A. Clair, A. Major, R. B. Moore, S. A. Norton, and J. B. Shanley. 2005. Factors influencing mercury in freshwater surface sediments of northeastern North America. Ecotoxicology 14:101-111.

Lynch, D. D. and N. B. Dise. 1985. Sensitivity of stream basins in Shenandoah National Park to acid deposition. U.S. Geological Survey Water-Resources Investigations Report 85-4115.

Mason, R. P., K. R. Rolfhus, and W. F. Fitzgerald. 1995. Bioaccumulation of mercury and methylmercury. Water, Air, and Soil Pollution 80:915-919.

Mason, R. P., J. M. Laporte, and S. Andres. Factors controlling the bioaccumulation of mercury, methylmercury, arsenic, selenium, and cadmium by freshwater invertebrates and fish. Archives of Environmental Contamination and Toxicology 38:283-297.

Nicoletto, P. F. and A. C. Hendricks. 1988. Sexual differences in accumulation of mercury in four species of centrarchid fishes. *Canadian Journal of Zoology* 66:944-949.

Qian, S. S., W. Warren-Hicks, J. Keating, D. R. J. Moore, and R. S. Teed. 2001. A predictive model of mercury fish tissue concentrations for the southeastern United States. *Environmental Science and Technology* 35:941-947.

Shanley, J. B., N. C. Kamman, T. A. Clair, and A. Chalmers. 2005. Physical controls on total and methylmercury concentrations in streams and lakes of the northeastern USA. Ecotoxicology 14:125-134.

Stafford, C. P. and T. A. Haines. 1997. Mercury concentrations in Maine sport fishes. *Transactions of the American Fisheries Society* 126:144-152.

Ullrich, S. M., T. W. Tanton, and S. A. Abdrashitova. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. *Critical Reviews in Environmental Science and Technology* 31:241-293.

USEPA (U.S. Environmental Protection Agency). 1991. Methods for the determination of metals in environmental samples. USEPA, EPA/600/4-91/010. Office of Research and Development, Washington, D.C.

USEPA (U.S. Environmental Protection Agency). 2000. Guidance for assessing chemical contaminant data for use in fish advisories. Volume 2, 3rd edition. Risk Assessment and Fish Consumption Limits. EPA 823-B-00-008. Office of Water, Washington, DC. Http://www.epa.gov/ost/fish/guidance.html.

USEPA (U.S. Environmental Protection Agency). 2001. Fact sheet: Mercury update: Impact on Fish advisories. EPA-823-F-01-011. Office of Water, Washington DC.

Wiener, J. G., D. P. Krabbenhoft, G. H. Heinz, and A. M. Scheuhammer. 2002. Ecotoxicology of mercury. In Handbook of Ecotoxicology, 2nd edition (D. J. Hoffman, B. A. Rattner, G. A. Burton, Jr., and J. Cairns, Jr., editors). CRC Press.

Figure 1

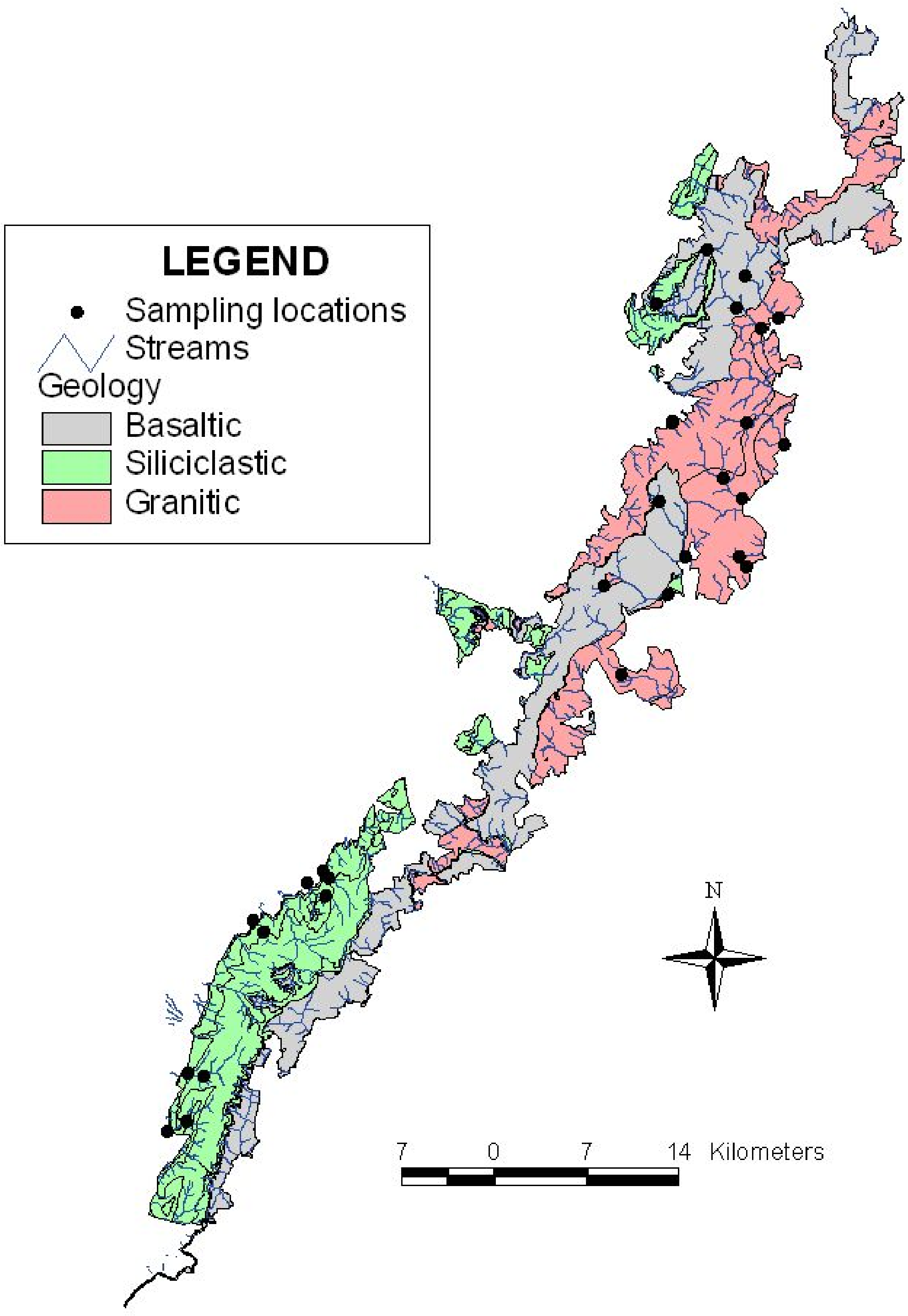

Figure 1. Map of Shenandoah National Park depicting locations of sampling sites. Major geologic bedrock types are also shown.

Figure 2

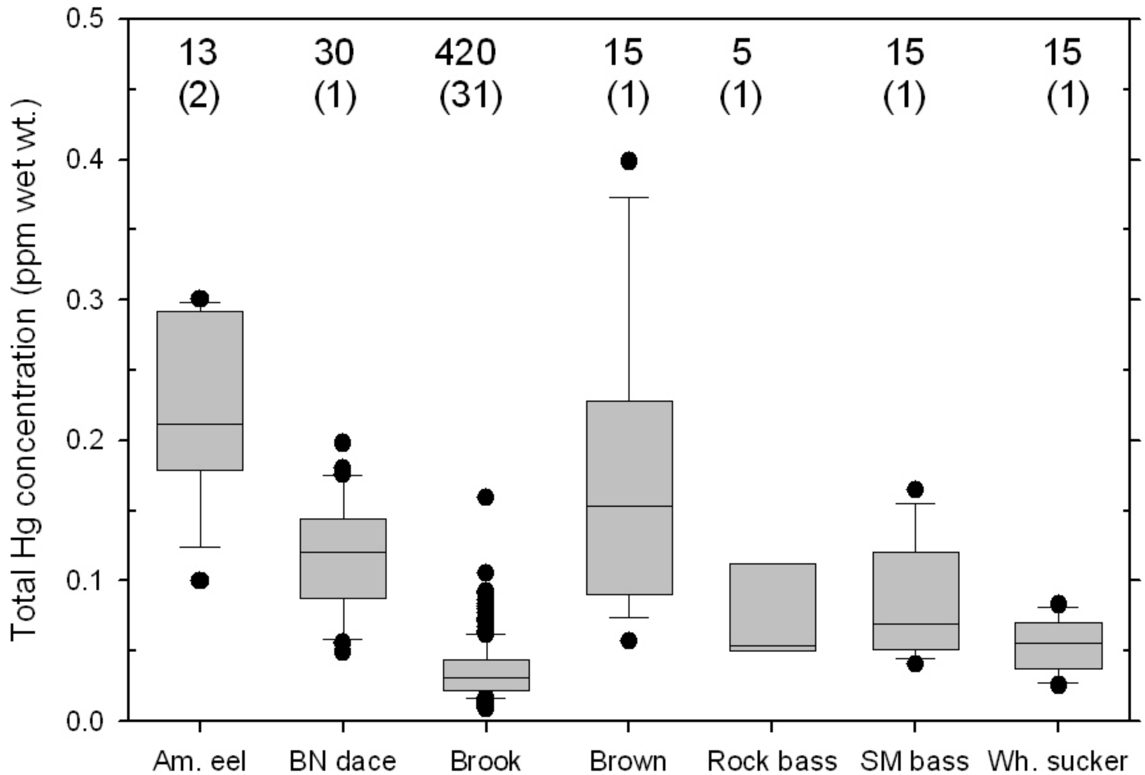

Fig. 2. Hg concentrations in seven fish species in Shenandoah NP. For each box plot, 50% of all values are defined by the limits of the box, 90% of the values are defined by the limits of the whiskers, and the remaining values are shown with closed symbols. The total number of fish collected and the number of sites (in parentheses) are shown above each box plot.

Figure 3

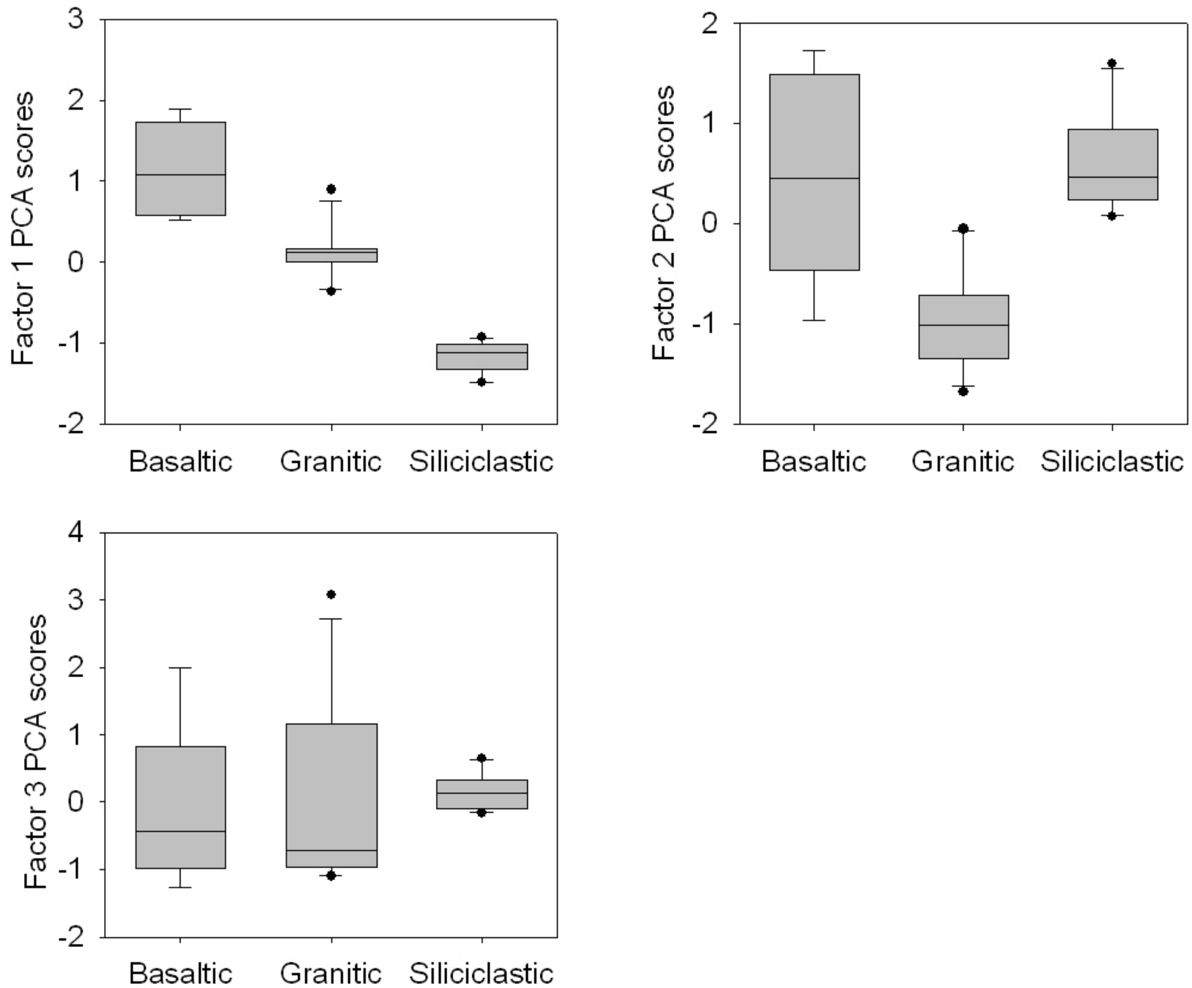

Figure 3. Comparison of Principal Components Analysis (PCA) factor scores among bedrock types. PCA scores were determined by ordinating 12 water chemistry variables. PCA factor 1 scores were correlated with calcium, alkalinity, pH, sodium, specific conductance, silica, magnesium, and potassium. PCA factor 2 scores were correlated with sulfates, and factor 3 scores were correlated with chlorides and nitrates.

Figure 4

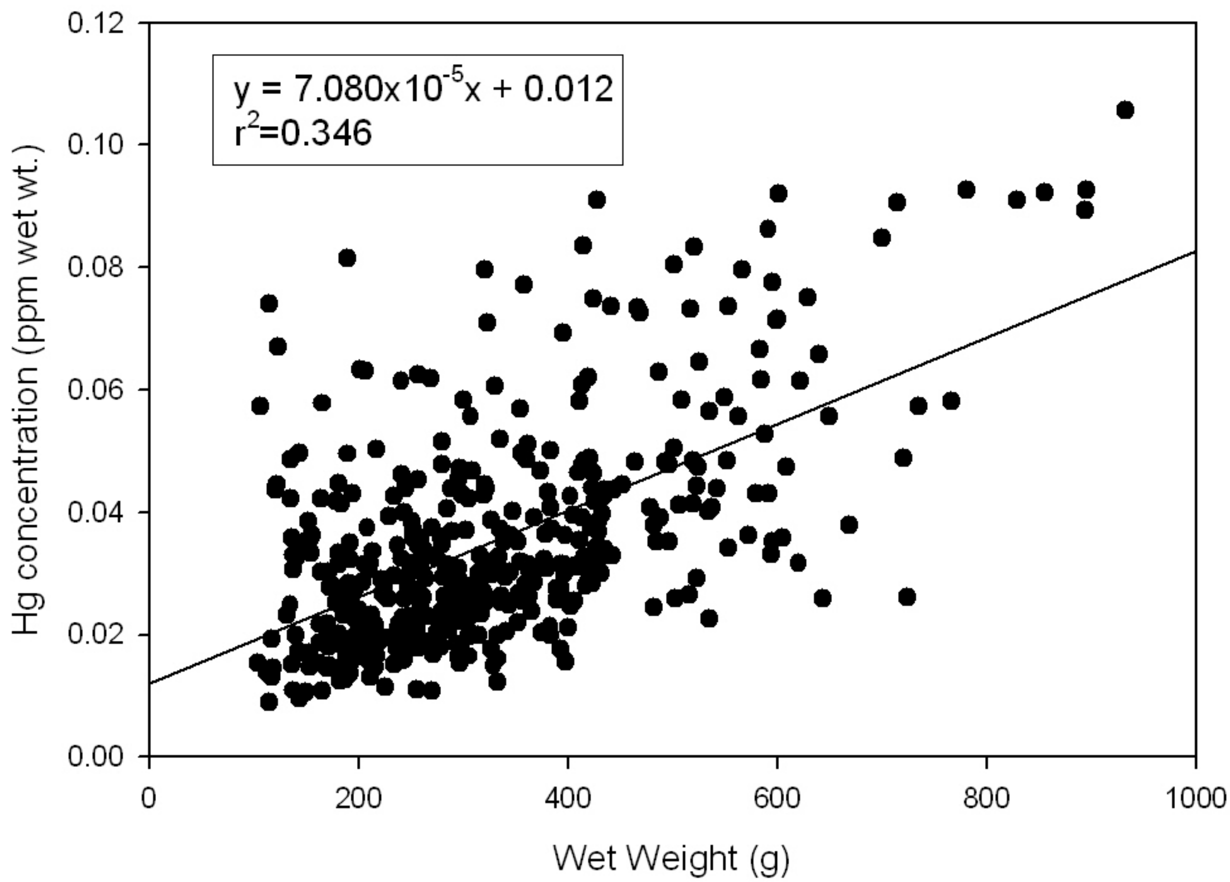

Figure 4. Mercury concentrations in brook trout collected in SNP streams as a function of body size.

Figure 5

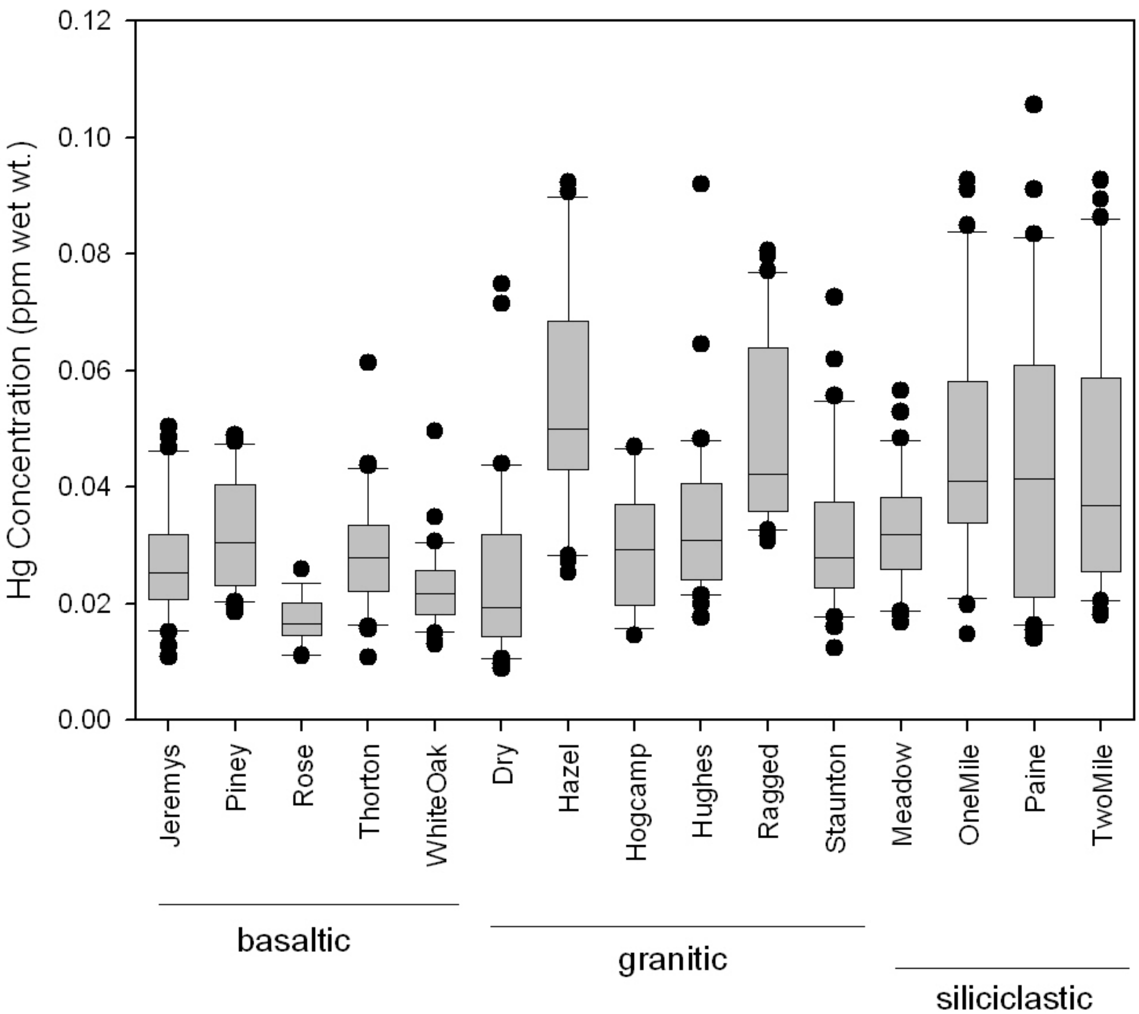

Figure 5. Comparison of Hg concentrations in brook trout among 15 watersheds in SNP. A total of 30 fish were collected from all streams except for the Rose River (N=13) and Hogcamp Run (N=23). Sites are grouped by underlying bedrock type from left to right.

Figure 6

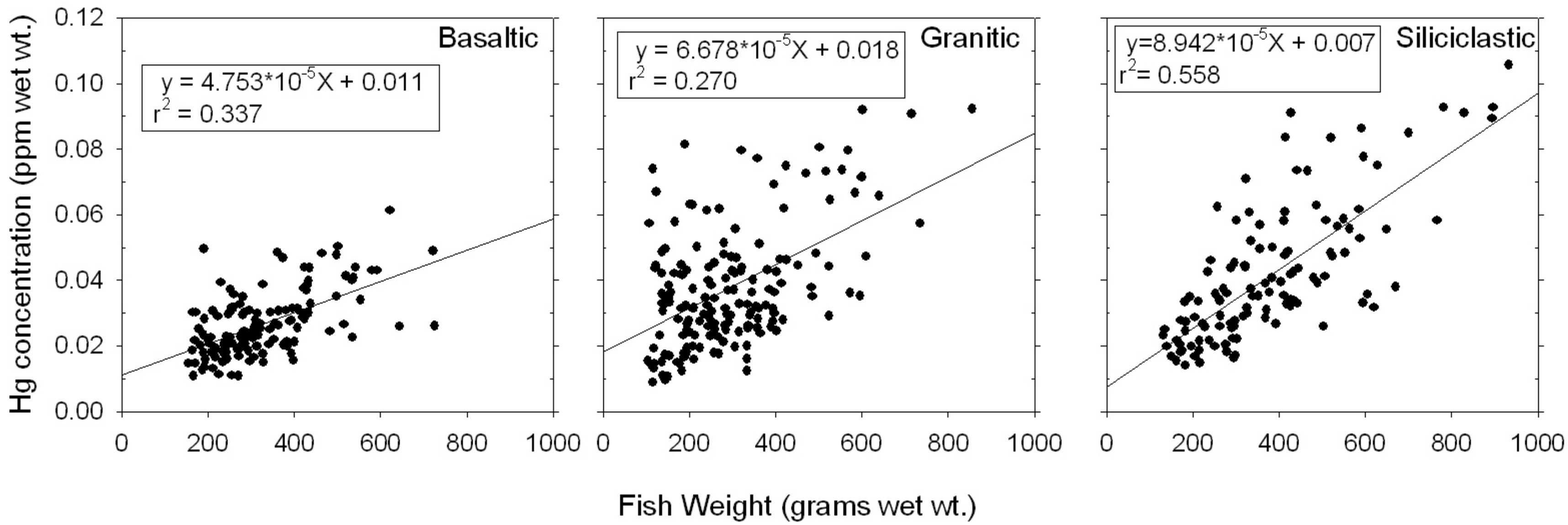

Figure 6. Comparison of Hg accumulation rates in brook trout among predominant bedrock types underlying streams. Regression equations and coeficients of determination (r^2) are shown in the insets of each graph.

Figure 7

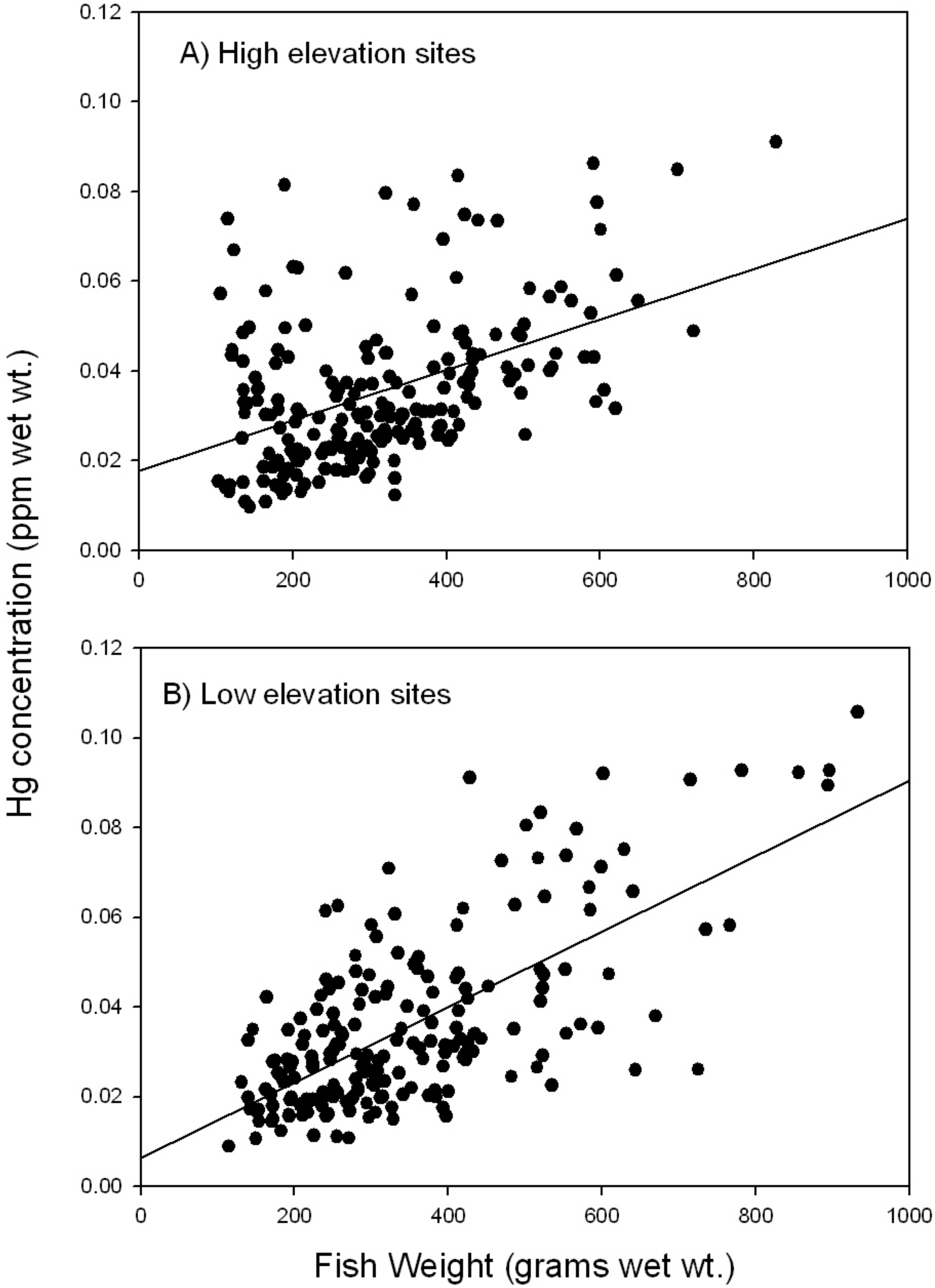

Figure 7. Comparison of Hg accumulation rates of brook trout among high and low elevation sites in SNP.

Figure 8

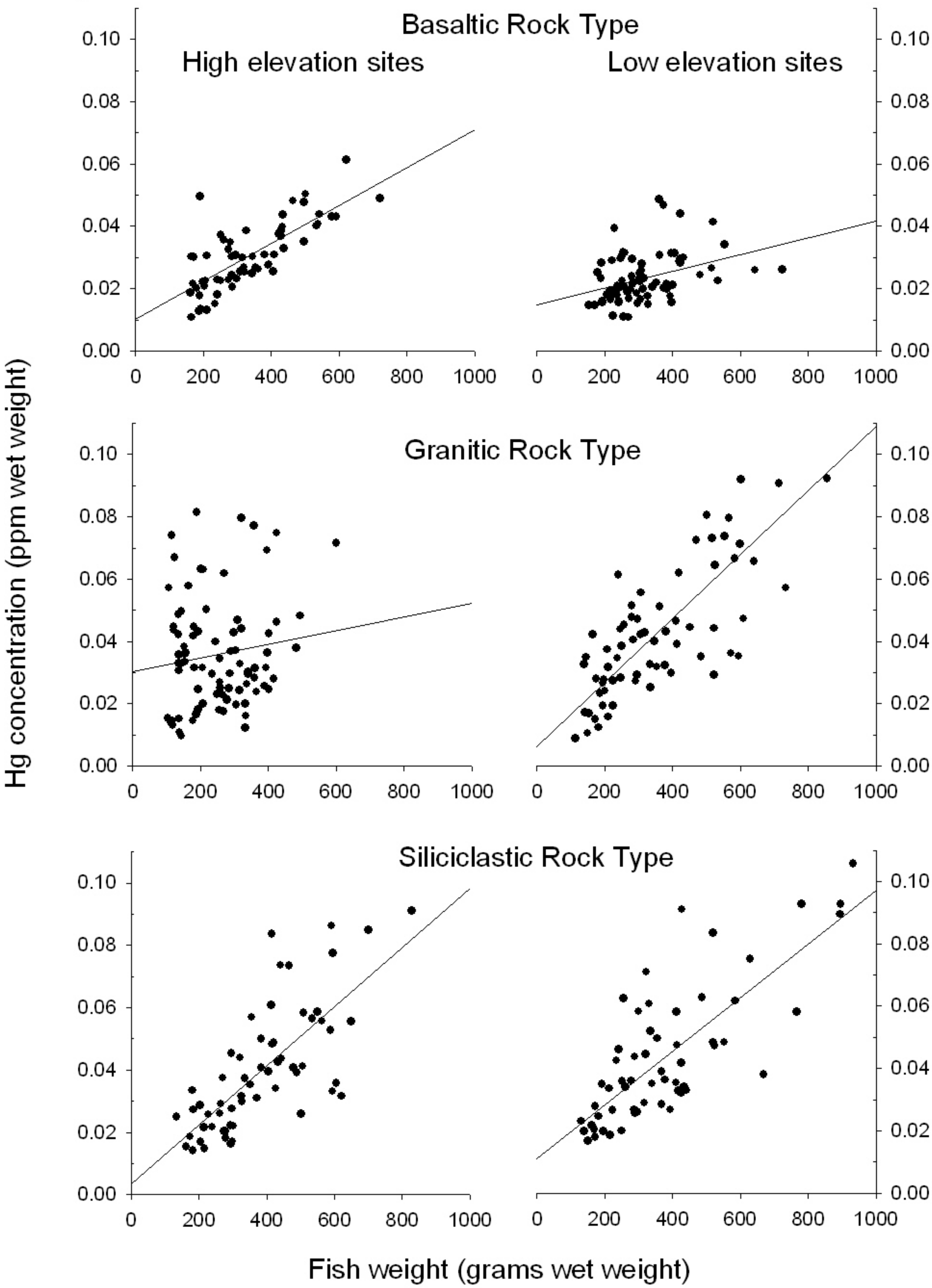

Figure 8. Comparisons of Hg accumulation rates between high elevation and low elevation sites within three bedrock types.

Figure 9

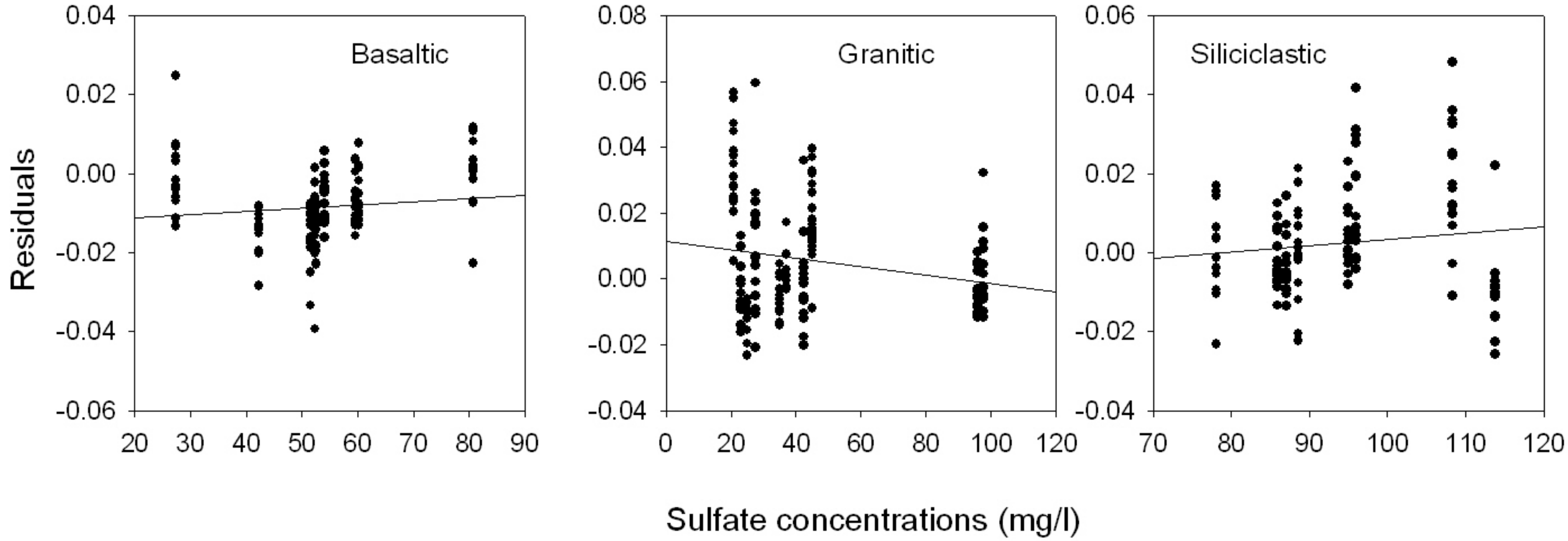

Figure 9. Relationships between the residual variation in Hg concentrations in brook trout after accounting for size (residuals) as a function of sulfate concentrations observed in stream water at the time of sampling. Comparisons are made within each bedrock type.

Figure 10

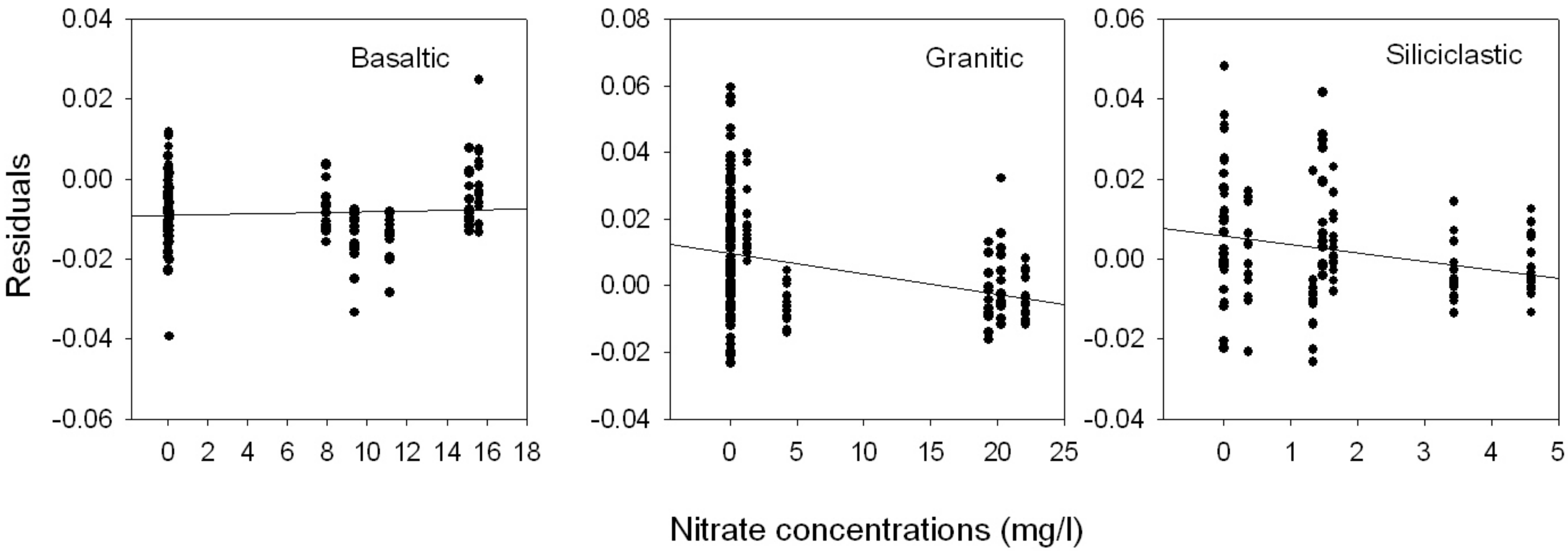

Figure 10. Relationships between the residual variation in Hg concentrations in brook trout after accounting for size (residuals) as a function of nitrate concentrations observed in stream water at the time of sampling. Comparisons are made within each bedrock type.