

Metal Loading of the B. Everett Jordan Reservoir

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DISCLAIMER STATEMENT

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ABSTRACT

Filterable and non-filterable Zn, Cd, Pb, Cu and Hg concentrations were examined in streams which form the B. Everett Jordan Reservoir, N.C. Stream samples were collected to coincide with low and high flow events. Zinc, Cu, Pb and Hg were transported principally in the non-filterable fraction and at high flow, whereas less than 20% of the Cd was transported in that fraction. Metal loadings were estimated from flow-weighted mean metal concentrations and mean stream flow data and indicated the importance of sampling during high flow events. Metal concentrations at high flow depended less on flow magnitude than the time relative to peak flow when the sample was collected.

The order of metal loading was Zn>Cu>Pb>Cd>Hg with the industrialized Haw River sub-basin contributing more metals Zn (19.7×10^3 g/km²-yr), Cd (32.4×10^1 g/km²-yr), Pb (5.0×10^3 g/km²-yr), Cu (8.8×10^3 g/km²-yr), and Hg (4.2×10^1 g/km²-yr) than the New Hope River sub-basin Zn (5.0×10^3 g/km²-yr), Cd (6.1×10^1 g/km²-yr), Pb (1.4×10^3 g/km²-yr), Cu (2.1×10^3 g/km²-yr) and Hg (2.5 g/km²-yr).



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SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Filterable and non-filterable Zn, Cd, Pb and Cu concentrations were examined in six streams which supply over 90% of the flow into the B. Everett Jordan Reservoir: New Hope River, Third Fork Creek, Morgan Creek, Northeast Creek in the New Hope sub-basin and Robeson Creek and the Haw River in the Haw River sub-basin. Stream samples were collected to coincide with low flow and high flow events during the sampling period (February 1980 - May 1981). Relationships between metal concentrations and data collected on suspended sediment concentrations, flow, DO, pH and temperature were examined. Metal loadings were estimated from metal concentrations and flow.

Metal concentrations varied with both site and stream-flow. The highest Zn, Pb and Cu concentrations were observed in streams which enter the reservoir from the New Hope sub-basin. Third Fork Creek had greater mean total Zn (58 $\mu\text{g/l}$) and Pb (17 $\mu\text{g/l}$) concentrations and Northeast Creek had greater Cu concentrations (26 $\mu\text{g/l}$). Robeson Creek had significantly less Zn (7.7 $\mu\text{g/l}$), Pb (1.4 $\mu\text{g/l}$) and Cu (7.1 $\mu\text{g/l}$) than the other streams. Cadmium concentrations varied little among streams and averaged less than 1 ppb.

Significant percentages of the total average Zn (50-72%), Cu (33-54%) and Pb (>94%) were transported in the non-filterable fraction, whereas less than 20% of the Cd was observed in this fraction. Considerable more Zn, Pb and Cu was found during high flow events and via suspended sediments than during low flow and the soluble form.

Negative linear correlations were observed between suspended sediment concentrations and suspended sediment associated Zn, Pb and Cu concentrations. Positive linear correlations were found between filterable Zn and filterable

Cd, Pb and Cu and between suspended sediment associated Zn and suspended sediment associated Pb and Cu. Strong positive correlation coefficients were observed between flow and non-filterable Zn and Pb at Site 6.

The order of metal loading is Zn>Cu>Pb>Cd. The Haw River sub-basin contributed more Zn (19.7×10^3 g/km²-yr), Cd (32.4×10^1 g/km²-yr), Pb (5.0×10^3 g/km²-yr) and Cu (8.8×10^3 g/km²-yr) to the Jordan Reservoir per unit area of drainage basin than the New Hope River sub-basin (Zn, 5.0×10^3 g/km²-yr; Cd, 6.1×10^1 g/km²-yr; Pb, 1.4×10^3 g/km²-yr; Cu, 2.1×10^3 g/km²-yr).

Mercury was also determined over a seven month sampling period, September 1982-March 1983. One site was added in the New Hope sub-basin, Little Creek, which receives urban runoff from Chapel Hill. Polkberry was used as a control site for Hg and Robeson was not sampled.

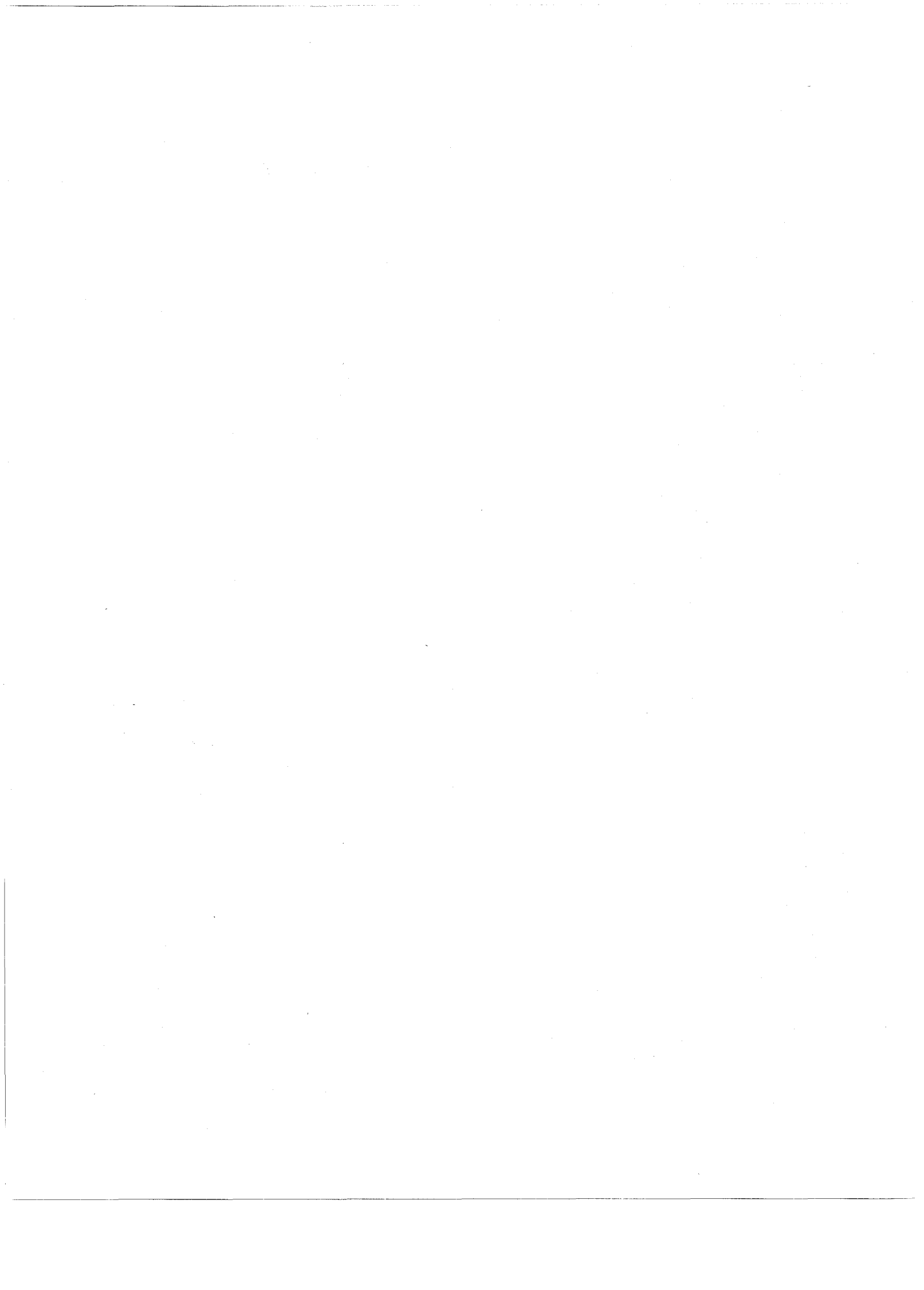
As with the other metals the highest mean total Hg concentrations were observed at sample sites in the New Hope sub-basin (165 ng/l) and the lowest (84 ng/l) at the control site. Mean total Hg concentrations decreased at high stream flows in the five streams of the New Hope sub-basin. In contrast, total Hg concentrations in the Haw River and Polkberry Creek were independent of stream flow. This pattern of Hg transport indicates a nonpoint source of Hg for the Haw River and Polkberry Creek, and point source input for the remaining five streams. Mercury levels in bottom sediment samples collected along Morgan Creek, for example, were elevated above background at the outfall and decreased with distance downstream of the Chapel Hill treatment plant, indicating that the plant is a point source. Grab samples of effluent were higher by a factor of four than concentrations found in samples upstream of the plant.

About one half of the Hg transported to the reservoir was on suspended particles, with the percentage slightly higher at high flow (52-65%) than at low flow (43-57%). About 99% of the Hg entering Jordan currently comes from the Haw River, with almost 90% of the input occurring during high flow events.

Metal concentrations were fairly typical for streams receiving municipal and industrial wastewater effluent and were below recommended levels for drinking water. Metals will have little direct impact on aquatic organisms but will lead to high sediment concentrations. Recycling of metals from the sediment to the water column may elevate concentrations in segments of the lake north of Highway 64 where water circulation is constrained and where eutrophic conditions are anticipated.

Recommendations

1. Metal concentrations should be studied at varying depths of Jordan Lake and at all seasons to determine to what extent metals are recirculated from sediment into overlying waters.
2. Organisms at all trophic levels should be examined over a period of several years for total Hg and methyl mercury concentrations.
3. An intensive study of metal recycling should be made in segments of the lake where eutrophic conditions exist.



INTRODUCTION

The 14,300 acre B. Everett Jordan Reservoir, located in the Cape Fear River Basin, North Carolina, impounds waters of the New Hope and Haw Rivers which receive industrial and municipal waste discharges from Greensboro, Reidsville, Burlington, Haw River, Durham and Chapel Hill. These discharges contain Cd, Cu, Pb, Hg and Zn which at elevated concentrations are hazardous to aquatic life and human health.

Metals in U.S. rivers are transported principally by suspended sediments. A large proportion of these suspended sediments are discharged to an estuary, lake or reservoir during high flow storm events and are deposited into bottom sediments when the flow rate of water carrying them is suddenly decreased. Jordan Lake is expected to receive metals principally from the suspended sediments discharged to the reservoir during high flow and to have elevated metal concentrations in bottom sediments.

There is no reliable estimate of metal loading (the total annual input) to Jordan Reservoir. Previous metal analyses were limited to filtered or unfiltered samples of Jordan Lake's source waters. No direct analyses of suspended sediments has been made although this information is necessary to estimate metal loading and to assess the impact of metals on the water quality of the reservoir.

Filling of the lake began in the fall of 1981. A debate about the suitability of the reservoir as a water supply has centered around questions concerning the eventual concentrations of certain metals and organic constituents. Two features of the reservoir provide conditions for metal remobilization from bottom sediments to overlying waters. The lake is shallow, with mean depths ranging from 2.1 to 6.7 meters and it receives high

nutrient and organic loads, characteristics which are expected to create eutrophic conditions. Dissolved oxygen concentrations in parts of the lake may become low enough to reduce and release sediment-bound metals with subsequent increase of metal concentrations in the water column.

During litigation of the B. Everett Jordan Project, it was suggested that elevated Hg concentrations would reduce the usefulness of the reservoir as a potential water supply. Weiss et al., (1972) monitored total Hg in streams feeding the impoundment for several years and found concentrations of 3.0 to 80 $\mu\text{gHg/liter}$. Preimpoundment studies by the Corps of Engineers (1975) also found Hg levels exceeding the recommended limit of 2 $\mu\text{gHg/liter}$ for raw water supplies.

The work reported here was initiated to provide reliable metal concentration and metal loading data for Jordan Reservoir and to examine the effect of stream flow and suspended sediment concentrations on loading.

OBJECTIVES

The objectives of this research were to:

1. Collect reliable analytical data on the concentrations of Zn, Cd, Pb, Cu and Hg in solution and on suspended sediments entering B. Everett Jordan Reservoir.
2. Establish the primary transport phase for each metal.
3. Obtain metal concentrations at both high and low stream flow.
4. Use metal concentration and flow data to generate metal loading data for Jordan Lake as a first step in understanding the effects of metal input on the water quality of Jordan Reservoir.
5. Verify earlier Hg data for water and attempt to locate sources of mercury by sampling water and bottom sediment upstream of the dam.

MATERIALS AND METHODS

The analysis of environmental Hg present the analyst with a different set of problems than does the analysis of Cd, Cu, Pb and Zn. The discussion below is separated to reflect those differences. Also, sampling dates for Hg did not coincide with the others metals.

A. Sample Collection and Storage: Cd, Cu, Pb and Zn

1. Sampling Sites. New Hope River (NH), Northeast Creek (NE), Morgan Creek (MC) and Third Fork Creek (TF) in the New Hope sub-basin and the Haw River (HR) and Robeson Creek (RC) in the Haw River sub-basin were selected for sampling (Table 1). Together these six streams represent 90% of the flow into the B. Everett Jordan Reservoir. Sampling sites were chosen downstream of point source discharges, upstream of the reservoir's conservation pool level and within access of roads.

Daily flow data for each sites was supplied by the Corps of Engineers, Wilmington District. Flows were based on drainage area ratios. The Bynum gauge station on the Haw River was used to estimate flows in the Haw River drainage and the Eno River at Durham gauge was used to estimate flows in the New Hope drainage.

Daily precipitation data was supplied by the National Oceanic and Atmospheric Administration (NOAA). Total watershed precipitation was calculated using station weights as determined by the Corps of Engineers (1975).

2. Sampling and Sample Storage: Streams were sampled from February of 1980 through May of 1981. Sampling dates were selected to coincide with low and high flow events. Each site was sampled at least ten times with New Hope and Third Fork sampled twelve times.

Several water quality parameters, pH, dissolved oxygen concentration and

Table 1. Sampling Sites

Stream	Location of Site	DA*	Significance
New Hope River (NH)	Highway 54 ¹ State Road 1107 ²	194.6	Receives wastewater treatment plant (WWTP) effluents from the New Hope and Sandy Creek Plants (2.5 and 1.0 mgd respectively).
Northeast Creek (NE1)	State Road 1731 ^{1,2}	89.6	Receives effluent from the Durham Triangle WWTP (3.0 mgd).
Northeast Creek (NE2)	State Road 1100 ¹		A site upstream.
Morgan Creek (MC)	State Road 1726 ^{1,2}	117.8	Receives effluent from Chapel Hill WWTP (8 mgd).
Third Ford Creek (TF)	Highway 54 ¹ Highway 751 ²	43.5	Receives effluent from Third Fork Creek WWTP (5.0 mgd) and Hope Valley WWTP (1.5 mgd).
Little Creek (LC)	State Road 1110 ²	61.4	Receives urban runoff from Chapel Hill
Robeson Creek (RC)	State Road 1943 ¹	76.1	Receives discharges from a chicken processing plant and Pittsboro WWTP (.25 mgd).
Polkberry Creek (PC)	State Road 1711 ²	30.7	Receives no known effluent discharge
Haw River (HR)	Highway 64 ¹ State Road 1713 ²	3333.1	Receives about 64 mgd of municipal and industrial waste from Burlington, Greensboro and Reidsville. The Haw River supplies 80% of the average annual flow to the reservoir.

*DA = Drainage Area in square kilometers

1. Cd, Cu, Pb, Zn

2. Hg

stream water temperature, were determined in the field. The pH was taken with a Model 401 Orion portable pH meter. Dissolved oxygen concentrations were determined by the Winkler Method (APHA, 1975).

Stream samples were taken in 5 liter linear polyethylene jerricans (Fisher) from stream edge at low flow and from bridges at high flow with a Nalgene bucket and transferred into jerricans. The jerricans were acid leached with dilute Mallinckrodt ACS grade Nitric Acid at pH=1 for at least 24 hours and rinsed three times with streamwater before sample collection. Samples were returned to the lab and stored at 4°C. The concentration of suspended sediments was determined from the mass collected on an acid cleaned 0.45 μm filter.

A simple study was designed to determine if metal concentrations changed during storage. Metal and suspended sediment concentrations in samples taken May 11, 1981 were determined within one week of collection and also after five months of storage at 4°C. No consistent trend in metal concentrations was found (Stokes, 1982) although in some cases increases could be attributed to contamination during filtration. The concentrations of suspended sediment and of Zn and Cu on suspended sediments were mostly within experimental error. No changes in metal concentrations could be attributed exclusively to gain or loss during storage.

B. Sample Pretreatment for Metal Analysis

Stream samples were divided by filtration into two fractions, a filterable fraction (that which passed through a 0.45 μm filter) and a non-filterable fraction (that which was retained on the filter). Filtering was done in a laminar flow clean hood (Environmental Air Control, Inc.) to reduce air contamination. Metal contaminants were leached from 0.45 μm pore size filters (Millipore) prior to sample filtration by soaking them in 1:4 nitric acid:DI water mixture. The Millipore filtering apparatus, all glass except

for a plastic frit, was acid cleaned and rinsed with distilled-deionized water between use. Four 250 ml aliquots of DI water were flushed through the apparatus and filter to remove traces of acid. A known volume of well mixed sample was then filtered under vacuum. The filtrate was poured into 125 ml Nalgene (LPE) bottles and stored at 4°C. The filters were removed with acid cleaned plastic tweezers, folded and put in 10 ml glass bottles with plastic caps and frozen. Both the Nalgene and glass bottles were acid soaked and DI water rinsed before they were used.

The digestion of filters was done using a procedure adapted from Florence (1977) and Figura and McDuffies (1980). The suspended sediments retained on the filters and the filters themselves were digested with 2 ml of 2 M HNO_3 /1.5 M HClO_4 mixture in a Labconcomicro Kjeldahl Digestion Unit equipped with 30 ml flasks (Figure 1). Baker's Ultrex Nitric Acid and Analytical Reagent Grade Perchloric Acid (Mallinckrodt's) were used. The Kjeldahl flasks were thoroughly cleaned initially and between digestions, first with hot dilute nitric acid, then refluxed for 30 minutes with concentrated nitric acid. They were then filled with dilute nitric acid, soaked overnight, rinsed three times with DI water and equilibrated with DI water for 30 minutes before use.

Digestion was complete after the disappearance of yellow nitric acid fumes and the appearance of white, perchloric acid fumes (≈ 45 minutes). The flasks were allowed to cool and were then reheated for 10 minutes after addition of 2 ml DI water. Cooled flasks were covered with Parafilm. Digestion blanks were prepared using a precleaned unused filter.

C. Analysis by Anodic Stripping Voltametry (ASV)

All sample manipulations and analysis were done under the laminar flow hood. The electrochemical sample cells were soaked with 1:4 nitric acid:DI water when not in use, and rinsed three times and filled with DI water 30 minutes before used. Large blanks resulted if the cells were simply rinsed.

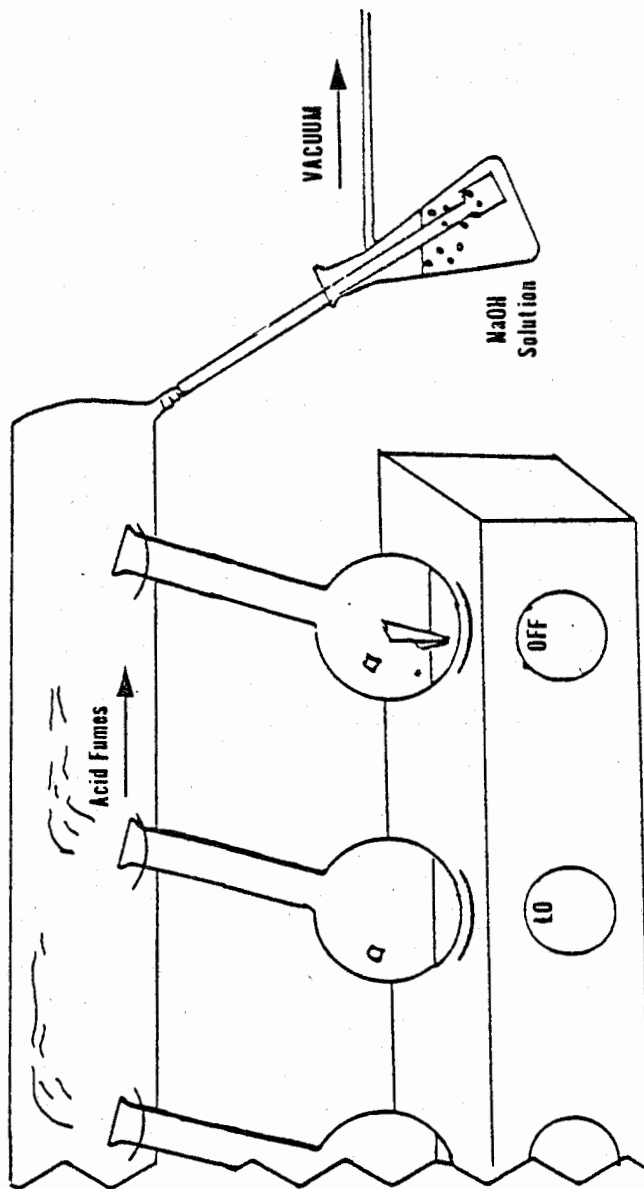


Figure 1. Apparatus Used for Filter Digestions. Labconco-micro Kjeldahl Digestion Unit equipped with 30 ml flasks was used. A vacuum pulled fumes through a NaOH solution to remove acids.

About 7 ml of filtered sample solution was equilibrated for 30 min. in the cell before analysis. This was discarded and 7 ml of fresh filtrate were Eppendorf pipeted into the cell. A 100 μ l aliquot of 1 M sodium acetate buffer was added to bring the pH to 4.5.

Digested sediments left a white precipitate, believed to be silicates. The supernatant was decanted directly into the cell and 3 ml of 2.5 M sodium acetate buffer was added to bring the pH to between 4.5 and 5.0. The sample volume was brought to 7 ml with DI water. An orange-brown color would often appear in the cell after addition of buffer to the digest. This could not be filtered but disappeared upon acidification. The color did not appear to cause interferences in the analysis and was believed to be hydrous ferric oxide.

Sodium acetate buffers were added to adjust pH and increase ionic strength. A 1 M acetate buffer, added to the filtrate, was adjusted to pH 4.5 with concentrated nitric acid. A 2.5 M acetate solution added to the digest had a pH of 8.9. Metals were removed from these solutions by stirring together with BioRad Laboratories Chelex 100 chelating resin for 24 hours and filtering the resin.

A PAR 174 Polarographic Analyzer was used together with a PAR 303 Static Mercury Drop Electrode. The smallest sized drop available on the 303 was used. Stripping current was recorded with a Hewlett-Packard 7004B X-Y Recorder. A Teflon coated stir-bar placed in the borosilicate glass sample cell was used with a Fisher stir plate to provide uniform stirring.

Samples were deaerated for 4 minutes with Seaford Nitrogen before pre-electrolysis. Pre-electrolysis potential at -1.2 volts (V) was carried out for 6 minutes with the filtrates and for 4 minutes with the digests. Stirring was stopped for 30 s prior to stripping at a scan rate of 50 mV/s.

Metals strip from the Hg drop at approximately -1.02 V for Zn, 0.64 V for Cd, -.48 V for Pb and -.04 V for Cu. The scan was halted momentarily after each peak to establish the baseline for the next peak. The Ariel and Eisner (1963) method was employed for measuring current peak heights. Triplicate determinations were run on each sample and on each addition.

Metal concentrations in filtrates were computed using two standard additions. Reagent blanks were subtracted to give the reported values. Mean metal concentrations in the reagent blanks were 1.1 $\mu\text{g/l}$ for Zn, 0.09 $\mu\text{g/l}$ for Cd, 0.93 $\mu\text{g/l}$ for Pb and 0.65 $\mu\text{g/l}$ for Cu.

Metal concentrations in digested samples were determined from a single standard addition using the following formula:

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1) V}$$

where C_u is the unknown concentration of the sample, i_1 is the sample stripping peak height, i_2 is the stripping peak height for the sample and spike, v is the spike volume, V is the sample volume and C_s is the concentration of the standard used for the spike. Metal concentrations, M_{ss} , of suspended sediments expressed in $\mu\text{g metal/g sed.}$ were determined from the following

$$M_{ss} = \frac{1000(C_u - R)V}{S F}$$

where R is the metal concentration of the filter blank (30 $\mu\text{g/l}$ for Zn, 19 $\mu\text{g/l}$ for Cd, 5.4 $\mu\text{g/l}$ for Pb and 5.4 $\mu\text{g/l}$ for Cu), S is the suspended sediment concentration (mg/l) and F is the volume of filtered water. These were multiplied by the suspended sediment concentration and divided by 1000 to obtain non-filterable metal concentrations ($\mu\text{g of Metal/l of sample}$).

The average relative standard deviation for triplicate ASV scans on filterable samples was 7% for Zn, 12% for Cd, 13% for Pb and 13% for Cu.

Relative standard deviations for the metal concentrations of suspended sediments averaged 4% for Zn, 16% for Cd, 6% for Pb and 4% for Cu.

The relative standard deviation in the computed metal concentrations for 4 separate aliquots of a filtered sample taken April 4, 1980 at Site HR, was 38% for Zn, 27% for Cd, 71% for Pb and 25% for Cu. Computed non-filterable concentrations for 5 aliquots of the same sample had relative standard deviations of 30% for Zn, 150% for Cd, 63% for Pb and 8% for Cu.

D. Statistical Analysis

A SAS computer program was used for statistical data analysis. Nonparametric analysis of variance (NPAR1WAY) was used to test for significant differences among sites. This package ranks all values before analyzing differences between variances. The sites whose values tend to be larger will have correspondingly larger ranks. Indication of significant difference through this test can descriptively be presented through the means. A .05 significance level was chosen as the threshold of statistical difference. Other packages used in the data analysis included the Spearman Correlations Procedure, the General Linear Modeling Procedure and the Stepwise Procedure.

E. Sample Collection and Storage, Hg:

1. Sampling Sites. New Hope River, Northeast Creek, Morgan Creek, Third Fork Creek, and Little Creek in the New Hope sub-basin and the Haw River and Polkberry Creek in the Haw sub-basin were selected for sampling (Table 1). Morgan and Northeast sites for Hg were identical to the sites for the other metals. Little Creek was added for Hg and New Hope, Third Fork and Haw River were sampled a short distance downstream. Polkberry in the Haw River sub-basin was used as a control station and Robeson was not sampled.

2. Sampling and Sample Storage. Streams were sampled from September of 1982 through May of 1983 on dates to include both low and high stream flows.

Each site was sampled ten times, five at low stream flow and five at high flow (Robinson, 1983).

Samples were collected from the banks and at about 10 cm depth just upstream of bridges and filtered immediately to avoid changes in equilibrium between dissolved and particulate Hg concentrations. Duplicates were filtered using a gasoline powered electrical generator (Craftsman) and two vacuum pumps (Doerr).

Borosilicate storage bottles (125 ml, Wheaton) were leached at least 48 hours in a cleaning solution of concentrated HNO_3 :10%(w/v) $\text{K}_2\text{Cr}_2\text{O}_7$: 0.15% (w/v) cysteine (0.5:0.4:0.1) and rinsed five times with deionized-distilled water to remove Hg and finally capped with a teflon/silicone septum (Pierce). Three reagents (HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and cysteine) were added to all filtrate sample bottles as a preservative (Batley and Gardner, 1977; Weiss, et al., 1976; Lo and Wai, 1975). One ml of concentrated HNO_3 (Ultrex) was added to the sample bottles using an oxford pipet whose tip had been soaked for five days in the cleaning solution and rinsed with deionized-distilled water. One ml of $\text{K}_2\text{Cr}_2\text{O}_7$ (10% w/v) and 1 ml of cysteine (0.15% w/v) were added using a glass syringe (Becton-Dickinson) that had been acid leached and rinsed and whose tip had been heated to 600°C.

Stream samples were collected for transfer in pre-treated bottles which had been rinsed with DI water five times and twice with stream water. Samples were filtered through 47 mm diameter membrane filters (0.45 μm . Millipore) at the stream site directly into the pretreated storage bottles containing the three preservation reagents.

Filters were soaked in the cleaning solution diluted 1:10 with deionized-distilled water for 48 hours, rinsed and then stored in deionized-distilled water until needed. The Millipore glass filter funnel was modified by

connecting the vacuum funnel end of a fritted disk filter assembly (Corning 33990) to the bottom of the Millipore funnel using an o-ring seal. A screw cap with a 13 mm hole drilled into the center was attached inside the ground glass joint of the vacuum funnel with silicon sealant so that filtrate ran directly into the storage bottles. The particulate samples on the filters were transferred to labeled Wheaton bottles using polyethylene tweezers and PVC gloves (Fisher) that had been soaked in diluted cleaning solution and in deionized-distilled water. All samples were sealed with a teflon/silicone septum under a bakelite cap and stored on ice for transport back to the laboratory. Field blanks were prepared by filtering DI water in the same fashion and collected at a minimum of three sites each sampling trip.

Soil samples were collected from each site approximately 25 meters from the stream bank and at a depth of 2-5 cm. Stream bank samples were collected from the top 2 cm on the bank. Stream bottom samples were collected from the top 2 cm of sediment along Morgan Creek above and below the wastewater treatment plant outfall.

Soil and sediment samples were collected in 10 ml polyethylene vials that had been soaked in the cleaning solution for one week, rinsed, and then soaked in deionized-distilled water until needed. They were stored at 4° C and frozen after return to the laboratory.

F. Sample Pretreatment for Mercury Analysis

One ml of KMnO_4 (10% w/v) was added through the teflon/silicone septum to all filtrates and to blanks immediately upon return to the laboratory from the field. The samples were then stored at 4° C and analyzed within 24 hours of collection. The KMnO_4 was added to digest organic Hg species.

Particulate samples on filters were stored at 4° C for 24-48 hours before digestion. The digestion procedure, adapted from the technique developed by Agemian and Chau (1976), consisted of adding 15 ml of a concentrated

H_2SO_4 : HNO_3 (2:1) mixture directly to the storage bottles and heating at 60°C for two hours in a water bath. After cooling, additional oxidants, 10 ml KMnO_4 10% (w/v) and 5 ml $\text{K}_2\text{S}_2\text{O}_8$ 5% (w/v), were injected through the septum using a syringe. Persulfate oxidation in addition to permanganate insures organo-Hg compounds are oxidized to mercuric ion. All samples were stored overnight at 4°C . Samples were diluted with DI water to 125 ml the following day and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (20% w/v) was added until the sample color was a faint pink, indicating complete reduction of excess oxidant.

Reagent contamination was minimized using procedures outlined in Table 2. All materials that would come in contact with the samples were soaked in the cleaning solution and rinsed with DI water. Reagent contamination was typically less than 1 ng Hg with these procedures.

G. Mercury Analysis by Modified Cold Vapor AA

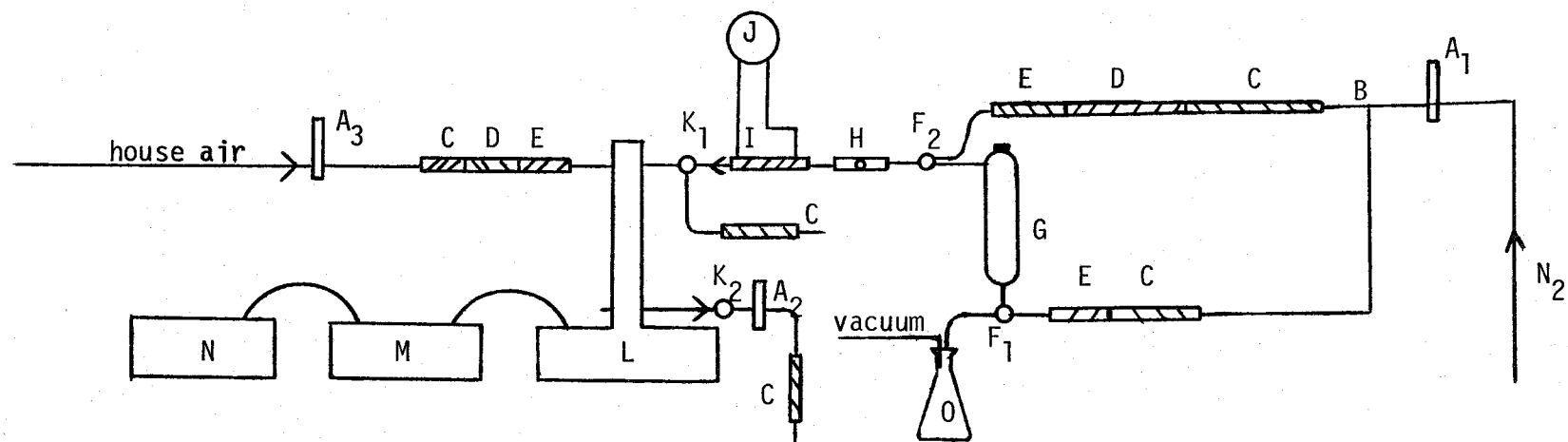
The cold vapor atomic absorption technique was developed by Hatch and Ott (1968). Mercury is reduced to metallic Hg in an acidic solution using stannous chloride, then volatilized by aeration and Hg vapor absorption measured at 253.7 nm. An additional step, amalgamation of the Hg on Au was introduced by Joensuu (1971) to reduce interferences from water vapor, volatile organics, sulfides and Cl_2 . The amalgam is heated in this procedure and the Hg vapor is carried into an absorption cell with an inert carrier gas such as N_2 .

1. Apparatus. A diagram of the gold sand amalgamation gas flow system used in this study is given in Figure 2. Nitrogen gas flow is adjusted by rotometer A_1 , and diverted by stopcocks F_1 and F_2 through a clean-up step (traps C and E) before entering sample reaction vessel G. Stannous chloride and Hg containing sample are injected into the reaction vessel through a septum located at the top and aerated to reduce Hg and removed it from solution. The N_2 with Hg vapor flows across gold column I where Hg is collected

Table 2. Purification of Reagents

Reagent	Purification Method	Typical post-Purification Hg Concentration ng/l
H ₂ SO ₄ (conc)	add 50 ml SnCl ₂ (10% w/v) to 2 liters of reagent, aerate for 5 hours with air scrubbed with activated carbon	32
KMnO ₄ (6%)	Boil solution, allow it to cool and filter through pyrex wool before each use*	60
NH ₂ OH-HCl (20%)	add 25 mg of SnCl ₂ and aerate for 2 hours with air scrubbed with activated carbon	10
SnCl ₂ (10%)	aerate for 2 hours with air scrubbed with activated carbon	10
HNO ₃ (Ultrex)	NONE	100
K ₂ Cr ₂ O ₇ (10%)	NONE	80
cysteine (0.15%)	NONE	20
water	Deionized-Distilled	10
K ₂ S ₂ O ₈ (5%)	NONE	40

* This filtering is done to remove Hg adsorbed to MnO₂ crystals.



A₁, A₂, A₃) Flow Meters

B) Pyrex "T"

C) Activated Carbon

D) Silica Gel

E) Gold Coated Sand

F₁, F₂) 3-Way Stopcock

G) Reaction Vessel

H) Hg Vapor Injection Port

I) Gold Furnace

J) Variable Transformer

K₁, K₂) 2-Way Stopcock

L) Mercury Optical Unit with 30 cm Cell

M) Mercury Control Unit

N) Strip Chart Recorder

O) Waste Bottle

Figure 2. Gold Amalgamation/Cold Vapor Apparatus.

and concentrated while other volatile interfering compounds are diverted out of the system by stopcocks K_1 and K_2 . Flow is then directed around the reaction vessel to prevent H_2O vapor from entering the optical cell while it is connected to the gas train. Traps C, D and E remove interfering compounds and Hg from the N_2 before passing across the Au column. The optical cell is connected to the gas train by stopcocks K_1 and K_2 and flow is readjusted by rotometer A_2 . The Au column is heated with high resistance wire connected to variable transformer J to remove the amalgamated Hg which is then swept into the optical cell. Peak height is noted on strip chart recorder N. The aerated sample is removed from the reaction vessel to waste bottle O by stopcock F_1 . Mercury vapor calibration injections were made through septa H to insure reproducibility throughout the analysis. The reference side of the system used house air which was cleaned up in the same manner as the N_2 .

Absorption measurements were made using a dual absorption cell Laboratory Data Control Mercury Monitor (Model 1235). All tubing that might come in contact with Hg vapor was 6 mm i.d. quartz or Vycor. Joints were sealed with heat shrinkable teflon tubing (Berghof/America). The reaction vessel into which samples were placed was borosilicate glass and had a screw cap top and a 3-way teflon stopcock bottom. The sample injection port at the top of the reaction vessel was capped with a teflon/silicone septum. A rubber septum was placed over the teflon/silicone septum to insure a good seal. A bakelite cap with a hole drilled in the center held the septa securely. The Hg vapor injection port placed downstream of the reaction vessel was made from a Pyrex T capped with a rubber sleeve stopper.

Seaford nitrogen was used as the carrier gas for all experiments. A filter train of activated carbon, silica gel and gold coated sand prevented the introduction of organic vapors, water and mercury vapor into the system.

Three-way teflon stopcocks allowed the reaction vessel to be bypassed during Hg measurements to prevent water vapor in the vessel from entering the absorption cell.

Sea sand (Fisher, 20-30 mesh) was given a very thin gold coating by vapor deposition of Au wire (0.008" dia.). A Denton Vacuum Evaporator (Model DV 502) located at the Botany Department at UNC-Chapel Hill was used to evaporate gold onto the sand. This procedure coats approximately 75% of the particle if deposition is repeated five times and the sand is shaken after each deposition.

The tube holding the Au plated sand was made of 100 mm x 6 mm (i.d.) Vycor and was wound with 3 meters of Nichrome wire (8.43 Ohms/m) for heating. A 40 mm length of Au coated sand held in place with quartz wool was used to collect and concentrate the Hg vapor. A variable transformer (Superior Electric) controlled heating. The temperature inside the collection furnace was calibrated with an API thermocouple which in turn was calibrated against the boiling points of H₂O (100° C) and Na₂CO₃ (851° C). Flow meters were calibrated with a soap bubble meter. A Perkin Elmer strip chart recorder set to a 10 mV range and a chart speed of 5 mm/minute was used to record absorption.

Mercury saturated air was used for calibration and was prepared by allowing a small amount of elemental Hg (1 ml) to equilibrate with air in a closed pyrex test tube. The tube was fitted with a sleeve rubber stopper for syringe extraction and immersed in a constant temperature water bath at 51° C ± 0.1° C. The concentration of Hg-saturated air was calculated from the ideal gas law. Known volumes of Hg vapor were withdrawn using a gas-tight constant rate syringe (Hamilton CR700). Mercury injections into the gas train were made either into the reaction vessel for standard curve determinations or through the pyrex T septum for calibration during analyses.

2. Procedure. The SnCl_2 (10% w/v) used for reduction is first put in the reaction vessel and purged of Hg. A 10 ml aliquot is injected into the reaction vessel through the top septum using a Becton-Dickinson syringe. The flow rate through the reaction vessel is adjusted to 300 ml minute using the #1 flow meter. The N_2 gas is bubbled through the Sn Cl_2 solution and Hg contamination trapped by the Au column. The variable transformer is set at 10 volts (Au column = 100°C) to prevent water vapor which accompanies the Hg vapor from condensing onto the gold sand. The N_2 flow through the reaction vessel and across the gold sand is not allowed to go through the Hg monitor but is diverted by the 3-way stopcocks out of the system. This prevents water vapor from entering the monitor where it would interfere with Hg measurements. The SnCl_2 is aerated for a total of one minute to remove all trace Hg in the reagent and in the system. The flow is then diverted, using stopcocks, to bypass the reaction vessel and gold sand is heated for 30 seconds at 80 volts (1000°C) to remove all Hg and contaminants from the Au column. After 30 seconds the voltage is turned off and an air stream is blown directly across the hot Au column for 45 seconds to cool the system. Next, 100 ng Hg is withdrawn from the calibration tubes and injected into the system at the pyrex T to condition the gold sand for subsequent injections. It was found when Au is fired to 1000°C or above that this preconditioning was necessary. The gold column is heated for 12 seconds at 80 volts (600°C) to remove the Hg adsorbed on the surface. Cooling air is turned on for 30 seconds to bring the column to room temperature.

The SnCl_2 solution and the system have now been purged of all Hg and after calibration, quantitative analysis can be carried out. The calibration is done first by connecting the gas train to the Hg monitor and adjusting the N_2 flow to 100 ml/minute using the #2 flow meter. The variable transformer is once again set at 10 volts and a precise amount of Hg vapor

is withdrawn from the calibration tube and injected into the system at the pyrex T. The gold column is heated for 12 seconds at 80 volts and the response recorded. After the gold column has cooled, the monitor is disconnected and the N₂ flow diverted around the optical cell.

A 50 ml sample is withdrawn from the storage bottle with a gas tight 50 ml Hamilton syringe and is injected into the reaction vessel containing the purged SnCl₂. The N₂ flow is adjusted to 1000 ml/minute and put back through the reaction vessel. After a one minute aeration the N₂ flow is diverted around the reaction vessel and across the Au column for 30 seconds to remove the water vapor that may have condensed on the Au sand. The monitor is reconnected and the flow through the monitor adjusted to 100 ml/minute. The Au column is heated by applying 80 volts for 12 seconds and Hg absorption recorded. This procedure is repeated for all samples. Soil, bank and bottom sediment samples were digested using the same procedure as the particulate samples. Digested samples were injected into the reaction vessel and analyzed as above. Total time for each sample is nine minutes.

Peak heights were measured and the amount of Hg in the sample was determined from a standard curve. Hg concentrations were calculated in the dissolved fraction by the formula:

$$\text{Hg/l} = \text{Hg in aliquot} \times \frac{1000 \text{ ml/l}}{\text{volume of aliquot in ml}}$$

Mercury concentrations in the particulate fraction were calculated by the formula:

$$\text{Hg/l} = \frac{125 \text{ ml}}{\text{vol. of aliquot}} \times \frac{\text{Hg in aliquot}}{\text{mg. of particulates in total sample}} \times \frac{\text{mg particulates}}{\text{liter}}$$

3. Standard Curves. Standard curves were initially prepared with both vapor phase and aqueous Hg standards. Aqueous Hg standards were prepared from a stock solution (0.1354 g HgCl₂ + 10 ml concentrated HNO₃ diluted to 100 ml with DI water) by serially diluting to obtain a working standard range between 1-20 ng Hg. Aqueous standards were analyzed using the procedure described above. Each standard concentration was analyzed in triplicate and at least five different concentrations were run.

Vapor phase standard curves were prepared by aerating 10 ml SnCl₂ and 50 ml DI water in the reaction vessel for ten minutes to remove any traces of Hg in the vessel and system. The Au column was heated to release Hg. A precise volume of Hg vapor was withdrawn from the calibration tube and injected into the reaction vessel through the septa located at the top. Aeration was carried out for one minute. The Au column was heated and peak height recorded. Other volumes of Hg vapor were injected into the same SnCl₂/water solution to establish the curve. Every point was done in triplicate.

There was good agreement between the two methods for establishing a standard curve (Figure 3). Mercury concentrations in the aqueous samples gave slightly greater responses than vapor samples probably because of trace Hg contamination from glassware and from handling during dilutions. Aqueous Hg standards, both stock and working solutions, show variability and instability (McNerney, 1983) with sources of error coming from weighing solid HgCl₂ and from contamination from labware used in the preparation of the standards. Vapor standards involve less processing and proved to be superior to aqueous standards with respect to convenience, precision and accuracy.

Vapor standard curves were used for all Hg determinations. Vapor standard curves were prepared before each set of analyses by a series of

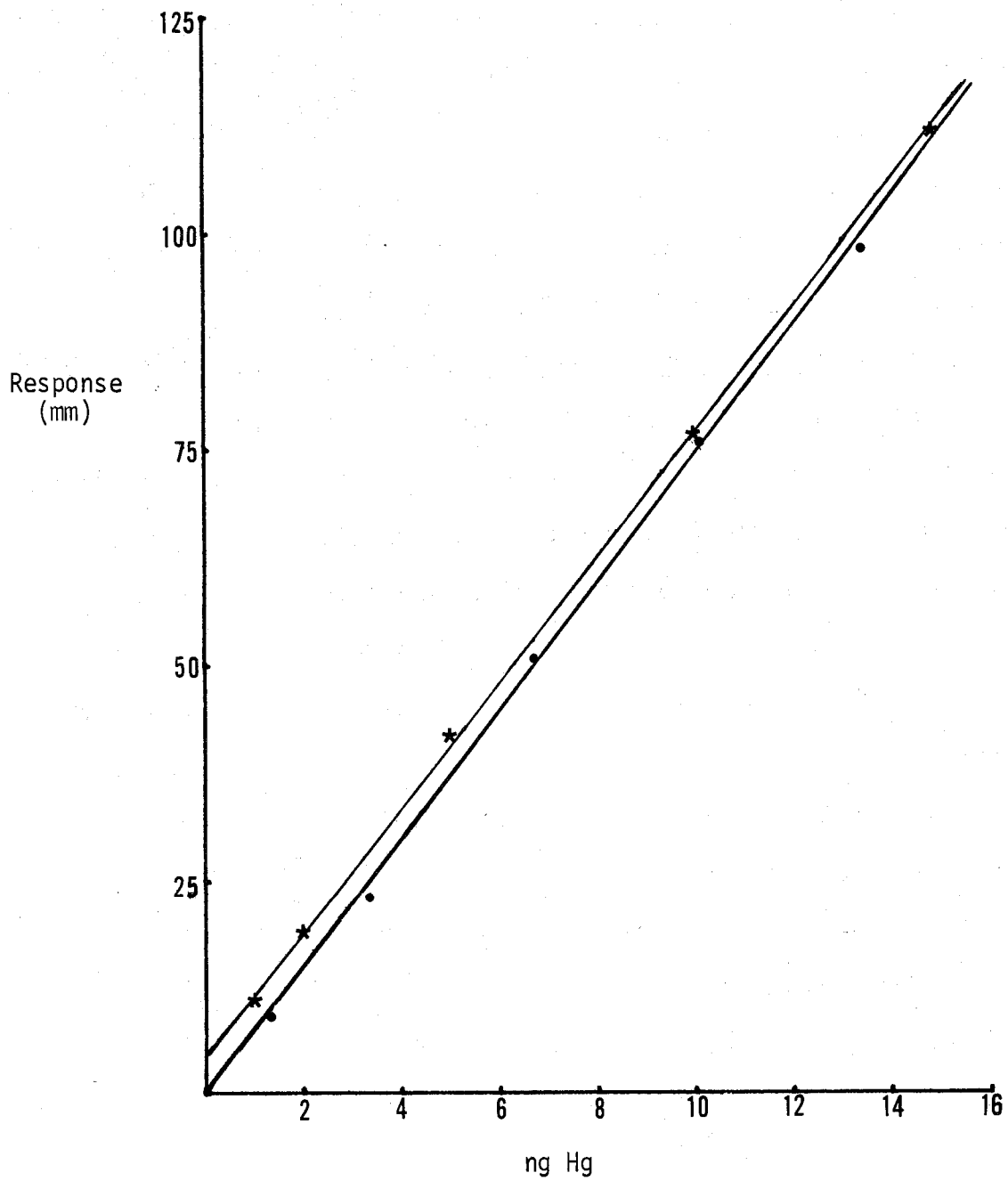


Figure 3. Standard curves for vapor phase and aqueous Hg standards.
(• = vapor phase Hg response, * = aqueous phase Hg response)

injections into the reaction vessel as described above. A calibration was carried out before each analysis within a set by injecting Hg vapor into the system through the pyrex T injection port and the response compared to that of five identical injections made before sample analyses had begun to determine whether instrument response had deteriorated. Injections during the analysis fell within this range or the system cleanup procedure was repeated until the value did fall within the range. Mercury levels recorded from injections into the T injection port were typically 5-10% greater than corresponding Hg levels recorded from injections into the reaction vessel.

4. Optimization of System Parameters. Largest peak heights were obtained at low N₂ gas flow. Very low flows cannot be used, however, because of sensitivity to small variations in flow. At the other extreme, high flow rates disrupt plug flow and lead to smaller peak heights. A flow rate of 100 ml/min was found to be a good compromise. The flow meter positioned at the exit port of the optical cell controlled carrier gas flow precisely enough at 100 ml/minute to give 1% coefficient of variation in peak height at a mean Hg level of 1 ng.

The effect of Au column temperature on peak height was examined at a constant carrier gas flow rate of 100 ml/min. Heating at temperatures below 300° C resulted in incomplete recovery of Hg from the column. Response increased rapidly between 300 and 500° C and leveled off about 600° C. Heating above 600° C did not improve signal height but instead led to a second peak. The broad shape of the second peak suggests the presence of materials other than Hg which desorb slowly. The peak is believed to be due to non-volatile organic compounds that coat the gold and vaporize at higher temperatures.

The aeration rate of the sample in the reaction vessel must be high to facilitate proper mixing with the reducing agent. Slow rates (750 ml/min)

do not appear to remove all of the mercury from solution and rates above 1250 ml/min cause turbulence which ejects droplets out of the reaction vessel and interferes with Hg analysis. An aeration rate of 1000 ml/min. prevented excess sample turbulence yet removed the maximum amount of Hg vapor from solution.

5. Precision and Accuracy. The accuracy of the procedure was evaluated by analyzing USEPA water pollution quality control samples and USGS standard reference materials. The precision of the method was evaluated from 5 replicate analyses of both dissolved and particulate fractions of a single sample from Morgan Creek. These replicates showed a coefficient of variation of 6.4% at a mean Hg level of 49.6 ng/l for the dissolved fraction and 14.4% at a mean level of 70.4 ng/l for the particulate fraction.

The limit of detection was defined as a signal that gave twice the blank value and was estimated to be 20 ng/l for a 50 ml sample size. One day and five day storage experiments were conducted to determine the reliability of the preservation technique. Mercury concentrations changed less than 1.2% over 5 days.

RESULTS AND DISCUSSION

A. Cd, Cu, Pb and Zn

Mean filterable metal concentrations are listed in Table 3 by sampling site. Filterable Zn concentration ranged from below 1.1 to 105 $\mu\text{g}/\text{l}$ and significant differences were observed among sites. Cadmium concentrations were consistently low ranging from undetectable ($<.02 \mu\text{g}/\text{l}$) to 2.2 $\mu\text{g}/\text{l}$ with no significant differences observed among sites. Lead concentrations were above the detection limit of .93 $\mu\text{g}/\text{l}$ for only 27% of the samples analyzed. The highest concentration, 3.3 $\mu\text{g}/\text{l}$, was found in samples from Robeson Creek and Haw River collected February 12, 1981. The area had received over an inch of rain the day before and there was high flow at all six streams. The highest filterable Pb concentrations for 4 of the 6 sites were found in samples collected on this day. No significant differences in the mean concentrations were observed among sites. Copper concentrations ranged from below 1.3 $\mu\text{g}/\text{l}$ to 51 $\mu\text{g}/\text{l}$. The mean concentration at Northeast Creek (14 $\mu\text{g}/\text{l}$) was significantly higher than the mean at the other 5 streams. Metal concentrations generally decreased in the order Zn>Cu>Cd>Pb except for Robeson Creek where they decreased in the order Cu>Zn>Pb>Cd.

Mean concentrations of non-filterable metal are listed in Table 3. These decrease in the order Zn>Pb>Cu>Cd for New Hope Creek, Morgan and Third Fork Creeks and Zn>Cu>Pb>Cd for Robeson and Northeast Creeks and the Haw River. Zinc concentrations ranged from .88 to 220 $\mu\text{g}/\text{l}$. Cadmium was detectable in only 17% of the 64 samples with the highest concentration, 1.8 $\mu\text{g}/\text{l}$ observed at the Haw River on February 12, 1981. Lead concentrations ranged from 0.27 to 120 $\mu\text{g}/\text{l}$, and Cu from 0.37 to 62 $\mu\text{g}/\text{l}$. Significant differences were observed among site non-filterable Zn, Pb and Cu

Table 3. Mean and Range of Metal Concentrations by Sub-basin and Site ($\mu\text{g/l}$)

Site	Zn		Cd		Pb		Cu	
	F	NF	F	NF	F	NF	F	NF
New Hope River Sub-basin								
NH	8.9 ^b (3.1-21.)	21. ^b (5.2-92.)	.35 (.02-.99)	.04 (n.d.-.54)	.11 (n.d.-1.1)	9.5 ^b (1.4-27.)	4.8 ^b (1.7-8.7)	7.4 ^b (.43-30.)
MC	7.2 ^b (.79-24.)	12. ^b (1.9-66.)	.24 (n.d.-.47)	.03 (n.d.-.32)	.10 (n.d.-.94)	5.5 ^b (.71-28.)	3.9 ^b (1.7-9.0)	4.6 ^b (.63-27.)
TF	22. ^a (2.8-53.)	36. ^b (2.5-220)	.65 (n.d.-2.2)	.13 (n.d.-.79)	.32 (n.d.-1.7)	17. ^a (2.3-120)	6.6 ^b (3.9-14.)	9.9 ^b (1.2-62.)
NE ₁ /NE ₂	18. ^a (.38-105)	26. ^b (5.5-102)	.53 (.12-1.2)	n.d.	.24 (n.d.-2.1)	7.2 ^b (1.7-28.)	14. ^a (1.3-51.)	12. ^b (2.7-60.)
Haw River Sub-basin								
RC	3.9 ^c (n.d.-15.)	3.6 ^c (.88-11.)	.32 (n.d.-1.1)	.03 (n.d.-.33)	.34 (n.d.-3.3)	1.1 ^c (.27-3.3)	5.5 ^b (n.d.-28.)	1.6 ^c (.37-5.3)
HR	6.3 ^b (1.1-21.)	21. ^b (1.7-104)	.52 (.16-1.1)	.20 (n.d.-1.8)	.35 (n.d.-3.3)	6.3 ^b (.64-29.)	3.2 ^b (1.3-6.8)	9.6 ^b (.86-61.)
Overall Mean	11.	20.	.44	.07	.24	7.8	6.3	7.5

a. Concentrations significantly higher than concentrations at sites designated b.

c. Concentrations significantly lower than b, F=filterable metals, NF=non-filterable metals, n.d.=below the detection limit for all samples at this site, ()=concentration ranges.

concentrations. Concentrations were significantly smaller at Robeson Creek.

The percentages of total metal in the non-filterable and filterable fractions were determined and then averaged for each site (Table 4a). Most of the Zn, Cu and Pb were found in the non-filterable fractions, about 50-72% of the Zn, 50% of the Cu and greater than 94% of the Pb. Previous workers (Windom, et al., 1971; Kubota, et al., 1974) have observed similar metal transport distribution for Zn, Pb and Cu in U.S. streams. Cadmium, on the other hand, was found primarily (>80%) in the filterable phase which is similar to the observations of Kubota et al., (1974) for Cd in tributaries of Cayuga Lake.

The amount of metal in suspended solids (SS) expressed as μg metal/g sediment is shown in Table 4b. The concentration of Zn ranged from 99 $\mu\text{g/g}$ to 1400 $\mu\text{g/g}$. Cadmium was detectable in only 11 of the 64 samples analyzed with its highest concentration, 60 $\mu\text{g/g}$, collected during a period of low flow from New Hope Creek. Lead concentrations ranged from 39 to 710 $\mu\text{g/g}$ and Cu ranged from 45 to 620 $\mu\text{g/g}$. No differences were observed among sediment concentrations of Zn, Cd and Cu. However New Hope Creek and Third Fork Creek had higher average Pb concentrations, 250 and 240 $\mu\text{g/g}$ respectively, than either Robeson Creek (104 $\mu\text{g/g}$) or Northeast Creek (80 $\mu\text{g/g}$) ($p=.0001$).

Suspended sediment concentrations ranged from 1.30 mg/l to 730 mg/l. Northeast Creek contained significantly more SS (122 mg/l) than the New Hope (89 mg/l), Morgan Creek (69 mg/l) or Third Fork Creek (83 mg/l), and Robeson Creek contained significantly less (18 mg/l).

The Zn, Pb and Cu concentrations in SS plotted against SS concentrations are shown in Figure 4. Metal concentrations are seen to decrease sharply at very low SS concentrations and level off at 100 mg/l SS.

Table 4a. Percentages* of the total metal concentrations transported in each of the two fractions, filterable and non-filterable

Site	Zn		Cd		Pb		Cu	
	F	NF	F	NF	F	NF	F	NF
NH	35%	65%	97%	3%	1%	99%	48%	52%
MC	44%	56%	93%	7%	2%	98%	62%	38%
TF	49%	51%	85%	15%	3%	97%	56%	44%
NE1/NE2	29%	71%	100%	0%	3%	97%	54%	46%
RC	43%	57%	97%	3%	5%	95%	66%	34%
HR	44%	56%	89%	11%	2%	98%	47%	53%

* Mean of the Sample Percentages.

Table 4b. Means and ranges of metal concentrations in suspended sediments of the New Hope and Haw River systems

Site	µg/g			
	Zn	Cd	Pb	Cu
NH	500 (105-1400)	5.0 (n.d.-60.)	250 (48.-710)	140 (58.-620)
MC	380 (150-690)	.53 (n.d.-4.6)	170 (63.-460)	130 (58.-310)
TF	530 (140-1100)	4.4 (n.d.-31.)	240 (71.-560)	140 (45.-300)
RC	340 (120-1100)	.62 (n.d.-6.2)	104 (40.-420)	110 (63.-280)
HR	310 (99.-650)	.83 (n.d.-5.4)	150 (39.-500)	150 (84.-290)
NE	290 (150-460)	n.d.	80. (47.-140)	130 (52.-320)

() = ranges, n.d. = below detection

$\frac{\mu\text{g Metal}}{\text{g Suspended Sediment}}$

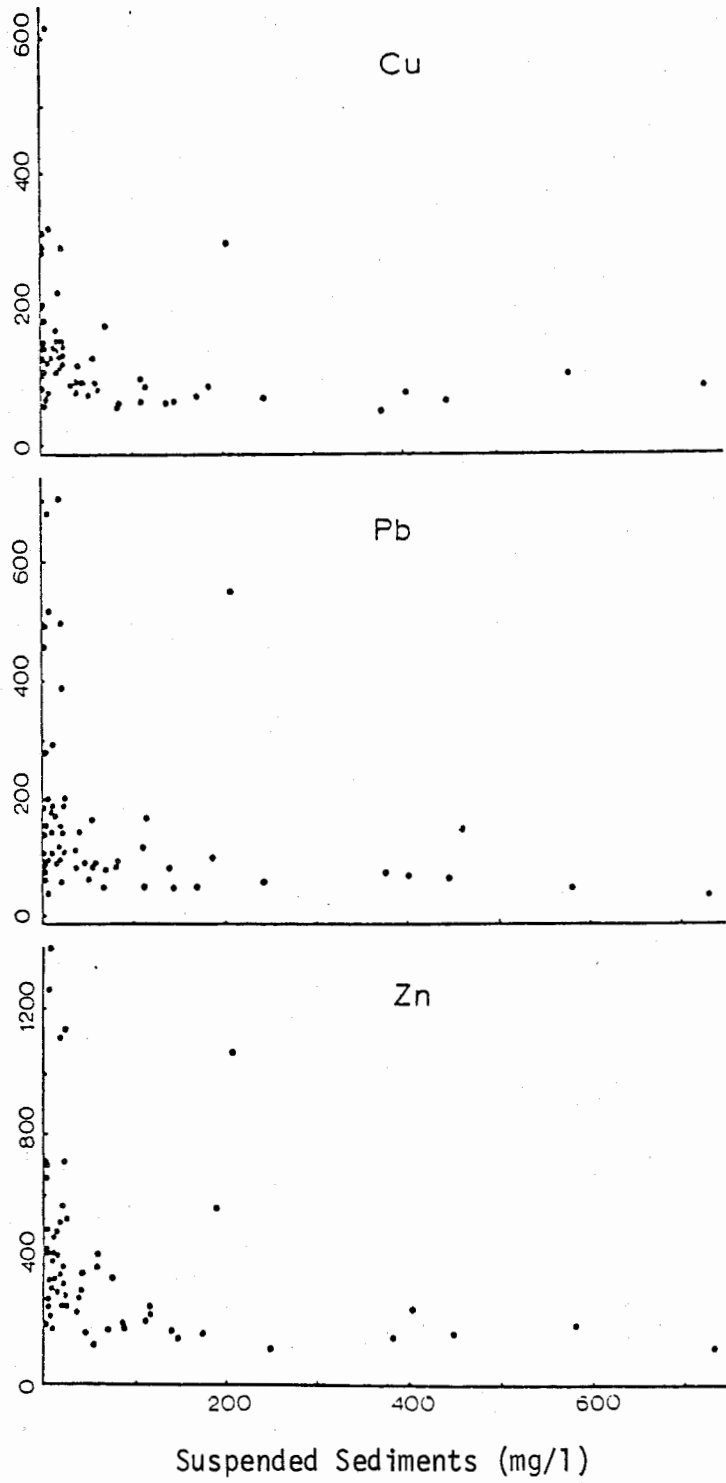


Figure 4. Metal concentrations in suspended sediments as a function of suspended sediment concentration.

Particle size could explain this relationship. Small buoyant particles are expected at low flow whereas at high flow larger particles predominate. The large area to volume ratios of smaller particles enable them to adsorb and carry more metal per gram of suspended sediment. Wilbur and Hunter (1979) observed such an increase in metal concentration with decreased particle size in bottom sediment of the Saddle River, New Jersey. The outlying point in each graph at 209 mg/l SS is the May 18, 1980, Third Fork Creek data point. The high metal concentration observed in this sample is likely due to the resuspension of treatment plant effluents which had settled in the bottom sediments during low flow and were resuspended during the sudden increase in flow that followed one inch of rainfall.

Concentration increases in one metal were often accompanied by increases in others. Positive linear correlations were observed between filterable Zn and filterable Cd, Pb and Cu and between suspended sediment associated Zn, Pb and Cu. The moderate correlations indicate metals are linked through a common factor, perhaps particulate size, or another variable not studied here.

Weak correlations were observed between suspended sediment concentrations and flows for the New Hope, Morgan Creek, Third Fork and Robeson Creek. Both filterable metal concentrations and SS associated metal concentrations were linearly correlated with flow at individual sites, but only Pb associated with the SS correlated with flow at more than one site.

The relationships between metal and suspended sediment concentrations and flow were examined further after the data was segregated into high and low flow (Table 5). The mean annual (March 1980-February 1981) flow was determined for each site (Table 1). Flows greater than the stream mean were classified high flow, while those less than or equal to the stream

Table 5. Mean Metal and Suspended Sediment Concentrations for High and Low Flows

		$\mu\text{g/l}$				mg/l			
		Cd		Pb		Cu		Suspended Sediments	
	Zn	High Flow	Low Flow	High Flow	Low Flow	High Flow	Low Flow	High Flow	Low Flow
Filterable	12.	7.8	.55	.46	.38	.10	5.3	6.0	
Non-Filterable	32. *	8.0	.12	.02	13. *	3.3	12. *	2.8	138. * 20.5

2

* Significantly different at $\alpha=.01$ using z statistic.

mean were classified low flow. All observations were combined to give the values in Table 5. The z test statistic was used to determine significant differences between the high/low flow mean concentrations at $\alpha = .01$.

Average high-flow filterable Zn, Cd and Pb concentrations were larger than low-flow concentrations but differences were not significant. Low flow filterable Cu was larger than high flow, but again this difference was not significant. Average non-filterable Zn, Pb and Cu concentrations were significantly larger in samples taken during high flow than at low flow. It is obvious from this table that considerably more Zn, Pb and Cu enter the reservoir during high flow events and via suspended sediments than during low flow and in soluble form.

Concentrations of suspended sediment and total metal at high flows appear to rely on the sample time relative to peak flow rather than on actual flow (Figures 5 and 6). Samples collected at peak flow (May 18, 1980 and May 11, 1981) from New Hope Creek had much higher suspended sediment concentrations and metal concentrations due to the particulate fraction than those collected when flows were actually higher but were on the falling stage of an event (March 22, 1980 and February 12, 1981) (Figure 5). Studies on several watersheds have indicated that the rising stage of a high flow event carries higher concentrations of suspended sediment and particulate forms of phosphorous (Yaksich et al., 1980), Si, Fe and Al (Mulholland et al., 1981) than the falling stage. Concentrations often peak before peak streamflow. This same relationship between concentrations and flow may hold true for Zn, Pb and Cu. Suspended sediments varied little during low flow for both the New Hope and the Haw Rivers (Figures 5 and 6).

Total annual Zn, Cd, Pb and Cu and suspended sediment loading of the

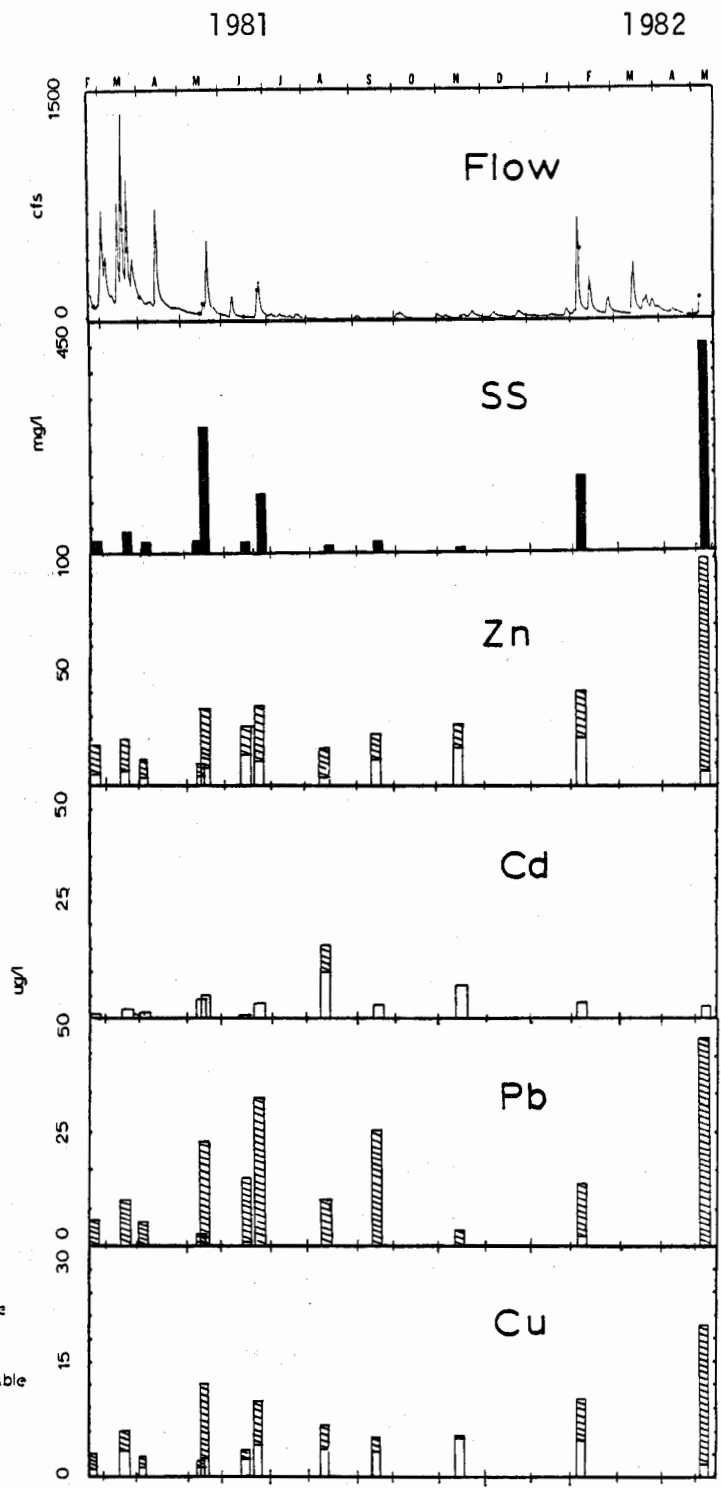


Figure 5. Flow (cfs), suspended sediments (mg/l), Zn ($\mu\text{g/l}$), Cd ($\mu\text{g/l}$), Pb ($\mu\text{g/l}$) and Cu ($\mu\text{g/l}$) as a function of sampling date for New Hope Creek.

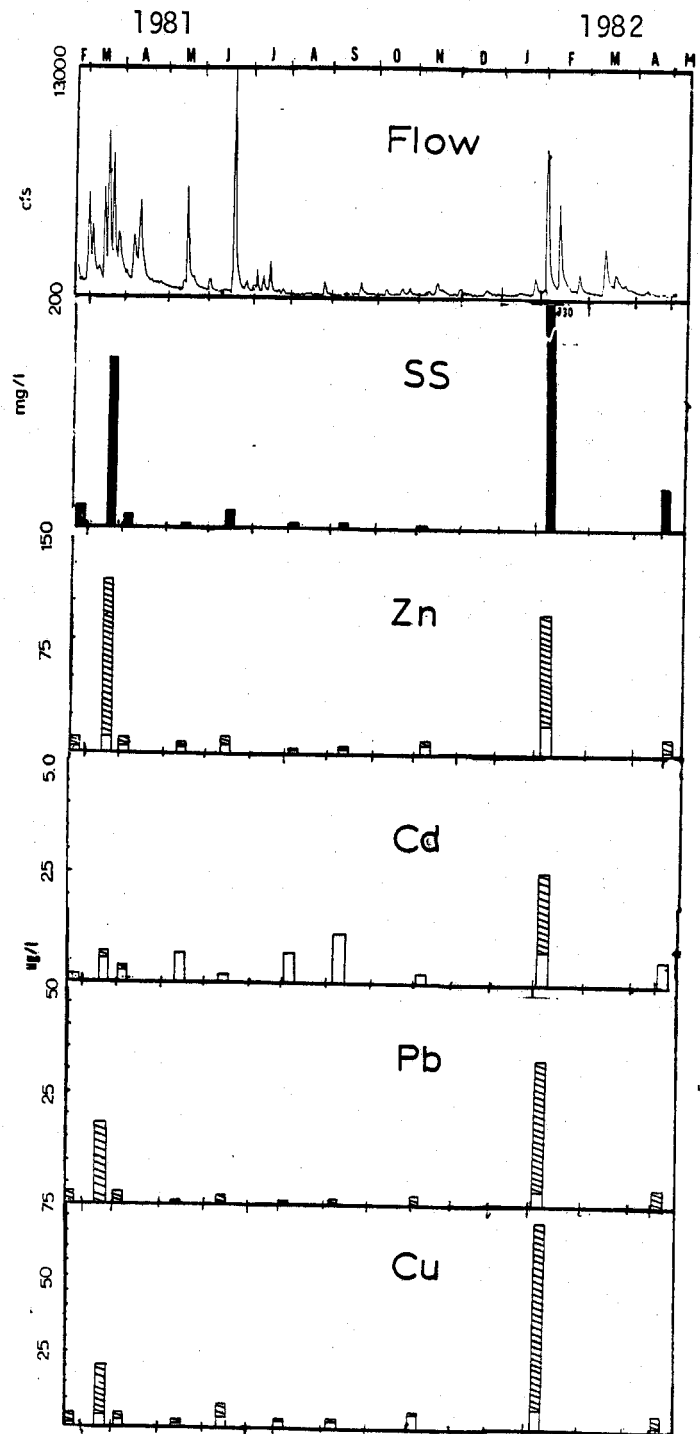


Figure 6. Flow (cfs), suspended sediments (mg/l), Zn ($\mu\text{g/l}$), Cd ($\mu\text{g/l}$), Pb ($\mu\text{g/l}$) and Cu ($\mu\text{g/l}$) as a function of sampling date for the Haw River.

B. Everett Jordan Reservoir were computed for each of the streams sampled by multiplying the average annual site flow by flow-weighted mean concentrations, $\bar{y}_w = \frac{\sum w_i y_i}{\sum w_i}$; where \bar{y}_w is the flow weighted mean concentration, w_i is the flow for the i th observation, y_i is the metal concentration for the i th observation, \bar{w} is the mean flow and n is the number of observations. Yaksich et al. (1980) suggested that flow-weighted mean concentrations are preferred for estimating loading so that the higher concentrations during short time high flow events can be properly accounted for and the lower concentrations at low flow will not predominate the calculation.

The order of metal loading is Zn>Cu>Pb>Cd (Table 6). Annual loadings were normalized with respect to drainage area (Table 7) for comparison of the different streams. Zinc entering the reservoir was similar for New Hope Creek (3.6×10^3 g/km² yr), Morgan Creek (5.7×10^3 g/km²-yr) and Northeast Creek (5.9×10^3 g/km²-yr). The Haw River contributes 20.1×10^3 g/km²yr, about 3-4 times as much Zn per km² as the New Hope, Morgan Creek or Northeast Creek. Robeson Creek contributes 2.4×10^3 g/km²-yr, or about half as much. New Hope Creek, Morgan Creek and Northeast Creek again contribute approximately the same amount of Pb. The Haw River contributes more Pb, while Robeson Creek contributes less. The Haw River contributes the most Cu 9.0×10^3 g/km²-yr with little variation among the other streams. Greater than 60% of the total Zn, Pb and Cu entering the reservoir is in the particular fraction.

The Army Corps of Engineers (1975) prediction for suspended sediment loadings of Jordan Lake is in the range 50 tons/mi²-yr (17.6×10^6 g/km²) to 550 tons/mi²-yr (193×10^6 g/km²-yr). One particular study in the Corps report estimated a sediment yield of 230 tons/mi²-yr (81×10^6 g/km²-yr) for the Haw River and 90 tons/mi²-yr (31×10^6 g/km²-yr) for the New Hope

Table 6. Metal and Suspended Sediment Loadings into the B. Everett Jordan Reservoir

Site	Metals (kg/yr)				Suspended Sediments
	Zn	Cd	Pb	Cu	
NH	710	5.6	200	300	2.4×10^6
MC	670	6.6	180	230	2.1×10^6
TF	310	4.0	110	140	7.0×10^5
NE1/NE2	530	11	130	280	2.2×10^6
RC	180	5.8	37	170	4.5×10^5
HR	67,000	1,100	17,000	30,000	3.1×10^8
<u>Total Loads by Sub-basin</u>					
New Hope Sub-basin					
	2,220	27	620	950	7.4×10^6
Haw River Sub-basin					
	67,200	1,100	17,000	30,200	3.1×10^8

* Weighted means were used to calculate loads

Table 7. Unit Area Contribution of Total Metals and Suspended Sediments by Sub-basin and Site

Site	g/km ² -yr				Suspended Sediments
	Zn	Cd	Pb	Cu	
NH	3.6 X 10 ³	2.8 X 10 ¹	1.0 X 10 ³	1.5 X 10 ³	12 X 10 ⁶
MC	5.7 X 10 ³	5.6 X 10 ¹	1.5 X 10 ³	1.9 X 10 ³	18 X 10 ⁶
TF	7.1 X 10 ³	9.1 X 10 ¹	2.5 X 10 ³	3.2 X 10 ³	16 X 10 ⁶
NE1/NE2	5.9 X 10 ³	12.2 X 10 ¹	1.5 X 10 ³	3.1 X 10 ³	25 X 10 ⁶
RC	2.4 X 10 ³	7.6 X 10 ¹	0.5 X 10 ³	2.2 X 10 ³	6 X 10 ⁶
HR	20.1 X 10 ³	33.0 X 10 ¹	5.1 X 10 ³	9.0 X 10 ³	93 X 10 ⁶

Unit Area Contribution (Total Load/Total Area) by Sub-basin

New Hope Sub-basin

4.98 X 10³ 6.1 X 10¹ 1.4 X 10³ 2.1 X 10³ 16.6 X 10⁶

Haw River Sub-basin

19.7 X 10³ 32.4 X 10¹ 5.0 X 10³ 8.8 X 10³ 90.6 X 10⁶

River. The calculated unit area contributions of suspended sediments from New Hope River, 16.6×10^6 g/km²-yr, and Haw River 91×10^6 g/km²-yr are quite close to these estimates.

B. Mercury

The relationship between Hg concentration and stream flow was examined after the data was segregated into high and low flows. The mean annual flow was estimated for each site using a relationship developed by the Corps of Engineers for North Carolina.

$$\text{Mean Annual Flow (ft}^3/\text{sec)} = \frac{\text{Drainage Area (miles}^2\text{)}}{0.96}$$

Flows greater than the stream mean were classified high flow, while those less than or equal to the stream mean were classified low flow.

Dissolved Hg concentrations in the Haw and New Hope River systems varied with both sampling site and flow (Table 8). Values ranged from 24.1 ng/l (Polkberry; March 2, 1983) to 124.6 ng/l (Little; September 28, 1982). Control site concentrations were significantly lower than all other sites at low stream flows. They were also significantly lower for three out of the five sample dates at high stream flows.

Four streams (Haw, Morgan, Little, Third Fork) had significantly lower mean dissolved concentrations at high flow than low flow. Dissolved Hg concentrations found in the six streams receiving municipal and urban effluent are in agreement with values reported in the literature (Smith et al., 1971; Turner and Lindberg, 1978; Cranston and Buckley, 1972; Jackson et al., 1982). Background levels found in the control stream are in agreement with some studies but are considerably higher than other studies (e.g. Jackson et al., 1982). The observed differences can be attributed to differences in the geochemistry of the watersheds, the differences in the amount of dissolved

Table 8. Means and Ranges of Dissolved Mercury Concentrations in Waters of the New Hope and Haw River Systems

Stream	Low Flow Dates (ng/l)	High Flow Dates (ng/l)	All Dates (ng/l)
Polkberry (Control)	39.9 (34.9-47.4)	34.3 (24.1-41.3)	37.1 (24.1-47.4)
Haw	62.1 (51.6-68.4)	47.5 (42.1-51.9)	54.8 (42.1-68.4)
Morgan	87.5 (66.1-105.3)	49.4 (43.8-53.3)	68.5 (43.8-105.3)
New Hope	78.4 (60.5-116.9)	61.3 (41.6-85.1)	69.9 (40.6-116.9)
Northeast	72.4 (55.7-102.7)	55.9 (34.1-71.5)	64.2 (34.1-102.7)
Third Fork	64.1 (56.4-72.2)	43.6 (28.4-60.0)	53.9 (28.4-72.2)
Little (Urban Runoff)	81.3 (65.4-124.6)	42.8 (28.4-51.9)	62.1 (28.4-124.6)

organic matter in the water, the amount of Hg discharged into each river and the proximity of the sample site to discharge outfall.

Particulate Hg concentrations ranged from 25.5 ng/l (Little Creek; October 26, 1982) to 135.3 ng/l (Haw River; October 26, 1982) (Table 9). The control site had significantly lower concentrations than any other site at low stream flows but was significantly lower only 2 of the 5 dates at high flow.

The mean particulate concentrations for four of the seven sites (Morgan, Northeast, Third Fork, Little) were lower at high flow than at low flow but not significantly. On the other hand, the Haw River had significantly higher mean concentration at high flow than low flow. Mean concentrations for the New Hope River and Polkberry Creek did not change significantly for the two flows.

The levels found are higher than those of Smith *et al.*, (1971) but are in agreement with Turner and Lindberg (1978). Differences are due to the size, organic content and amount of particles collected on the filter.

The Hg concentrations of particulates expressed as μg Hg per gram of particulate are compared in Table 10a. The mean concentrations are significantly less for high flow than low flow at all streams. These concentrations plotted as a function of suspended particulate concentration show a sharp decrease with increasing SS load (Figure 7). Concentration variability also decreased dramatically at loads above 100 mg/l were Hg concentrations never exceed 2.5 $\mu\text{g}/\text{g}$. One possible explanation for the decrease of Hg concentration with SS concentration is that the organic matter content is regulating Hg concentration. However, data of Weiss *et al.*, (1983) collected during the same sampling period showed loss on ignition to be almost constant with flow and particulate load. Size fractionation of particulates was conducted to determine whether particle size could explain the relationship (Table 10b).

Table 9. Means and Ranges of Mercury Concentrations Due to the Particulate Fraction in Waters of the New Hope and Haw River Systems

Stream	Low Flow Dates (ng/l)	High Flow Dates (ng/l)	All Dates (ng/l)
Polkberry (Control)	43.5 (35.0-47.3)	48.5 (29.6-56.7)	46.0 (29.6-56.7)
Haw	60.5 (55.0-67.4)	86.3 (70.3-135.3)	73.4 (55.0-135.3)
Morgan	73.4 (62.2-94.8)	69.3 (60.7-90.2)	71.4 (60.7-94.8)
New Hope	94.1 (72.3-107.1)	94.7 (83.0-108.9)	94.4 (72.3-108.9)
Northeast	71.9 (51.9-89.1)	60.1 (46.2-77.0)	66.0 (46.2-89.1)
Third Fork	82.2 (71.6-97.0)	61.9 (44.7-73.1)	72.1 (44.7-97.0)
Little (Urban Runoff)	60.3 (49.2-70.1)	46.9 (25.5-75.5)	53.6 (25.5-75.5)

Table 10a. Means and Ranges of Mercury Concentrations on Particulates Per Unit Weight

Stream	Low Flow*	High Flow*	Both Flows*
Polkberry Creek (Control)	11 (5.5-22.7)	1.2 (0.2-2.3)	6.0 (0.2-22.7)
Haw	8 (3.5-20.8)	1.0 (0.4-1.1)	4.5 (0.4-20.8)
Morgan	24 (5.0-33.4)	2.0 (0.4-2.5)	13.0 (0.4-33.4)
New Hope	3 (1.7-5.4)	1.2 (0.4-2.5)	2.0 (0.4-5.4)
Northeast	6 (2.8-12.8)	0.8 (0.5-0.8)	3.0 (0.5-12.8)
Third Fork	5 (3.2-6.1)	1.0 (0.2-1.5)	3.0 (0.2-6.1)
Little (Urban Runoff)	21 (6.8-48.4)	1.1 (0.4-1.8)	11.0 (0.4-48.4)

* μgHg
g Sus. Sed.

Table 10b. Particle Size Fractionation of Suspended Particulate Matter in Morgan Creek

Diameter (μM)	Hg Concentration ($\mu\text{g Hg/g Part.}$)	Number of Samples	Weight % of Total Sample	% of Total Hg
0.45-8	7.05	6	11.9	48.2
8-20	1.36	6	46.7	36.2
20	0.66	6	41.4	15.6

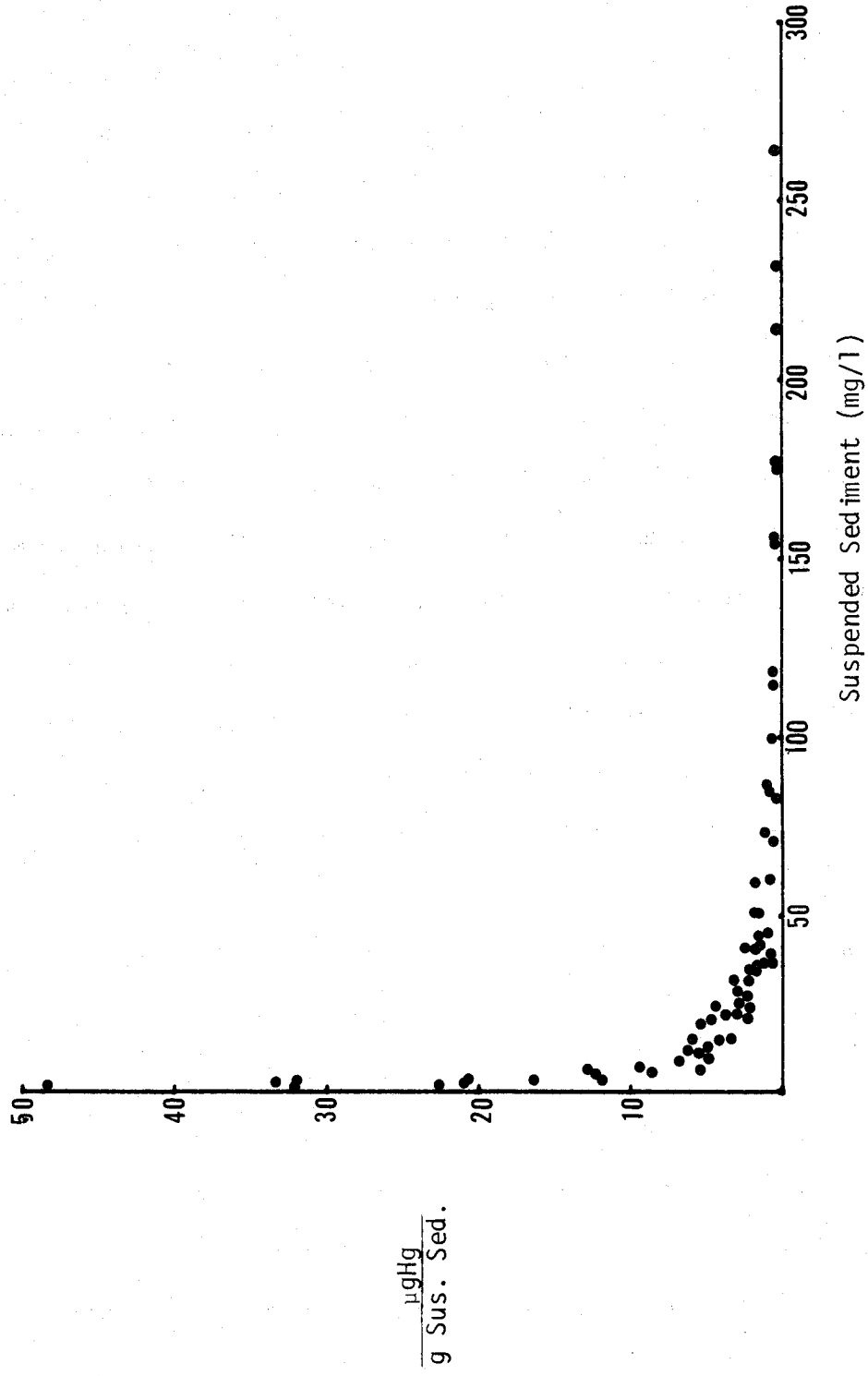


Figure 7. Mercury concentrations in suspended sediments as a function of suspended sediment concentrations.

The smaller sized particles (0.45-8 μm) had 10 times the concentration of Hg than the larger sized particles (>20 μm). Millward and Herbert (1981) and Nelson et al., (1977) found Hg values in the finest size fraction to be much higher than the course fraction of particulate matter. Although the largest size fraction (>20 μm) accounted for 41% of the material collected in this study, only 15% of the total Hg was associated with it. This is in agreement with Cranston and Buckley (1972) who found the same size fraction (>20 μm) to contain 13% of the total Hg found in the sample.

The New Hope River had the highest mean total Hg concentrations (defined as the mean dissolved plus mean particulate) of all sites for both high and low flows (Table 11). Polkberry Creek had the lowest of all sites for both flows. All streams in the New Hope sub-basin has significantly lower mean total concentrations at high stream flow than low flow, whereas the Haw River showed a significantly higher mean concentration at high flow. Polkberry Creek showed no change with flow.

The percentage of total Hg transported in each of the two fractions, dissolved and particulate, is given in Table 12. This table indicates that most of the Hg is on particulates at high flow and about evenly distributed at low flow.

The Hg concentration on bottom sediments collected above and below the municipal wastewater outlet on Morgan Creek are given in Table 13. Concentrations double at the outfall and decrease with distance downstream. This is not surprising since municipal waste appears to be a source of Hg. Van Loon (1974), for example, found sediment concentrations below a municipal wastewater treatment plant outfall to be larger by a factor of five than upstream sediment concentrations. The concentrations found upstream are reasonable for this environment. Miller et al., (1978) found 80 ng/g in

Table 11. Total Mercury Concentrations in Waters of the New Hope and Haw River Systems

Site	Total Hg (ng/l)		Mean for Both Flows (ng/l)
	High	Low	
Polkberry Creek (Control)	82.80	83.46	83.13
Haw River	133.84	122.68	128.26
Morgan Creek	118.76	160.92	139.84
New Hope River	156.02	172.44	164.23
Northeast Creek	116.04	144.26	130.15
Third Fork Creek	105.42	148.38	126.9
Little Creek (Urban Runoff)	89.7	141.62	115.66

Table 12. Percentages of Total Mercury Concentrations Transported in Each of the Two Fractions, Dissolved and Particulate

Stream	Low Flow		High Flow	
	Dissolved (%)	Particulate (%)	Dissolved (%)	Particulate (%)
Polkberry	47.9	52.1	41.4	58.6
Haw	50.7	49.3	35.5	64.5
Morgan	54.4	45.6	41.6	58.4
New Hope	45.4	54.6	39.3	60.7
Northeast	50.2	49.8	48.2	51.8
Third Fork	43.2	56.8	41.3	58.7
Little	57.4	42.6	47.7	52.3

Table 13. Bottom Sediment Mercury Concentrations Above and Below the Wastewater Outfall on Morgan Creek

Sample Site	Hg Concentration ($\frac{\text{ngHg}}{\text{gram sediment}}$)
200 meters upstream	186.4
OUTFALL	371.8
10 meters downstream	292.3
100 meters downstream	260.9
1000 meters downstream	201.1
5000 meters downstream	197.3

sandy sediment and 270 ng/g in unpolluted sediments with high organic content.

Samples were collected from soil and stream banks near each site in order to determine Hg levels expected from erosion. The concentrations varied with no particular pattern. Soil levels ranged from 19.0 ng/g at Little Creek to 95.7 ng/g at the Haw River with a mean for all sites of 47.5 ng/g. Stream bank concentrations ranged from 27.0 ng/g at Northeast Creek to 114.4 ng/g at the New Hope River with a mean of 68.1 ng/g.

Weiss et al., (1972) found a mean of 54 ng/g and a range of 11.6-1,015 ng/g for soils around a sub impoundment of Jordan Reservoir. Shere (1975) reported a mean Hg level for a large number of South Carolina soils to be 62 ng/g.

Total annual mercury loading of the B. Everett Jordan Reservoir was computed for each of the streams sampled (Table 14) by multiplying the average annual site flow by the flow weighted mean concentrations as done for the other metals. Mercury loading per unit drainage area is also indicated in Table 14. As with other metals studied, the Haw sub-basin contributes a greater amount per unit drainage area than the New Hope.

As noted above, total Hg concentrations increased significantly with flow in the Haw River while they decreased significantly with flow in the five streams representing the New Hope sub-basin. Andelman's (1973) hydrodynamic model suggest that the Haw River receives non-point Hg inputs while the five streams in the New Hope water shed receive point source inputs.

Wastewater effluent appears to contribute considerable amount of Hg into the reservoir. Wastewater treatment plants discharge a total of 64

Table 14. Mercury Loading of the B. Everett Jordan Reservoir

Stream	Hg Loading (grams/year)			Both Flows	g/km ² -yr.	% of Total Load		
	High Flow	Low Flow	High Flow			Low Flow	Total Flow	
Polkberry (control)	10.8	0.7	11.5		0.4	0.1	0.1	0.1
Haw	119,963.1	15,388.6	135,351.7		40.6	99.0	99.5	99.0
Morgan	182.0	14.8	197.7		1.7	0.2	0.1	0.2
New Hope	922.0	52.0	974.0		5.0	0.8	0.3	0.7
Northeast	31.7	2.4	34.1		0.4	0.1	0.1	0.1
Third Ford	14.4	2.1	16.5		0.4	0.1	0.1	0.1
Little (urban)	28.7	1.8	30.5		0.5	0.1	0.1	0.1
TOTALS	121,150	15,460	136,610			0.1	0.1	0.1
New Hope Sub-basin					2.5			
Haw Sub-basin					40.2			

million gallons/day into the Haw River sub-basin and 21 million gallons/day into the New Hope sub-basin. Using Hg concentrations found in Morgan Creek effluent, wastewater treatment plant discharges account for 100% of the yearly Hg loading from the New Hope sub-basin and 27% from the Haw sub-basin.

Water from the Haw River has a short residence time in the reservoir. The Hg on suspended particles will settle to bottom sediments only if sedimentation and scavenging rates are fairly high. Circulation patterns will carry some of the particulate matter, especially small particles, up the New Hope arm of the Reservoir and deposit them there. The reducing environment expected along the bottom sediment in the lower part of the reservoir will likely immobilize Hg whereas spring and fall turnover periods will distribute Hg throughout the reservoir.

Mercury entering from the New Hope sub-basin will be retained there until flushed towards the dam during high flow events. The waters furthest from the dam will be well mixed and facilitate bacterial conversion to methyl-mercury.

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