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Chemical and Toxicological Characterization of the Upper York River, Virginia The Mattaponi and Pamunkey Rivers

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ABSTRACT

This study describes the most extensive effort to characterize the chemistry, toxicology and community of the sediments of the Mattaponi and Pamunkey Rivers. This was accomplished using a study design modified to expand the number of stations occupied by reducing the cost of analyses by compositing replicate samples collected from each study site rather than performing toxicity tests on these samples individually. In previous studies, the variability in field replicate samples was equivalent to the variability in laboratory replicates. This design has long been used to analyze samples for various chemical contaminants as a cost savings endeavor.

While the concentration of several metals in bulk sediment analyses exceeded the ER-L, only Mn exceeded the ER-M. Thus the sediments sampled were free of serious metals contamination. Of the simultaneously extracted metals when analyzing acid volatile sulfide, only copper, lead, nickel and zinc were present in some samples at concentrations above the detection limit. The SEM/AVS ratios suggest substantial capability of the sediments to accommodate additional metals.

The concentrations of various organic contaminants including PAHs, organophosphate and organochlorine pesticides, PCBs and herbicides were all well below concentrations likely to produce adverse impacts.

No statistically significant impacts on survival in sediments were observed in the three invertebrate species tested (*Hyalella azteca*, *Chironomus tentans*, and *Ceriodaphnia dubia*). There was lower final weight in *C. tentans* at two stations in the Mattaponi River than at any other stations, but in both cases, the final weight exceeded the initial weight. Thus there was no evidence of sediment toxicity in any sample.

There were some minor differences between the benthic communities in the two rivers, but in the final analysis, the B-IBI yielded good results at all stations except at mile 11.88 in the Pamunkey River. The degraded condition resulted from low individuals/meter^2, ash-free dry weight, and number of bivalves at this station. There is no corresponding evidence of chemical or toxicological concerns. There was lower abundance and diversity of invertebrate fauna throughout the Pamunkey River than in the Mattaponi. No random stations were located in the vicinity of the industrial discharges into the Pamunkey River, so no attribution of the cause of the bad B-IBI at one station can be made.

The data from this study are generally consistent with previous limited results produced by Hall *et al.* (1998a), McGee *et al*. (2001) and Wright *et al*. (2002). None of the stations examined by these investigators showed any substantial chemical contamination or sediment toxicity, consistent with the present results. The B-IBIs in the study by McGee *et al*. evidenced some depression, but this was not clearly attributable to the local industry, but may instead reflect runoff from the city streets of West Point.

In summary, there is no evidence of degraded health in these tributaries due to toxicological stressors even with the application of the expanded sampling design.

ACKNOWLEDGMENTS

Any study of this complexity requires the participation of an array of professionals with specific expertise to accomplish the task. This study is not exception.

Support for sampling during the present study was provided by the Water Quality Standards and Biological Programs within the Water Division of DEQ. Rick Browder from that office coordinated the effort and operated the vessel used for sampling. Stu Torbeck provided technical support during each cruise. Through their efforts, the sampling was accomplished within the necessary time window.

Toxicity tests were performed by Georgi Briggs, Lynda Lawrence and John Clements with Coastal Bioanalysts, Inc. These tests were accomplished within the prescribed time window, which requires that all pre-test preparations be accomplished according to a very tight schedule, and thereafter, completion of each task of the test with precision and timeliness.

Scott Winters and Michael Noe of the Division of Consolidated Laboratories for the Commonwealth of Virginia provided analytical support for the chemical characterization of the sediment samples. Timely performance of the necessary analyses involved a phalanx of chemist, under the direction of Ed Shaw.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

1.1 Need for Regional Characterization

For over a decade, the Chesapeake Bay Program, through its Toxics Subcommittee, supported a series of studies designed to characterize sections of the Bay from both a chemical and toxicological perspective. Beginning with the pilot studies of Hall *et al.* (1991, 1992, 1994 and 1997) and continuing through the ambient toxicity reports of 2000 (Hall *et al.* 1998a, 1998b, 2000a, 2000b, Roberts *et al.* 2000, McGee *et al.* 2001, Roberts *et al.*, 2002, Roberts *et al.*, 2003), many areas of the Bay system have been characterized from the mouth to the tidal limits.

In the characterization report for the Chesapeake Bay (U.S. EPA, 1999), some significant areas were identified as lacking sufficient data to be characterized. Included among these areas in Virginia were the Pamunkey and Mattaponi Rivers that form the head waters of the York River, VA. Only two stations, both in the lower Pamunkey River, had been occupied in this region during the decade-long characterization studies. Both were included in the 5th study year along with two stations located some 15 miles downstream in the York River.

Since the characterization report, two studies have examined a few stations in the Mattaponi and Pamunkey Rivers (McGee *et al.* 2001; Wright *et al.* 2002). Investigators in both studies were based in Maryland where most of their research was focused.

While these studies provide insight into these Virginia systems that did not exist when the characterization report was produced, the Virginia DEQ deemed a focused study essential to characterize these waters. A major expectation of this study was to evaluate extended reaches in each river using a series of randomly chosen stations.

1.2 Objectives

- Assess ambient sediment chemistry and toxicity in the Pamunkey and Mattaponi Rivers
- Assess the condition of the benthic community
- Characterize the condition of sediment in this segment of the Chesapeake Bay.

2.0 MATERIALS AND METHODS

2.1 Station Selection

Roberto Llanso of Versar specified 25 random station locations within each of the Upper York River tributaries, the Mattaponi and Pamunkey Rivers. The sampling cruise for the benthic community sampling, which predated the sampling cruise for the remaining portions of the study, constituted a reconnaissance cruise for the chemical and toxicological sampling. Three criteria were defined for station selection: 1) accessibility (depth sufficient to allow the research vessels to access the location), 2) sediment texture (sand content <70-80%) and 3) anaerobic layer present (a dark layer indicating substantial TOC, low oxygen content and high sulfides in sediments). The latter two criteria define areas where various contaminants are likely to be accumulated. The second criterion cannot be strictly applied as there is no accurate field method for measuring sand content. The third criterion is imprecise, but is taken to be any station at which a grab sample of sediment include some amount of anaerobic sediment identifiable as dark brown to black in color and sulfurous in aroma.

Adhering to the above criteria, random station locations were visited until a total of 7 stations were selected. Final station selections are listed in Table 2.1 and plotted in Figure 2.1 and 2.2. As will be demonstrated later in this report, the sediment texture criterion was not consistently applied.

2.2 Sediment Collection

Samples were collected from three randomly chosen points within a 100 by 100 m grid centered on the coordinates for each station. The upper 2 cm of sediment were retained for chemical analyses and toxicological tests. Multiple grabs were made at each point with a Ponar grab until sufficient sediment had been collected for both chemical and toxicological characterizations. Equal quantities of sediment from each point in the grid were then homogenized and distributed among the sample containers. The compositing of sediment from three points in the grid for chemical analyses is consistent with prior studies in this series, but the compositing of sediment for particle size, total organic carbon (TOC) and toxicological samples is a deviation from prior practice. This change was made to increase the number of stations that could be sampled without dramatically increasing the cost of analysis. AVS/SEM samples were collected and stored separately, but composited under nitrogen in order to avoid oxidation of the material immediately prior to analysis.

All samples were placed on ice and transported to the testing laboratories with delivery of analytical samples the following day and toxicological samples within 2-3 days of collection. Toxicological samples held over in the DEQ laboratory were kept in a dark refrigerator at 4°C. Once in the testing laboratories, all sediment was maintained in a 2-4°C cold room prior to processing and analysis. The samples for toxicity evaluations were tested within the 14-day holding time specified in the protocols.

Table 2.1. Station Locations in the Mattaponi and Pamunkey Rivers.

Station Designation	Random Station Number	Latitude	Longitude	Major Landmarks	Depth at MLW (ft)
Mattaponi River					
8-MPN000.86	3	37° 31' 54.96"	-76° 47'9.8"	Near eastern shore upstream from River Mouth.	3
8-MPN001.10	12	37° 32' 5.55"	-76° 47' 20.4"	Eastern Edge of channel downstream from Rt.33 bridge.	10
8-MPN001.33	11	37° 32'18.47"	-76° 47'21.65"	Immediately upstream of Rt. 33 bridge.	18
8-MPN004.31	2	37° 34'15.2"	-76° 47'30.2"	Mid-channel southeast of Muddy Point.	15
8-MPN020.58	4	37° 41'9.38"	-76° 54'55.38"	Mid-channel south of Mantapike.	16
8-MPN020.75	5	37° 41'18.12"	-76° 54'55.38"	Mid channel south of Mantapike.	17
8-MPN024.81	1	37° 41'47.05	-76° 58'17.61	Western shore near Mantua Ferry.	14
Pamunkey River					
8-PMK009.39	5	37° 33'38.45"	-76° 51'34.33"	Left side of channel east of Hill Marsh.	12
8-PMK011.64	3	37° 34'44.61"	-76° 52'18.32"	Left bank north of Hill Marsh.	1
8-PMK011.88	1	37° 34'41.09"	-76° 52'32.57"	Left side of channel north of Hill Marsh.	12
8-PMK012.00	2	37° 34'39.82"	-76° 52'40.31"	Left side of channel north of Hill Marsh.	12
8-PMK013.06	7	37° 34'5.49"	-76° 52'59.21"	Near right bank, west of Hill Marsh.	6
8-PMK020.31	15	37° 33'15.80"	-76° 56'35.44"	Mid-channel east of Cohoke Marsh.	14
8-PMK033.04	4	37° 34' 8.34"	-77° 1' 5.56"	Northwest of Rockahock Bar, east side of Island.	3

Figure 2.1. Station Locations for the Mattaponi River. Stations were sampled in random order sequence until a total of 7 were attained for characterization.

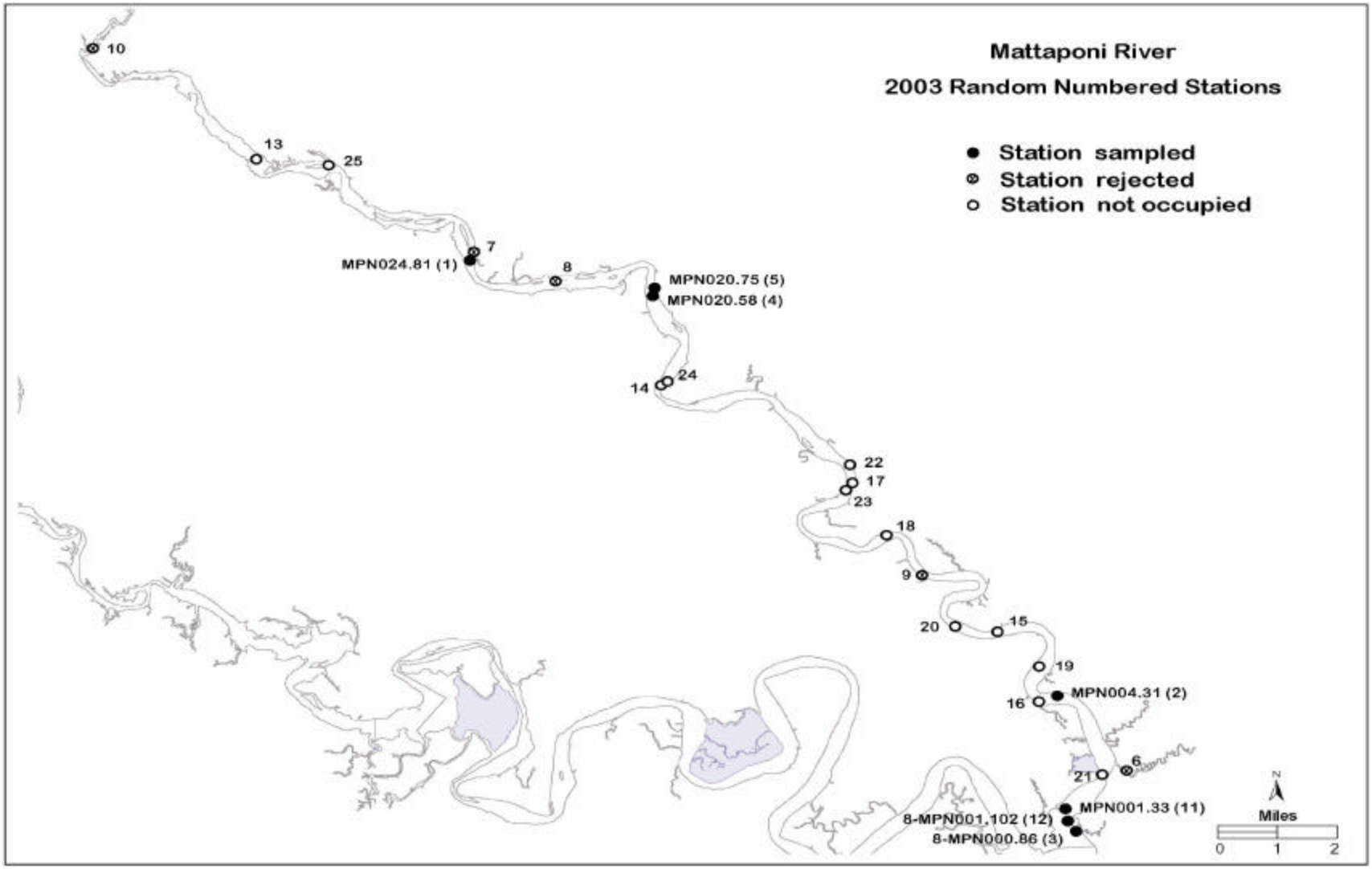
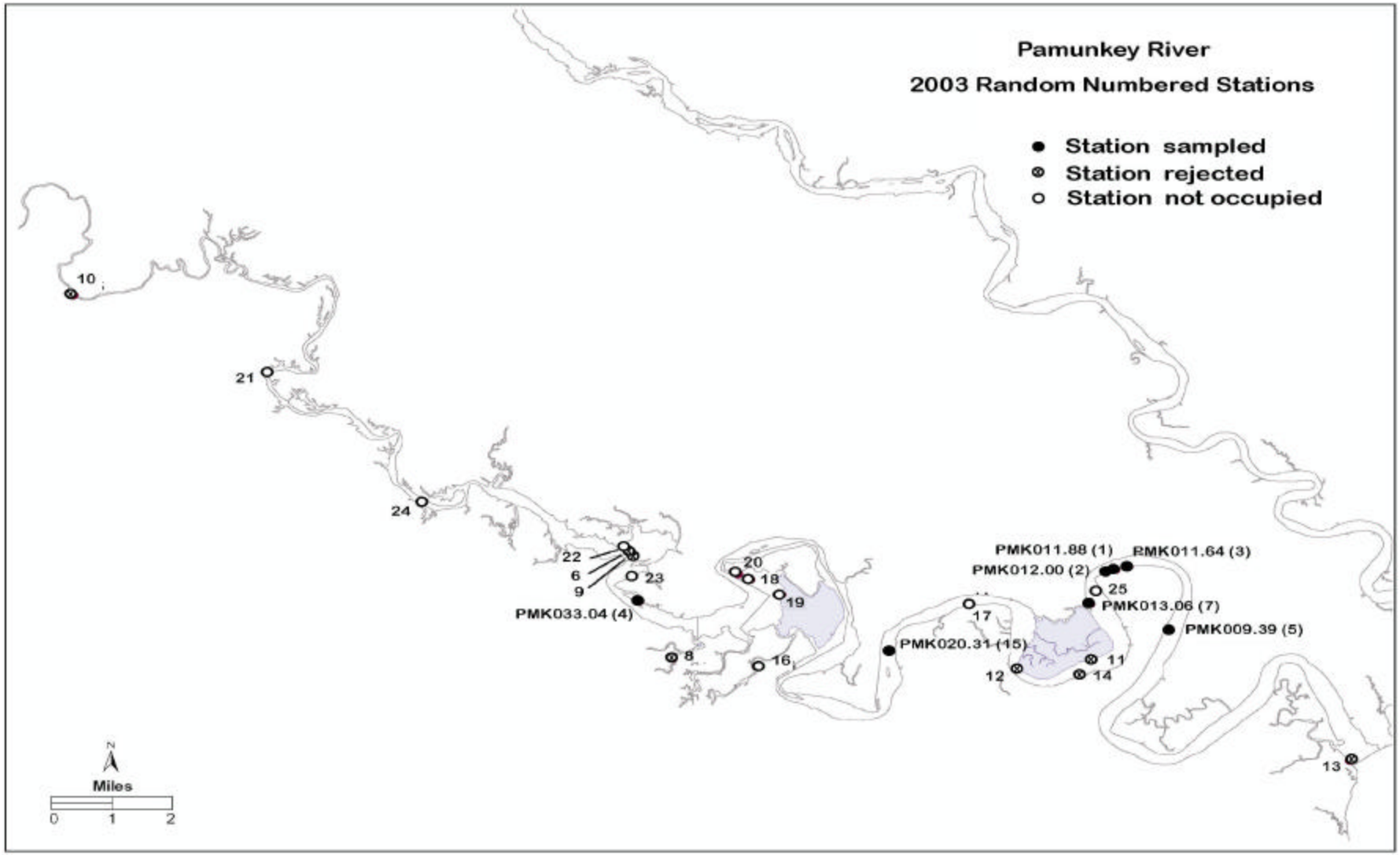


Figure 2.2. Station Locations for the Pamunkey River. Stations were sampled in random order sequence until a total of 7 were attained for characterization.



While at each station, a Hydrosonde III was deployed to measure surface and bottom temperature (°C), conductivity (µmhos/cm^2), salinity (g/kg), dissolved oxygen (mg/l), pH (S.U.) and sampling depth (m). Surface conditions were measured at ca 0.5 m below the water surface, and bottom conditions at about 1 m above the sediment.

2.3 Chemical Analyses

Sediment samples for bulk metal analyses were oven dried, weighed, and digested in nitric and hydrochloric acids by microwave technology. After cooling, the samples were brought up to 50 ml volume, mixed and allowed to settle overnight prior to analysis. From the digested sample, metals are analyzed by ICPMS. The following elements are analyzed by this method: Al, Sb, As, Be, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, and Zn. In addition, acid volatile sulfides and simultaneously extractable metals (AVS/SEM) were determined on separate sediment aliquots using the methods of Leonard *et al*. (1996, 1999). These aliquots consisted of the composite of three independent samples, one from each substation, that were homogenized under nitrogen in the analytical laboratory.

Various organic chemicals in sediments were determined including semi-volatile organic compounds (SVOC), organophosphate pesticides, organochlorine pesticides, polychlorinated biphenyls (PCB), and herbicides. For SVOCs, sediment samples were ground with anhydrous sodium sulfate and Soxhlet extracted with methylene chloride for 18 to 24 hours. The extracts were concentrated and the sulfur content reduced using high performance GPC on porous styrene-divinylbenzene copolymer gel. The extracts were then concentrated and fractionated on a semipreparative aminosilane HPLC using step gradients; this resulted in three fractions containing broad compound classes ranging from aliphatic to polar. The fractionated extracts were then analyzed by capillary gas chromatography / mass spectrometry.

A flame photometric detector (FPD) operating in the phosphorous mode was used to identify and quantitate organophosphates. A halogen specific detector (XSD) was used to measure organochlorine pesticides and polychlorinated biphenyls (PCB).

Portions of the extracts were subjected to water/methylene chloride partitioning to remove residual acid and water-soluble interferences. The extracts are then methylated, concentrated to volume, and analyzed by gas chromatography utilizing a halogen specific detector (XSD) to identify and quantitate herbicides.

Methods are fully described in the work plan submitted for this project.

2.4 Sediment Analyses

Sediment texture on composite samples from the field stations was determined by the Division of Consolidated Laboratory Services (DCLS) using the Folk (1980) method. A sediment sample is dried and passed through geological screens: 4 mm and 62.5 µm. Material retained on the 4 mm sieve represents gravel (weight not determined), and that passing the 4 mm sieve but retained on the 62.5 µm sieve is sand. The remainder of the sediment passing through the finest sieve is

moistened and suspended in water. At fixed times after complete mixing, samples are drawn from specified depths, placed in tared weighing pans, dried and weighed. From this information, the amount of silt and clay can be calculated.

A subsample of the sediment was dried, weighed, incinerated, and reweighed to determine the dry weight and ash-free dry weight. The difference is the total organic carbon that is then expressed as a percentage of the original sample weight.

Coastal Bioanalysts measured percent porewater, porewater ammonia, and porewater pH for each sediment replicate from each station used for the toxicity tests. This provided the information to assess whether there was a toxicologically significant amount of ammonia released from the sediment or a deleterious pH.

2.5 Toxicological Analyses

Sediment and Water Preparation and Characterization

Samples, received in the laboratory from 10/2/03 to 10/9/03, were processed for testing in accordance with CBI SOP STS002B. In the laboratory a test I.D. value from 1-16 was randomly assigned to each sample and laboratory control sediment; for pore water tests with *Ceriodaphnia* laboratory I.D. values from 17-19 were also assigned to fresh and brackish control waters. Laboratory control sediment was collected on 10/9/03 from a retention pond (37°28'42.0"N, 76°31'30.1"W) in an unnamed tributary feeding Beaver Dam Reservoir, Gloucester, VA. Sediment from this site has been successfully used in previous 10-d and 42-d tests with *H. azteca* and 10-d tests with *C. tentans*. Sediment samples were stored in the dark at 2-4^{o} C until used in toxicity tests.

Prior to use in testing, samples were homogenized and large debris (e.g. sticks and shell) was removed. Samples were also examined for the presence of potential predators and species similar to the test species. No predators or other interfering organisms were noted to occur in the samples. Aliquots of homogenized sample were collected for measurement of percent water/solids and pore water pH, salinity (i.e. conductivity) and ammonia nitrogen. For all water quality measurements, conductivity was measured as a surrogate for salinity. A portion of the laboratory control sediment was salinity-adjusted using brine (deionized water and Forty Fathoms brand synthetic sea salts) to provide brackish water control sediment for those sediments determined to have saline pore water.

For *Ceriodaphnia* 3-brood tests, pore water was collected from the control sediment and all test sediments having pore water salinity values within the expected tolerance range for this species (i.e. $\leq$ 2 g/kg; all stations except 8-MPN000.86, 8-MPN001-33, 8-MPN004.31). Pore water was collected by placing approximately 250 ml of sediment in an appropriate number of 250-ml polyethylene jars and centrifuging at 2150 times gravity for 30 min using an IEC model K2 centrifuge. A few samples (8-MPN020.58, 8-PMK020.31, 8-PMK033.04 and Beaver Dam Control) required a second centrifugation of the supernatant due to the high turbidity of the initial sample. Laboratory control waters consisted of moderately hard synthetic freshwater

(MHSFW) made with ASTM Type I deionized water and ACS reagent grade chemicals and two brackish waters (target salinities 0.7 and 1.2 g/kg) selected to bracket the range of test sample pore water salinity values. Brackish waters were prepared by adding synthetic sea salts (Forty Fathoms brand) to MHSFW. Pore water was also collected from Beaver Dam control sediment for use as a pore water control.

For amphipod and chironomid tests, approximately 100 ml of homogenized sediment and 175 ml of dilution water were added to each 300-ml lipless borosilicate glass beaker the day prior to testing (test day –1). The sediment surface was smoothed by gently tapping the chamber prior to addition of laboratory control water. Laboratory control water consisted of carbon filtered well water or (for brackish samples) filtered well water with sufficient synthetic sea salts (Forty Fathoms brand) added to provide a final salinity of ca. 1.5 g/kg. Water quality characteristics of the freshwater control were: conductivity 346 µS/cm, pH 7.98, hardness 150 mg/l as $CaCO_3$ and alkalinity 178 mg/l as $CaCO_3$. Characteristics of the brackish water control were: conductivity 3120 µS/cm, pH 8.21, hardness 410 mg/l as $CaCO_3$ and alkalinity 171 mg/l as $CaCO_3$.

Test Organisms:

Hyalella azteca, 13-14 days old, were obtained from Chesapeake Cultures, Gloucester, VA. Animals were hand delivered to the laboratory the day prior to use in toxicity tests. During the grow-out/holding period amphipods were fed a combination of YCT and maple leaves and were monitored for unusual mortality and behavior (none observed). Photoperiod and temperature for both amphipods and chironomids (see below) were maintained at 16:8 L:D and 23 ± 1^{o}C respectively. The water used for grow out and testing of both these species was carbon filtered well water of moderate hardness (138 mg/l $CaCO_3$).

Chironomus tentans egg cases were obtained from Aquatic Biosystems, Fort Collins, CO on 10/2/03. Egg cases (deposited 10/1/03) were hatched in 10 cm culture dishes; each dish contained approximately 200 ml of well water and 2-3 egg cases. When hatching began, approximately 1 ml of algae (*Selenastrum capricornutum*) concentrate (ca. $1x10^8$ to $5x10^8$cells/ml) was added to each dish. When hatching was approximately 50-75% complete, larvae were transferred to plastic bins containing 7-8 L of well water and a thin (0.5-1 cm) layer of washed #1 silica. Larvae were fed algae (2 ml of concentrate) and Tetramin slurry (60 mg) four times per week until used in tests. Appropriate instar (3^{rd}) was assessed by head capsule width measurements of twenty individual animals archived at the beginning of the test.

Ceriodaphnia dubia, 19 to 23.5 hours old, were obtained from in-house cultures. Animals were cultured at 25^{o} C in moderately hard synthetic freshwater and fed YCT and *S. capricornutum* at the same concentrations used in testing (Table 2.2c). Test animals were selected from broods produced by females which had previously produced at least 3 broods and were less than two weeks of age. All test animals used for a given replicate within the test were from a single brood (i.e. the test was blocked by known parentage).

Test protocols:

Whole sediment tests (*C. tentans* and *H. azteca*) were conducted in accordance with EPA Methods 100.1 and 100.2 (EPA 2000; see also Tables 2.2a-c). Pore water tests (*C. dubia*) were conducted in accordance with EPA method 1002.0 (EPA 2002) except that the exposure volume was reduced from 15 ml to 5 ml per replicate (Table C3). Tests were conducted in temperature-controlled rooms maintained within 1^{o} C of the target test temperature and with a photoperiod of 16:8 L:D. Copies of laboratory bench sheets and other raw data containing documentation of all test procedures are provided in Appendix D. General procedures are described below.

For whole sediment tests sediment and water were added to exposure chambers the day prior to addition of animals. A modified Zumwalt (Zumwalt *et al.* 1994) water delivery system was used for automatic renewal of overlying water in the test chambers over the course of the test. Separate 1000-L fiberglass vats contained fresh or brackish waters. Dilution water splitter boxes delivered a controlled flow of ca 175 ml twice daily (i.e. approximately two test chamber volumes per day, delivered at 1005 and 2205). Notches cut in the tops of the beakers and covered with 316 stainless steel mesh allowed flow of water through the chamber while retaining test organisms. The ends of the glass delivery tubes from each pipette tip were situated approximately 1 cm below the water surface in each chamber, sufficiently above the sediment surface to avoid sediment re-suspension.

Tests were initiated on 10/14/03 by adding 10 amphipods or chironomids to each chamber. Initial weights (dry weight for *H. azteca*, ash-free dry weight for *C. tentans*) were determined on 8 groups of 10 animals each for both species. In addition a subset of 20 chironomids was preserved in sugar formalin for later measurement of head capsule width to verify instar stage. Each chamber was checked for floaters shortly after addition of animals (none observed). Conductivity, temperature, pH, total ammonia, hardness, alkalinity and dissolved oxygen were measured in each treatment on 10/14/03 (before animals were added) and at test end on 11/24/03. Dissolved oxygen, temperature, pH and conductivity were measured daily in one replicate of each treatment and the control. The numbers of dead and emergent animals were recorded daily. Observations regarding any unusual behavior of amphipods or chironomids were also made daily and recorded if noted. Animals were fed, immediately after the morning renewal cycle, 1 ml of YCT/beaker (amphipods) or Tetramin (6 mg) suspension (chironomids).

Tests were ended after ten days by wet sieving sediments using 0.410 mm mesh sieves and counting the number of live animals. Animals from each chamber were rinsed and placed in 30 ml Solo cups containing ca. 20 ml of well water; approximately 1 ml of 1N HCl was added to each cup and the animals were removed as soon as death was noted. Amphipods were placed in tared aluminum pans, dried at 60°C overnight and weighed to the nearest 0.01 mg. Chironomids were similarly dried and weighed prior to ashing at 550°C for 2 h and re-weighing. Ash-free dry weight was calculated as the difference between the dry and ash weights.

For pore water tests, ten replicates of 5 ml each were tested using borosilicate glass scintillation vials as test chambers. Each chamber contained a single *Ceriodaphnia* neonate (< 24-h old). Test solutions were renewed daily by transferring test animals to new vials containing fresh solution and food (YCT and *Selenastrum).* Water quality was monitored daily both before and

after renewal of the test solutions. The number of live cladocerans and the number of offspring were recorded daily at the time of renewal. The test endpoints are survival and reproduction. The test was terminated when 60% of the control (MHSFW) organisms had produced their third brood (after 6 days).

Data Analysis:

Endpoints were total proportion surviving (number survivors/number exposed in replicate) and dry weight (pooled replicate dry weight/number survivors in replicate) for amphipods and chironomids and proportion surviving and reproduction (mean offspring per female exposed) for *Ceriodaphnia.* For amphipods and chironomids the total number observed emergent (i.e. on the sediment surface for *H. azteca* or on the water surface for *C. tentans)*, a measure of sediment avoidance, was not assessed due to lack of response (no emergent chironomids, maximum mean response of 3.1 for amphipods).

Test data were analyzed using the Minitab (1995; version 10Xtra) statistical software package. Proportionate data (e.g. survival) were transformed as the arcsine of the square root of the proportion to attain a more normal distribution. Growth data sets which did not exhibit a normal distribution in the untransformed state were transformed using the base 10 logarithm. Data were tested for normality and homogeneity of variance using the Ryan-Joiner (similar to Shapiro-Wilk) and Bartlett's tests ($p = 0.01$), respectively, prior to hypothesis testing to determine if the assumptions of the test method were met. Parametric tests used were ANOVA and Dunnett's or Tukey's multiple comparison tests and Student's t-test. Non-parametric tests used were Kruskal-Wallis rank test, Moods median test and the Mann-Whitney U-test for comparison of two samples. Survival data for *Ceriodaphnia* were not analyzed because of the "all or nothing" response (all treatments $\geq$ 90% or 0% survival). Because the design employed several different control groups and test salinity values, several different hypotheses were tested as described later.

Quality Control:

A reference toxicant test was conducted concurrently with each sediment toxicity test using the same lot of organisms. Potassium chloride was used as the reference toxicant. Tests were static and 96 in duration for all test species. LC50 values of the concurrent reference toxicant tests were compared with the mean value and 95% confidence limits of reference toxicant tests conducted previously in this lab using the same species and exposure duration.

A reference toxicant test was conducted concurrently with each whole sediment toxicity test using the same lot of organisms. Monthly 3-brood *Ceriodaphnia* reference toxicant tests are conducted and values for the reference tests preceding and following the sediment pore water test are provided. Potassium chloride was used as the reference toxicant. Tests were static 96 h (amphipods and chironomids) or 6 days (*Ceriodaphnia*) in duration. LC50 (96-h tests) or IC25 values (6-day tests) of the reference toxicant tests were compared with the mean value and 95% confidence limits of reference toxicant tests conducted previously in this lab using the same species and exposure duration

Table 2.2a. Required conditions for 10-day sediment toxicity tests with *H. azteca.*

TEST TYPE:	Whole sediment toxicity test
TEMPERATURE:	$23 \pm 1^{o}C$
PHOTOPERIOD:	16L:8D
ILLUMINANCE:	500-1000 lux
TEST CHAMBERS:	300 ml lipless glass beakers (with 1 cm^2 square cut off top and covered with 100 um stainless steel screen)
SEDIMENT VOLUME:	100 ml
OVERLYING WATER VOLUME:	175 ml
OVERLYING WATER:	Well water
RENEWAL OF OVERLYING WATER	1 volume addition/12 h
WATER QUALITY:	Measure total water quality (hardness, alkalinity, ammonia, pH, conductivity, D.O., temperature) days 0 and 10 each treatment; temperature and D.O. daily on one replicate
AGE OF AMPHIPODS:	7-14 days
NUMBER OF ORGANISMS/ CHAMBER:	10
REPLICATES:	8
FEEDING:	1.0 ml YCT/chamber/day
AERATION:	None
TEST DURATION:	10 days
ENDPOINTS:	Survival, growth (dry weight)
TEST ACCEPTABILITY:	Control survival $\geq$ 80%, measurable growth of controls

Table 2.2b. Required conditions for 10-day sediment toxicity tests with *C. tentans*.

TEST TYPE:	Whole sediment toxicity test
TEMPERATURE:	$23 \pm 1^{o}C$
PHOTOPERIOD:	16L:8D
ILLUMINANCE:	500-1000 lux
TEST CHAMBERS:	300 ml lipless glass beakers (with 1 cm^2 square cut off top and covered with 100 um stainless steel screen)
SEDIMENT VOLUME:	100 ml
OVERLYING WATER VOLUME:	175 ml
OVERLYING WATER:	Well water
RENEWAL OF OVERLYING WATER:	1 volume addition/12 h
WATER QUALITY:	Measure total water quality (hardness, alkalinity, ammonia, pH, conductivity, D.O., temperature) days 0 and 10 each treatment; temperature and D.O. daily on one replicate
AGE OF MIDGES:	3^{rd} instar (head capsule width 0.33 to 0.45 mm) to 2^{nd} instar
NUMBER OF ORGANISMS/CHAMBER	10
REPLICATES:	8
FEEDING:	6.0 mg dry wt. Tetramin/chamber/day
AERATION:	None
TEST DURATION:	10 days
ENDPOINTS:	Survival, growth (ash-free dry weight)
TEST ACCEPTABILITY:	Mean control survival $\geq$ 70% and AFDW $\geq$ 0.48 mg

Table 2.2c. Required conditions for 10-day sediment toxicity tests with *C. dubia.*

TEST TYPE:	Static renewal (daily)
TEST CONCENTRATIONS (%):	100% pore water.
REPLICATES:	10 with 1 animal each (i.e. 10 animals/sample)
RANDOMIZATION:	Test chambers oriented in randomized block (by replicate/known parentage)
TEST CHAMBERS:	30-ml borosilicate glass
TEST VOLUME:	5 ml
TEMPERATURE:	25 $\pm$ 1^{o} C (max-min 3^{o} C maximum)
LAB CONTROL WATER:	Moderately hard synthetic freshwater (SFW)
PHOTOPERIOD:	16 h light/8 h darkness
LIGHT INTENSITY:	10-20 µE/m^2/s (50-100 ft-c) (ambient laboratory illumination)
AGE:	< 24-h old, all released within 8 h
D.O.:	$\geq$4.0 mg/l, aeration not applicable. Do not aerate
FEEDING:	0.1 ml YCT + 3.5E6 cells *Selenastrum* per 15 ml
CLEANING:	New (clean) chambers used daily
TEST DURATION:	Until 60% of surviving control females have 3 broods (8 days max)
ENDPOINTS:	Survival, reproduction
TEST ACCEPTABILITY:	Controls: 80% survival, 60% of surviving females with $\geq$ 3 broods, avg. 15 offspring/surviving female, 80% remaining after exclusion of males/blocks

2.6 Benthic Community Sampling

Stations were sampled if there was a near-surface anaerobic layer (suggesting the presence of TOC) and sand content judged to be less than 70-80%. These criteria were applied based on subjective evaluations rather than objective determinations since the latter were not possible while in the field. Stations were sampled in random order sequence until a total of seven were attained in each water body.

Two Young grab samples (area of 440 cm^2) were obtained from each station. One sample was sieved through a 0.5 mm screen, and the retained material was preserved in the field by adding Rose Bengal in formaldehyde. The specimens were removed from the sediment, sorted to taxon, enumerated, and identified to the lowest possible taxon. Each taxon was then dried, weighed, and reweighed after incineration to determine ash-free dry weight biomass (AFDW). The second sample was used to characterize the texture of the sediment using the method of Folk (1980). Percent silt-clay, percent sand, and volatile solids were calculated.

2.7 Benthic Community Analysis

Weisberg *et al.* (1997) defined the Benthic Index of Biotic Integrity (B-IBI) for various habitats in the Chesapeake Bay system. The index is based on various metrics (Shannon-Wiener Diversity Index, abundance, species numbers, life mode, pollution tolerance, pollution sensitivity, ash-free dry weight, and other community parameters (Dauer and Rodi, 2001; Alden *et al.* 2002) which are scored and averaged. These measures are compared to values expected at non-polluted sites of similar water and sediment quality, a rank is established for each measure and the mean range calculated as the B-IBI.

3.0 RESULTS

3.1 Water quality:

Water temperature at the sampling sites was relatively uniform from surface to bottom (Table 3.1). When the most downstream stations in both the Mattaponi and Pamunkey were sampled, the surface temperature ranged from 20.5°C to 22.5°C. A week later when the most upstream stations were sampled, the temperature had dropped to 17.5-19°C at the surface and 17.1-19°C at the bottom. The water was fresh (conductivity <100 µmhos/cm, salinity <0.5 g/kg) except at 8-MPN000.86 where the water was slightly brackish (conductivity ca 150µmhos/cm, salinity 0.7 g/kg). Dissolved oxygen concentrations were low (3.7-6.6 mg/l in the Mattaponi and 3.7-6.8 mg/l in the Pamunkey). The higher oxygen concentrations were observed in the second week of sampling, and may reflect temporal changes rather than upstream – downstream differences. pH at all stations was in the low to mid 6 units. Both these latter parameters may well be in part related to the paper mill located at the confluence of the two study rivers, but likely also reflect effects of the adjacent marshlands. However, the effect of Hurricane Isabel on river flow, water quality, and possibly sediment quality cannot be totally discounted. The hurricane passed through the area on 18-19 September 2003, less than two weeks before sampling for this study. However, there is no way to identify effect of the hurricane from the available data.

3.2 Sediment Characteristics:

Sediment texture at the stations sampled ranged from 13% sand to 90% sand in the Mattaponi and 6% sand to 83% sand in the Pamunkey. Total Organic Carbon (TOC) was below 1% in sediments with high sand content with the exception of the sample from station 8-PMK012.00 where the sand content was only 6%. Acid Volatile Sulfur (AVS) was below 11 µmole/g wet weight at all stations with low TOC and higher as stations with TOC above 1%.

Anecdotal information is available for three other random stations (Mattaponi 7 and 8 located near MPN020.75 and MPN024.81; Pamunkey 14 located south of the Sweet Hall Marsh) for which "sand" was given as the reason for station rejection. All other rejected stations were not sampled because of accessibility issues (upstream of low railroad bridge, too shallow, or located in marsh). Other random stations were not occupied after identifying the number of stations (7) for each river required in this study.

Table 3.1a. Water quality from stations located on the Mattaponi River at the time of sample collection.

Sampling Date	Station	Sample Location	Temp. (° C)	Conductivity (µmhos/cm)	DO (mg/L)	pH	Depth Meters	Salinity (g/kg)	Weather Condition
10/1/2003	8-MPN000.86	Surface	21.9	150.8	4.44	6.55	0.5	0.07	Cloudy, mid 60's
		Mid-depth	21.9	151.1	4.31	6.49	1.5	0.07	
		Bottom	21.9	151.4	4.29	6.47	2.1	0.07	
	8-MPN001.10	Surface	21.7	88.9	4.48	6.42	0.5	0.03	Cloudy, mid 60's
		Mid-depth	21.6	89.7	4.16	6.33	2.5	0.03	
		Bottom	21.6	90.1	3.98	6.31	4.1	0.03	
	8-MPN001.33	Surface	21.6	89.7	3.97	6.42	0.5	0.03	Cloudy, low 60's
		Mid-depth	21.6	91.1	3.84	6.34	4.0	0.03	
		Bottom	21.6	91.5	3.73	6.33	6.8	0.03	
	8-MPN004.31	Surface	21.4	75.7	3.88	6.15	0.5	0.03	Cloudy, low 60's
		Mid-depth	21.4	76.5	3.85	6.19	3	0.03	
		Bottom	21.4	76.5	3.78	6.19	5	0.30	
10/6/2003	8-MPN020.58	Surface	17.8	49.6	5.56	5.96	0.5	0.01	Sunny, mid 60's
		Mid-depth	17.8	49.8	5.53	6.18	3	0.01	Northwest wind
		Bottom	17.8	49.8	5.32	6.12	5.9	0.01	
	8-MPN020.75	Surface	18.0	49.9	6.58	6.32	0.5	0.01	Sunny, low 70's
		Mid-depth	17.9	49.9	5.25	6.23	3.0	0.01	
		Bottom	17.8	49.9	5.20	6.23	5.9	0.01	
	8-MPN024.81	Surface	17.5	51.6	6.30	6.27	0.5	0.01	Sunny, mid 70's
		Mid-depth	17.2	52.1	5.82	6.23	2.3	0.01	
		Bottom	17.1	51.9	5.82	6.21	4.5	0.01	

Table 3.1b. Water quality from stations located on the Pamunkey River at the time of sample collection.

Sampling Date	Station	Sample Location	Temp. (° C)	Conductivity (µmhos/cm)	DO (mg/L)	pH	Depth Meters	Salinity (g/kg)	Weather Condition
9/30/2003	8-PMK009.39	Surface	21.9	75.9	3.96	6.64	0.5	0.03	Partly Cloudy, mid 60's
		Mid-depth	21.9	76.1	3.84	6.50	3	0.03	
		Bottom	21.9	76.4	3.78	6.44	5.4	0.03	
	8-PMK011.64	Surface	22.5	72.6	4.37	6.61	0.1	0.02	Partly Cloudy, mid 60's
	8-PMK011.88	Surface	22.1	68.8	4.25	6.79	0.5	0.02	Partly Cloudy, mid 60's
		Mid-depth	21.6	70.0	4.05	6.48	2.2	0.02	
		Bottom	21.4	71.2	3.85	6.40	4	0.02	
	8-PMK012.00	Surface	21.4	68.1	4.33	6.60	0.5	0.02	Partly Cloudy, low 60's
		Mid-depth	21.3	68.6	3.69	6.50	2.5	0.02	
		Bottom	21.3	68.8	3.62	6.48	4	0.02	
	8-PMK013.06	Surface	20.6	75.4	3.84	6.52	0.5	0.02	Partly Cloudy, mid 50's
		Mid-depth	20.5	75.9	3.75	6.50	1.5	0.03	
		Bottom	20.4	75.7	3.70	6.50	2.3	0.03	
10/8/2003	8-PMK020.31	Surface	19.0	85.1	5.88	6.48	0.5	0.03	Sunny, low 70's
		Mid-depth	19.0	85.7	5.71	6.54	3.1	0.03	
		Bottom	19.0	85.5	5.73	6.60	6.4	0.03	
	8-PMK033.04	Surface	19.0	95.1	6.84	6.47	0.5	0.04	Sunny, mid 70's
		Mid-depth	18.8	95.5	6.21	6.63	1.5	0.04	
		Bottom	18.9	95.2	6.25	6.60	2.5	0.04	

Table 3.2. Characteristics of sediment from each station sampled. Each station is represented by 3 field replicates selected randomly from within a grid centered on the station coordinates, and composited prior to laboratory analysis.

Station	Percent (%) TOC	Acid Volatile Sulfide (µmole/g wet wt)*	Percent (%) Sand	Percent (%) Silt	Percent (%) Clay
Mattaponi River					
8-MPN000.86	2.71	20.947	30.6	29.3	40.1
8-MPN001.10	0.41	10.685	86.7	4.4	8.9
8-MPN001.33	3.29	24.378	13.1	24.4	62.5
8-MPN004.31	2.45	50.300	19.4	23.2	57.4
8-MPN020.58	0.60	8.531	62.8	20.7	16.5
8-MPN020.75	2.98	16.755	17.6	23.3	59.1
8-MPN024.81	0.28	8.625	90.4	3.1	6.5
Pamunkey River					
8-PMK009.39	1.44	20.218	51.7	13.9	34.4
8-PMK011.64	2.86	14.871	8.9	25.9	65.2
8-PMK011.88	1.19	16.019	64.3	10.3	25.4
8-PMK012.00	0.88	10.730	5.9	75.2	18.9
8-PMK013.06	2.51	36.801	14.9	21.7	63.4
8-PMK013.06 FD	2.53	26.729	15.9	22.4	61.7
8-PMK020.31	0.54	10.465	83.2	4.6	12.2
8-PMK033.04	2.08	15.643	32.3	26.1	41.6

FD = Field Duplicate

* Acid Volatile Sulfide was measured after all three field replicates were composited in the laboratory.

3.3 Chemical Characterization

3.3.1 Metals

Several metals exhibited exceedances of the ER-L for freshwater sediments (Ingersoll, *et al.*, 1996) or saline sediments (Long *et al.*, 1995), but only Mn exhibited an exceedance of the ER-M (Table 3.3). While most metals were detected at levels above the detection limit, exceedances of sediment guidelines were relatively infrequent. Arsenic exceeded the ER-L at one station in the Mattaponi but none in the Pamunkey. While detectable at most stations in both rivers, copper, iron, lead, and nickel exhibited no exceedances. Chromium and zinc exceeded the ER-L at one station in the Mattaponi and 2 stations in the Pamunkey. Manganese exceeded the ER-L at 3 of 4 stations in the lower 5 miles of the Mattaponi, but the exceedance of the ER-M occurred at mile 20.75. Manganese exceeded the ER-L at 4 of 7 stations in the Pamunkey. Antimony, beryllium, cadmium, mercury, selenium, silver and thallium were never present above the detection limit at any station in either river.

Copper, nickel and zinc were above the detection limit in the simultaneously extracted metals fraction of the AVS samples from several stations in the Mattaponi and Pamunkey. Lead was also detected in some samples from the Pamunkey (Table 3.4).

Despite the presence of various metals in both rivers, the occurrences were not sufficient to suggest a possible toxicological impact singly or collectively.

3.3.2 Semi-Volatile organic compounds (SVOC)

Various phthalates were verified present in samples from both rivers; only bis [2-ethylhexyl] phthalate was quantified. At only one station (8-PMK011.88) did the concentration approach or exceed 1 mg/kg (Table 3.5).

Low Molecular Weight PAHs were never above the detection limits at any station. High Molecular Weight PAHs above detection limits was observed only for Benzo[k]fluoranthene at station PMK012.00 and total HM PAHs at stations MPN024.81 and PMK012.00. In no case was there an exceedance of any ER-L or ER-M

3.3.3 Pesticides (Organophosphate and Organochloride)

A few organophosphate pesticides were identified in each river: carbophenotheion, Diazinon, disulfoton, monocrotophos, and TEPP in the Mattaponi and diazinon, disulfoton, leptophos, phosmet, TEPP, thionazin and trochlorate in the Pamunkey (Table 3.6). Only diazinon and disulfoton occurred at multiple stations in both rivers.

A few chlorinated pesticides were also identified in the sediments (Table 3.7): b,BHC, Hexachlorobenzene, Dibromochloropropane, Dieldin, Endosulfan Sulfate, g-BHC, Hexachlorocyclopentadiene, Methoxychlor, p,p'-DDD, and Toxaphene were identified from some stations in the Mattaponi and b,BHC, Endosulfan Sulfate, Hexachlorocyclopentadiene, p,p'-DDD, and Toxaphene were identified from some stations in the Pamunkey. No exceedances of the ER-L were found for the p,p'-DDD, one of two DDT derivatives for which a sediment guideline exists.

3.3.4 PCB

While a few PCB congeners were tentatively identified in a few samples, none could be quantified and only one was verified in a single sample from the Mattaponi (Table 3.8). The approximate concentrations were, in every case, less than 100 ng/g sediment. The total amount of 19 congeners in only two samples from the Mattaponi slightly exceeded 100 ng/g sediment.

3.3.5 Herbicides

Herbicide concentrations (Table 3.9) were below detection for all samples.

Table 3.3. Metal concentrations (µg/g) in sediment samples collected during fall 2003 from the Mattaponi and Pamunkey Rivers.

Station	Al	Sb	As	Be	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Se	Ag	Tl	Zn
Mattaponi River																
8-MPN000.86	15,400	< 5	7.61	< 5	< 1	32.1	13.9	29,700	17.9	*1,010*	< 0.1	13	< 1	< 1	< 5	95.5
8-MPN001.10	5,400	< 5	< 5	< 5	< 1	14.1	< 5	11,800	6.38	136	< 0.1	< 5	< 1	< 1	< 5	35.9
8-MPN001.33	17,300	< 5	7.87	< 5	< 1	30.9	15.5	27,700	20.9	*1,460*	< 0.1	14.8	< 1	< 1	< 5	100
8-MPN004.31	29,500	< 5	*10.2*	< 5	< 1	*47.7*	26.2	42,600	30.8	*1,260*	< 0.1	20.2	< 1	< 1	< 5	*163*
8-MPN020.58	5,910	< 5	< 5	< 5	< 1	13.9	< 5	9,590	5.7	271	< 0.1	5	< 1	< 1	< 5	22.1
8-MPN020.75	22,300	< 5	6.7	< 5	< 1	35.5	12	34,000	20.5	**3,380**	< 0.1	17.9	< 1	< 1	< 5	85.7
8-MPN024.81	2,130	< 5	< 5	< 5	< 1	6	< 5	6,620	< 5	474	< 0.1	< 5	< 1	< 1	< 5	22.2
Pamunkey River																
8-PMK009.39	13,200	< 5	< 5	< 5	< 1	28.3	14.6	21,800	16.6	453	< 0.1	10.6	< 1	< 1	< 5	87.3
8-PMK011.64	28,600	< 5	7.8	< 5	< 1	*44.8*	15.7	33,300	19.1	*1,270*	< 0.1	19.7	< 1	< 1	< 5	83.6
8-PMK011.88	9,650	< 5	< 5	< 5	< 1	17.4	10.5	14,700	10.2	*870*	< 0.1	6.78	< 1	< 1	< 5	61
8-PMK012.00	6,060	< 5	< 5	< 5	< 1	13.1	8.91	11,700	8.71	531	< 0.1	5.19	< 1	< 1	< 5	49.6
8-PMK013.06	21,600	< 5	6.17	< 5	< 1	35.4	22.7	27,900	24.1	*949*	< 0.1	15.4	< 1	< 1	< 5	*140*
8-PMK013.06FD	28,100	< 5	7.5	< 5	< 1	*44.1*	26.6	34,300	28.5	*1,190*	< 0.1	19.6	< 1	< 1	< 5	*160*
8-PMK020.31	6,600	< 5	< 5	< 5	< 1	16.4	8.2	14,700	8.9	416	< 0.1	6.5	< 1	< 1	< 5	62.7
8-PMK033.04	16,700	< 5	< 5	< 5	< 1	31.6	20.1	25,200	16.1	*1,170*	< 0.1	13.8	< 1	< 1	< 5	89.3
Detection Limit	5.0	5.0	5.0	5.0	1.0	5.0	5.0	5.0	5.0	5.0	0.10	5.0	1.0	1.0	5.0	5.0
ER-L[a]			8.2		1.2	81	34		46.7		0.15	20.9		1.7		271
ER-M[a]			70.0		9.6	370	270		218		0.71	51.6		3.7		410
ER-L[b]	14,000		13		0.7	39	41	200,000	55	730		24				110
ER-M[b]	58,000		50		3.9	270	190	280,000	99	1,700		45				550
TEC[c]			9.79		0.99	43.4	31.6		35.8		0.18	22.7				121
PEC[c]			33		4.98	111	149		128		1.06	48.6				459

Underlined and boldfaced values exceed the relevant ER-M or PEC
Italicized values exceed the relevant ER-L or TEC

FD = Field Duplicate
[a] Long, E.R. *et al*. 1995.
[b] Ingersoll, C.G. *et al.* 1996.
[c] MacDonald, DD, CG Ingersoll and TA Berger. 2000

Table 3.4. Sediment acid volatile sulfide and simultaneously extracted metals (expressed as µmole/g wet weight) for sediments collected during fall 2003 from the Mattaponi and Pamunkey Rivers.

Station	Acid Volatile Sulfide	Cadmium	Copper	Lead	Mercury	Nickel	Zinc	Sum SEM	SEM/AVS RATIO
8-MPN000.86	20.9468	< 0.0126	0.0999	< 0.0681	< 0.0001	0.06	1.3598	1.6004	0.0764
8-MPN001.10	10.685	< 0.0133	< 0.0276	< 0.0339	< 0.0001	< 0.03	0.436	0.4832	0.0452
8-MPN001.33	24.3778	< 0.0122	0.1081	< 0.0663	< 0.0001	0.07	1.166	1.4226	0.0584
8-MPN004.31	50.3004	< 0.0140	0.0868	< 0.0761	< 0.0001	< 0.07	1.9525	2.1294	0.0423
8-MPN020.58	8.5311	< 0.0060	< 0.0264	< 0.0323	< 0.0001	< 0.03	0.1317	0.17	0.0199
8-MPN020.75	16.7554	< 0.0110	0.0586	< 0.0599	< 0.0001	0.1	0.8218	1.0513	0.0627
8-MPN024.81	8.6249	< 0.0057	< 0.0253	< 0.0310	< 0.0001	0.04	0.2401	0.3168	0.0367
8-PMK009.39	20.2179	< 0.0093	0.0906	< 0.0505	< 0.0001	0.04	1.0091	1.1995	0.0593
8-PMK011.64	14.8713	< 0.0097	0.1887	0.0736	< 0.0001	0.08	1.6173	1.9693	0.1324
8-PMK011.88	16.0189	< 0.0114	0.293	0.0992	< 0.0001	0.09	2.0724	2.566	0.1602
8-PMK012.00	10.73	< 0.0070	0.0872	< 0.0382	< 0.0001	0.03	0.9019	1.0643	0.0992
8-PMK013.06	36.801	< 0.0153	0.1929	0.1014	< 0.0001	0.11	1.8479	2.2675	0.0616
8-PMK013.06 FD	26.7286	< 0.0133	0.2002	< 0.1083	< 0.0001	0.09	2.255	2.6668	0.0998
8-PMK020.31	10.4646	< 0.0055	0.0437	< 0.0298	< 0.0001	0.03	0.7591	0.8681	0.0830
8-PMK033.04	15.6434	< 0.0097	0.1292	< 0.0528	< 0.0001	0.07	1.2646	1.5263	0.0976

Table 3.5a. Semi-Volatile Organic Compounds (ng/g, dry weight) in sediment samples collected during fall 2003 from the Mattaponi River.

	ER-L	ER-M	8-MPN000.86	8-MPN001.10	8-MPN001.33	8-MPN004.31	8-MPN020.58	8-MPN020.75	8-MPN024.81
Analyte									
Dimethyl phthalate			64 *	< 69	< 169	< 151	< 74	< 35	< 63
Diethyl phthalate			< 73	< 69	< 169	< 151	18 *	< 35	< 63
Di-N-butylphthalate			< 73	19 *	< 169	35 *	28 *	11 *	< 63
Butylbenzylphthalate			< 73	48 *	48 *	57 *	39 *	17 *	42 *
Bis[2-ethylhexyl]phthalate			< 73	459	< 169	408	202	120	209
Di-N-octylphthalate			< 73	< 69	< 169	< 151	< 74	< 35	< 63
Low Molecular PAHs									
2-Methylnaphthalene	70	670	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Acenaphthylene	44	160	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Acenaphthene	16	500	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Anthracene	85.3	1,100	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Fluorene	19	540	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Naphthalene	160	2,100	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Phenanthrene	240	1,500	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Total LM PAHs	552	3,160	ND	ND	ND	ND	ND	ND	ND
High Molecular PAHs									
Benzo[b]fluoranthene			< 73	< 69	< 169	< 151	< 74	< 35	< 63
Benzo[k]fluoranthene			< 73	< 69	< 169	< 151	< 74	< 35	< 63
Benzo[g,h,i]perylene			< 73	< 69	< 169	< 151	< 74	< 35	< 63
Chrysene	384	2,800	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Dibenz[a,h]anthracene			< 73	< 69	< 169	< 151	< 74	< 35	< 63
Fluoranthene	600	5,100	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Indeno[1,2,3-cd]pyrene	63.4	260	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Pyrene	665	2,600	< 73	< 69	< 169	< 151	< 74	< 35	< 63
Total HM PAHs	1,700	9,600	ND	ND	ND	ND	ND	ND	117
Total PAHs	4,022	44,792	ND	ND	ND	ND	ND	ND	ND

* Presence of analyte verified but not quantified
ND = Not Detected

Table 3.5b Semi-Volatile Organic Compounds (ng/g, dry weight) in sediment samples collected during fall 2003 from the Pamunkey River.

	ER-L	ER-M	8-PMK009.39	8-PMK011.64	8-PMK011.88	8-PMK012.00	8-PMK013.06	8-PMK013.06	8-PMK020.31	8-PMK033.04
Analyte								FD		
Dimethyl phthalate			< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Dibenzofuran							< 134	< 35		
Diethyl phthalate			< 108	28 *	< 92	< 134	< 156	< 35	< 71	< 105
N-Nitrosodiphenylamine							< 134	< 35		
Di-N-butylphthalate			< 108	< 121	< 92	< 134	< 156	< 35	30 *	42 *
Butylbenzylphthalate			< 108	< 121	< 44	< 134	74 *	< 35	40 *	49 *
Bis[2-ethylhexyl]phthalate			371	< 121	2089	< 134	334	< 35	141	116
Di-N-octylphthalate			< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Low Molecular PAHs										
2-Methylnaphthalene	70	670	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Acenaphthylene	44	160	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Acenaphthene	16	500	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Anthracene	85.3	1,100	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Fluorene	19	540	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Naphthalene	160	2,100	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Phenanthrene	240	1,500	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Total LM PAHs	552	3,160	ND	ND	ND	ND	ND	ND	ND	ND
High Molecular PAHs										
Benzo[b]fluoranthene			< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Benzo[k]fluoranthene			< 108	< 121	< 92	40 *	< 156	< 35	< 71	< 105
Benzo[g,h,i]perylene			< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Chrysene	384	2,800	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Dibenz[a,h]anthracene			< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Fluoranthene	600	5,100	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Indeno[1,2,3-cd]pyrene	63.4	260	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Pyrene	665	2,600	< 108	< 121	< 92	< 134	< 156	< 35	< 71	< 105
Total HM PAHs	1,700	9,600	ND	ND	ND	40	ND	ND	ND	ND
Total PAHs	4,022	44,792	ND	ND	ND	40	ND	ND	ND	ND

* Presence of analyte verified but not quantified
ND = Not Detected

Table 3.6a. Organophosphate pesticide concentrations (ng/g, dry weight) in sediment samples collected during fall 2003 from the Mattaponi River.

Compound	8-MPN000.86	8-MPN001.10	8-MPN001.33	8-MPN004.31	8-MPN020.58	8-MPN020.75	8-MPN024.81
Bolstar	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Carbophenothion	< 6	< 3	73 *	< 6	< 3	< 8	< 3
Chlorfenvinphos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Chlorpyrifos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Chlorpyrifos (methyl)	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Coumaphos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Crotoxyphos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Demeton	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Diazinon	< 6	< 3	160 *	8 *	4 *	15 *	< 3
Dichlorvos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Dicrotophos	< 6	< 3	52 *	< 6	< 3	< 8	< 3
Dimethoate	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Dioxathion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Disulfoton	< 6	2 **	< 7	384 *	< 3	< 8	< 3
EPN	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Ethion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Ethoprop	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Famfur	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Fenitrothion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Fensulfothion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Fenthion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Folex	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Guthion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Leptophos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Malathion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Mevinphos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Monocrotophos	< 6	< 3	345 *	< 6	< 3	< 8	< 3
Monophos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Naled	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Parathion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Parathion(methyl)	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Phorate	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Phosmet	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Phosphamidon+Dichlorofenthion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Ronnel	< 6	< 3	< 7	< 6	< 3	< 8	< 3
TEPP	< 6	< 3	1 **	< 6	< 3	< 8	< 3
Terbufos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Tetrachlorvinphos	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Thionazin	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Tokuthion	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Trichlornate	< 6	< 3	< 7	< 6	< 3	< 8	< 3

Table 3.6b. Organophosphate pesticide concentrations (ng/g, dry weight) in sediment samples collected during fall 2003 from the Pamunkey River.

Compound	8-PMK009.39	8-PMK011.64	8-PMK011.88	8-PMK012.00	8-PMK013.06	8-PMK013.06	8-PMK020.31	8-PMK033.04
						FD		
	2.4	3.4	1.3					
Bolstar	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Carbophenothion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Chlorfenvinphos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Chlorpyrifos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Chlorpyrifos (methyl)	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Coumaphos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Crotoxyphos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Demeton	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Diazinon	< 5	< 5	6 *	4 *	< 7	< 6	< 3	5 *
Dichlorvos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Dicrotophos	< 5	< 5	3 *	< 3	< 7	< 6	< 3	< 4
Dimethoate	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Dioxathion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Disulfoton	312 *	< 5	2 **	6 *	17 *	30 *	< 3	< 4
EPN	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Ethion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Ethoprop	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Famfur	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Fenitrothion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Fensulfothion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Fenthion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Folex	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Guthion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Leptophos	< 5	< 5	< 4	< 3	17 *	< 6	< 3	< 4
Malathion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Mevinphos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Monocrotophos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Monophos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Naled	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Parathion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Parathion(methyl)	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Phorate	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Phosmet	< 5	10 *	< 4	< 3	< 7	< 6	< 3	< 4
Phosphamidon+Dichlorofenthion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Ronnel	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
TEPP	< 5	< 5	< 4	**7 ***	< 7	< 6	< 3	< 4
Terbufos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Tetrachlorvinphos	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Thionazin	4 *	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Tokuthion	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Trichlornate	11 *	< 5	< 4	< 3	< 7	< 6	< 3	< 4

Table 3.7a. Organochlorine pesticide concentrations (ng/g, dry weight) in sediment samples collected during fall 2003 from the Mattaponi River.

Analyte	ER-L	ER-M	8-MPN000.86	8-MPN001.10	8-MPN001.33	8-MPN004.31	8-MPN020.58	8-MPN020.75	8-MPN024.81
Aldrin			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Alpha-Chlordane			< 11	< 6	< 14	< 6	< 3	< 15	< 5
b-BHC			15 *	4 *	8 *	9 *	< 3	< 8	5 *
d-BHC			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Dibromochloropropane (DBCP)			< 6	< 3	< 7	< 6	< 3	< 8	288 *
Dieldrin			< 6	2 **	< 7	< 6	< 3	< 8	< 3
Endosulfan I			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Endosulfan II			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Endosulfan Sulfate			< 6	10 *	7	< 6	< 3	< 8	< 3
Endrin			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Endrin Ketone			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Gamma-Chlordane			< 11	< 6	< 14	< 13	< 6	< 15	< 5
g-BHC			< 6	< 3	< 7	< 13	5 *	11 *	7 *
Heptachlor			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Heptachlor Epoxide			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Hexachlorobenzene			< 6	< 3	< 7	< 6	< 3	< 8	7 *
Hexachlorocyclopentadiene			< 6	< 3	< 7	< 6	< 3	35 *	< 3
Isodrin			< 6	< 3	< 7	< 6	< 3	< 8	< 3
Methoxychlor			< 6	< 3	< 7	< 6	< 3	23 *	< 3
p,p'-DDD	2	20	< 6	< 3	< 7	< 6	5 *	12 *	8 *
p,p'-DDE			< 6	< 3	< 7	< 6	< 3	< 8	< 3
p,p'-DDT	1	7	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Toxaphene			< 112	< 57	< 141	< 126	< 61	< 151	< 52

* Presence of analyte tentatively identified at the approximated concentration.
** Presence of material verified but not quantified.

Table 3.7b. Organochlorine pesticide concentrations (ng/g, dry weight) in sediment samples collected during fall 2003 from the Pamunkey River.

Analyte	ER-L	ER-M	8-PMK009.39	8-PMK011.64	8-PMK011.88	8-PMK012.00	8-PMK013.06	8-PMK013.06	8-PMK020.31	8-PMK033.04
								FD		
Aldrin			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Alpha-Chlordane			< 9	< 10	< 8	< 7	< 13	< 13	< 6	< 9
b-BHC			6 *	< 5	9 *	7 *	40 *	9 *	< 3	< 4
d-BHC			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Dibromochloropropane (DBCP)			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Dieldrin			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Endosulfan I			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Endosulfan II			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Endosulfan Sulfate			< 5	9 *	< 4	< 3	< 7	< 6	< 3	< 4
Endrin			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Endrin Ketone			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Gamma-Chlordane			< 9	< 10	< 8	< 7	< 13	< 6	< 6	< 9
g-BHC			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Heptachlor			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Heptachlor Epoxide			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Hexachlorobenzene			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Hexachlorocyclopentadiene			< 5	< 5	< 4	< 3	< 7	< 6	15 *	19 *
Isodrin			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Methoxychlor			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
p,p'-DDD	2	20	< 5	< 5	< 4	< 3	< 7	< 6	< 3	5 *
p,p'-DDE			< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
p,p'-DDT	1	7	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Toxaphene			< 90	< 101	< 76	< 68	< 130	< 130	< 59	< 88

* Presence of analyte tentatively identified at the approximated concentration.
** Presence of material verified but not quantified.

Table 3.8a. Polychlorinated Biphenyl congener concentrations (ng/g, dry weight basis) in sediment samples collected during the fall 2003 from the Mattaponi River.

Analyte	8-MPN000.86	8-MPN001.10	8-MPN001.33	8-MPN004.31	8-MPN020.58	8-MPN020.75	8-MPN024.81
PCB 1	< 6	< 3	< 7	< 6	91 *	93 *	32 *
PCB 5	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 18	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 31	< 6	< 3	< 7	< 6	< 3	< 8	4 *
PCB 44	< 6	< 3	< 7	< 6	< 3	< 8	2 **
PCB 52	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 66	< 6	< 3	< 7	< 6	12 *	32 *	14 *
PCB 87	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 101	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 110	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 138	< 6	8 *	< 7	< 6	< 3	< 8	< 3
PCB 141	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 151	< 6	4 *	< 7	< 6	< 3	< 8	36 *
PCB 153	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 170	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 180	< 6	5 *	31 *	< 6	< 3	< 8	< 3
PCB 183	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 187	< 6	< 3	< 7	< 6	< 3	< 8	< 3
PCB 206	< 6	< 3	< 7	< 6	< 3	< 8	< 3
Total PCBs (as 19 Congeners)	< 6	17	31	< 6	103	125	88

***** Presence of analyte tentatively identified at the approximated concentration.
** Presence of analyte verified but not quantified

Table 3.8b. Polychlorinated Biphenyl congener concentrations (ng/g, dry weight basis) in sediment samples collected during the fall 2003 from the Pamunkey River.

Analyte	8-PMK009.39	8-PMK011.64	8-PMK011.88	8-PMK012.00	8-PMK013.06	8-PMK013.06	8-PMK020.31	8-PMK033.04
						FD		
PCB 1	< 5	< 5	5 *	< 3	< 7	<6	15 *	38 *
PCB 5	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 18	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 31	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 44	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 52	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 66	< 5	< 5	< 4	< 3	< 7	< 6	20 *	25 *
PCB 87	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 101	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 110	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 138	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 141	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 151	< 5	< 5	< 4	< 3	< 7	< 6	17 *	7 *
PCB 153	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 170	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 180	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 183	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 187	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
PCB 206	< 5	< 5	< 4	< 3	< 7	< 6	< 3	< 4
Total PCBs (as 19 Congeners)	< 5	< 5	5	< 3	< 7	< 6	52	70

***** Presence of analyte tentatively identified at the approximated concentration.
** Presence of analyte verified but not quantified

Table 3.9. Bulk herbicide concentrations (ng/g, dry weight) in sediment samples collected during fall 2003 from the Mattaponi and Pamunkey Rivers.

Analyte	8-MPN000.86	8-MPN001.10	8-MPN001.33	8-MPN004.31	8-MPN020.58	8-MPN020.75	8-MPN024.81
Mattaponi River							
DCPA Dacthal	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Dicamba	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
MCPP	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
MCPA	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Dichlorprop	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
2,4-D	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Pentachloroanisol	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
2,4,5-TP	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Chloramben	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
2,4,5-T	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Bentazon	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Picloram	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10
Acifluorfen	< 10	< 11.5	< 11.6	< 10	< 10	< 12.5	< 10

Analyte	8-PMK009.39	8-PMK011.64	8-PMK011.88	8-PMK012.00	8-PMK013.06	8-PMK013.06	8-PMK020.31	8-PMK033.04
						FD		
Pamunkey River								
DCPA Dacthal	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Dicamba	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
MCPP	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
MCPA	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Dichlorprop	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
2,4-D	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Pentachloroanisol	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
2,4,5-TP	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Chloramben	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
2,4,5-T	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Bentazon	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Picloram	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5
Acifluorfen	< 10	< 10	< 10	< 10	< 10.7	< 10.7	< 10	< 12.5

3.4 Toxicity Characterization

3.4.1 Pore Water Characterization

Sediment pore water ammonia was between 1.6 and 9.9 mg/l in all but one sample, that from Station MPN020.75 in which the concentration was 17.9 mg/l (Table 3.10). Even this concentration was not sufficiently high to produce toxicity in the amphipod or chironomid tests.

Pore water pH ranged from 6.9 to 7.5 in the Mattaponi River samples, and 6.4 to 7.0 in the Pamunkey River samples. These values were slightly above the values for the overlying water measured on station (Table 3.1). No adverse biological impact is attributable to these values.

The sediment samples varied in pore water conductivity within four narrow ranges. Salinity in sediment from two stations in each river was less than 500 µS/cm (MPN020.58, MPN024.81, PMK020.31, and PMK033.04); these were freshwater sites located 20 or more miles upstream. Sediment from 7 stations in the two rivers was between 1000 and 3000 µS/cm (MPN001.12, MPN20.75, PMK009.39, PMK011.64, PMK011.88, PMK012.00 and PMK013.06); these are slightly brackish sites. Sediment at three stations in the Mattaponi exceeded 5000 µS/cm ((MPN000.86, MPN001.33, and MPN004.31). The pore water in this last group of stations exceeded the upper tolerance limit for *C. dubia* as reported by EPA (1993). Therefore pore water from these samples was not tested with *C. dubia*. For the slightly brackish waters, two control samples are used for the *C. dubia tests*, one at 1680 µS/cm and one at 2720 µS/cm.

A preliminary examination of sediment from each station revealed no predatory invertebrates and only a few dead amphipods that are morphologically distinguishable from *H. azteca*. Therefore no sediment preparation was necessary to eliminate predators or indigenous animals of the same or similar species to the test species.

3.4.2 Amphipod Test:

In tests with the amphipod *H. azteca*, survival in all treatments was essentially the same as in the appropriate freshwater or brackish water control sediment (Table 3.11). Survival in all test cases ranged from 93 to 99%, well within the acceptable survival range for the controls.

In contrast, there was depression in growth in most field sediments compared to laboratory controls. Growth as an increase in final weight as compared to initial weight (0.186 mg dry weight) was observed only in sediment from MPN001.33, PMK011.88, and PMK012.00. The final weights for amphipods exposed to all other sediment samples were essentially unchanged from the initial weights or exhibited a weight loss (PMK013.06).

3.4.3 Chironomid Test:

There was no significant reduction in survival following exposure to field sediments when compared as a group to the relevant control (Table 3.11). However, the highest survival (in sediment from Station MPN004.31) was significantly greater than the lowest survival (in sediment from Station PMK013.06.

Growth of chironomid larvae was affected to only a limited extent. Growth was clearly depressed for larvae exposed to sediment from stations MPN001.12 and MPN020.75, but in both cases the final weight was greater than the initial weight (0.098 mg dry weight), i.e. positive growth occurred.

3.4.4 Ceriodaphnia Test:

As noted above, samples from three stations (MPN000.86, MPN001.33, and MPN004.31) were sufficiently brackish to be toxic to this species, and hence were not tested. Two additional stations with conductivity >2000 µS/cm may also have exhibited salinity stress as shown in the relevant control (SFW1.2). The only station at which there was significant reduction in survival or reproduction compared to controls was MPN020.75 where 50% mortality of the neonates was observed within 24 hours and complete mortality occurred within 96 hours. The toxicity of this sample may have resulted from elevated ammonia concentrations. Sediments from other stations with similar salinity did not produce significant reduced survival or reproduction.

3.4.5 Statistical evidence

Various hypotheses were assessed statistically to support the descriptive results presented above. The details of these statistical analyses are outlined in Table 3.12. The survival data is reasonably straightforward and intuitively obvious. The sub-lethal endpoints (growth and reproduction) are less straightforward from a statistical perspective. The weakness in these analyses lies in the repeated used of the same data in different configurations which in some sense reduces the power of the analyses. They are also reduced in value by the limited number of samples in some statistical cells and the limited replication. Despite these issues, the statistical analyses support the intuitive interpretation.

3.4.6 Reference Toxicity Test Results

Reference tests were performed with KCL as the reference toxicant for each species (Table 3.13). It is clear from these data that the test animals responded to the reference toxicant in a manner consistent with the control charts produced in the toxicity testing laboratory over years of work.

Table 3.10. Sediment pore water characteristics and percent water (modified from DeLisle 2003).

Station	Pore Water NH3 (mg/l)	Pore Water pH (S.U.)	% Water	Pore Water Conductivity (µS/cm)
FWC	7.3	7.03	67.0	447
Mattaponi River				
MPN000.86	7.5	7.28	66.8	7250
MPN001.12	1.6	7.45	34.9	1295
MPN001.33	9.9	7.23	73.0	7900
MPN004.31	5.8	7.12	68.9	5370
MPN020.58	1.8	6.88	76.2	269
MPN020.75	17.9	7.01	34.9	1416
MPN024.81	1.9	7.01	72.9	147
Pamunkey River				
PMK009.39	2.1	6.79	56.5	1729
PMK011.64	3.9	6.43	60.1	1788
PMK011.88	5.2	6.75	51.5	2640
PMK012.00	3.6	6.87	43.2	2160
PMK013.06	5.4	6.48	69.6	1560
PMK020.31	2.1	6.96	38.3	406
PMK033.04	1.8	6.80	73.5	257

Table 3.11. Summary of survival and final weight/reproduction data of three invertebrate species after a 10-day exposure to sediments from the Mattaponi and Pamunkey Rivers (modified from DeLisle 2003).

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	H. azteca		*C. tentans*		*C. dubia*	
Station	Survival (%)	Mean Dry Wt. (mg)	Survival (%)		Survival (%)	Mean No. of Offspring
BRCSED	98	0.207	88	2.298		
FWCSED	98	0.222	86	2.206	100	11
SFW0.0					90	18.4
SFW0.7					100	15.2
SFW1.2					80	12.1
MPN000.86	98	0.167	73	1.787		
MPN001.12	96	0.174	83	1.317	100	24.5
MPN001.33	94	0.231	80	1.748		
MPN004.31	93	0.187	93	1.812		
MPN020.58	98	0.168	73	2.49	100	11.8
MPN020.75	93	0.165	83	1.44	0	0
MPN024.81	96	0.175	78	1.987	90	15.3
PMK009.39	96	0.175	88	2.059	90	19.7
PMK011.64	99	0.158	84	1.649	100	16.3
PMK011.88	96	0.200	88	1.747	90	13.9
PMK012.00	96	0.225	85	1.614	100	18.4
PMK013.06	96	0.122	70	2.206	100	16.3
PMK020.06	96	0.182	78	2.095	100	16.4
PMK033.04	99	0.163	76	2.354	100	19.8

Controls and stations with pore water conductivity >1000 µS/cm
Controls and stations with pore water conductivity >2000 µS/cm
Stations with pore water conductivity >5000 µS/cm

BRCSED=brackish Beaver Dam control sediment
FWCSED=freshwater (unadjusted) Beaver Dam Control Sediment
SFWC=synthetic freshwater control
SFW0.7=synthetic freshwater with synthetic sea salts (1680 µS conductivity)
SFW1.2=synthetic freshwater with synthetic sea salts (2720 µS conductivity)

Note: Treatments are grouped, based on pore water salinity, with corresponding control sediment or water.

Table 3.12. Generalized Trends from Hypothesis Test Results for all species (modified from DeLisle 2003).

Hypothesis	Survival Endpoint	Sub-lethal Endpoint (growth, reproduction)
Control Groups Equal	NS[1]	*C. dubia:* Lab control (SFW) > FW control sediment
Freshwater Lab Control > Freshwater Field Sediments	NS	*H. azteca:* Lab control > All field sediments
Freshwater Field Sediments Equal	NS	NS
Brackish Lab Control > Brackish Field Sediments	*C. dubia:* Lab control > MAT19	*H. azteca:* Lab control > (MAT01, MAT02, MAT19, PAM02, PAM03, PAM07) *C. tentans:* Lab control > MAT02 *C. dubia:* Lab control > MAT19
Brackish Field Sediments Equal	*C. tentans:* MAT06>PAM07 *C. dubia:* All field sediments > MAT19	*H. azteca:* (MAT03, PAMO4, PAM05) > (MAT01, MAT02, MAT06, MAT19, PAM02, PAM03) > PAM07 *C. dubia:* MAT02 > (PAM03, PAM07); All field sediments > MAT19
Freshwater Lab Control > All Field Sediments	NS	*H. azteca:* Lab Control > (MAT01, MAT02, MAT18, MAT19, MAT21, PAM02, PAM03, PAM07) *C. tentans:* Lab control > (MAT02, MAT19)
All Field Sediments Equal	NS	*H. azteca:* (MAT03, PAMO4, PAM05) > (MAT01, MAT02, MAT06, MAT18, MAT19, MAT21, PAM02, PAM03, PAM12, PAM18) > PAM07 *C. tentans:* (MAT18, PAM02, PAM12) > (MAT02, MAT19) *C. dubia:* MAT02 > (MAT18, PAM03, PAM04, PAM05, PAM07, PAM12)

[1]NS=no significant (p=0.05) effect, i.e. accept null hypothesis.

Table 3.13. Reference toxicant test results for species used in aqueous toxicity tests (Reference toxicant: KCl, Sigma "Ultra" lot #29H00321; values in mg/l) (modified from DeLisle 2003).

H. azteca - 96-h Acute

Reference Test Dates:	10/30/03-11/2/03
Reference Toxicant:	KCl (Sigma "Ultra")
Test Concentrations:	307, 384, 480, 600, 750 mg/l
Control Survival:	100%
96-h LC50 Reference test (95% C.L.):	565.7 mg/l (524.0-614.8)
Control Chart 96-h LC50 (Accept. Limits):	483.9 mg/l (388.8-578.9)

C. tentans - 96-h Acute

Reference Test Dates:	10/30/03-11/2/03
Reference Toxicant:	KCl (Sigma "Ultra")
Test Concentrations:	10, 3.6, 2.2, 1.3, 0.78 g/l
Control Survival:	100%
96-h LC50 Reference test (95% C.L.):	5.6 g/l (5.0-6.3)
Control Chart 96-h LC50 (Accept. Limits):	4.9 g/l (3.3-6.5)

C. dubia – 3-brood Chronic

Reference Test Dates:	10/1/03-10/7/03
Reference Toxicant:	KCl (Sigma "Ultra")
Test Concentrations:	2000, 1000, 500, 250, 125 mg/l
Control Survival:	100%
IC_{25} Reproduction Reference test:	277 mg/l
Control Chart IC_{25} (Accept. Limits):	310 mg/l (256-365)
NOEC Survival Reference test:	250 mg/l
Control Chart NOEC Survival (Accept. Limits):	250 mg/l (125-500)

Reference Test Dates:	11/4/03-11/10/03
Reference Toxicant:	KCl (Sigma "Ultra")
Test Concentrations:	2000, 1000, 500, 250, 125 mg/l
Control Survival:	100%
IC_{25} Reproduction Reference test:	323 mg/l
Control Chart IC_{25} (Accept. Limits):	308 mg/l (252-363)
NOEC Survival Reference test:	250 mg/l
Control Chart NOEC Survival (Accept. Limits):	250 mg/l (125-500)

3.5 Benthic Community Analysis

Benthic samples collected for community analysis prior to the collection for chemical and toxicological analysis. Thus any differences in aqueous conditions during the August sampling (Table 3.14) and those during the October sampling (Table 3.1) can be attributed in part to seasonal differences. Clearly, sampling did not occur at identical locations since the water depths were different at the sites and in an amount that exceeds any difference that one can attribute to differences in tidal phase. Temperature at the times of sampling differed by 7°C or more on both rivers. The salinity at the three most downstream stations in the Mattaponi was substantially higher in August (2-9 g/kg) than October. Curiously, the salinity at 8-MPN000.86 (2.2 g/kg) was substantially lower than at the next two stations as one proceeds upstream (9.6 g/kg) during August. This may reflect an effect of sampling times and tidal phase. Similarly during August the four most downstream stations in the Pamunkey were more saline (1 to 4 g/kg) than the same stations in October (0.2-0.3 g/kg).

The sediment characteristics in samples collected independently for the benthic community analysis (Table 3.15) were more often different than consistent with those collected for the chemical and toxicological characterization (Table 3.2). Since there is often considerable variability within a station, it is not unreasonable that a single sample collected at an independent point within the station grid would differ from all others and the overall average. In this case, however, the differences lead one to characterize some stations as sandy during one sampling event and silt-clay during the other.

The species richness in the Mattaponi River stratum was generally higher than in the Pamunkey River stratum (Table 3.16). The abundance of individuals ranged from 1450 to 12,700 in the Mattaponi River stratum and from 400 to 3100 in the Pamunkey River stratum. It should be noted that there were no stations occupied on the Pamunkey River between mile 0 and mile 9, whereas there were on the Mattaponi. This is significant because the single largest identifiable source of potential contamination in these river systems occurs at West Point between mile 0 and mile 1. The actual discharge points are located on the lower Pamunkey, where all candidate stations were rejected. Nevertheless, it is clear that the Pamunkey River has a less diverse and less abundant benthic fauna.

Sediments in the Mattaponi River (Table 3.17) were dominated by Annelids (8 species), Arthropods (10 species) and Molluscs (7 species). Sediments in the Pamunkey River (Table 3.17), were also dominated by Annelid (5 species), Arthropods (16 species), and Mollusks (4 species). Three obvious differences are the absence of the bivalve *Corbicula flumea* in the Pamunkey River, the absence Spheridae (bivalves) in the Mattaponi, and the small number of insect species in the Mattaponi (2 versus 8 in the Pamunkey).

Substantial numbers of the amphipod, *Leptocheirus plumulosis*, were observed at some stations in both rivers during the benthic community sampling, but were not observed in sediments subjected to toxicological testing. In addition, a major amphipod predator, *Cyathura polita*, was observed in significant numbers in the benthic community samples from several stations, but was not observed in sediments collected for toxicological testing. This difference in sediments collected in August versus October is curious.

The Benthic Index of Biological Integrity (B-IBI) scores for stations in the Mattaponi River stratum, ranging from 3.0 to 5.0, place this region in the “meets goals” to “exceeds goals” categories. The B-IBI scores for stations in the Pamunkey River stratum were similarly high (3.0 to 5.0) with the exception of Station PMK011.88 with a score of 1.0. This station involved 4 species with low abundance (total of 18 animals). At the adjacent station PMK012.00, the B-IBI was in the “meets goals” range (4.6), but had only 5 species present (total of 20 animals), clearly dominated by 1 predatory isopod species (13 specimens). These seemingly minor differences had a profound impact on the scoring for the two stations.

Table 3.14 Physical Data for AMBTOX Project Monitoring Stations sampled in August 2003 (modified from Dauer & Rodi, 2004).

Station	Sampling Date	Depth (m)	Salinity (ppt)	Dissolved Oxygen (mg/l)	Temperature (°C)
Mattaponi River					
MPN000.86	8/21/2003	1.30	2.2	4.10	28.8
MPN001.10	8/27/2003	5.00	9.6	4.5	28.4
MPN001.33	8/27/2003	8.00	9.7	4.40	28.4
MPN004.31	8/21/2003	5.80	0.2	3.30	28.5
MPN020.58	8/27/2003	5.50	0.0	4.80	28.7
MPN020.75	8/27/2003	6.00	0.0	4.80	28.7
MPN024.81	8/27/2003	4.50	0.0	5.10	28.6
Pamunkey River					
PMK009.39	8/27/2003	4.50	4.2	4.70	28.9
PMK011.64	8/27/2003	5.00	1.6	4.70	29.0
PMK011.88	8/27/2003	5.50	1.2	5.00	29.0
PMK012.00	8/27/2003	5.00	1.0	5.30	29.1
PMK013.06	8/27/2003	1.00	0.4	5.40	29.2
PMK020.31	8/28/2003	4.50	0.1	5.60	29.1
PMK033.04	8/27/2003	2.00	0.1	5.60	29.4

Table 3.15 Sediment characteristics in sediment samples collected for benthic community analysis during fall 2003 (modified from Dauer & Rodi, 2004).

Station	Sand % Wt)	Silt-Clay (% Wt)	Volatile Solids (%)
Mattaponi River			
MPN000.86	1.2	98.8	3.0
MPN001.10	86.2	13.8	1.1
MPN001.33	40.4	59.6	2.1
MPN004.31	11.2	88.8	2.9
MPN020.58	73.3	26.7	1.1
MPN020.75	52.0	48.0	2.0
MPN024.81	80.2	19.8	1.3
Pamunkey River			
PMK009.39	23.4	76.6	3.6
PMK011.64	2.7	97.3	4.7
PMK011.88	32.2	67.8	4.7
PMK012.00	37.2	62.8	3.2
PMK013.06	31.7	68.3	3.0
PMK020.31	31.7	52.9	2.2
PMK033.04	4.80	95.2	3.5

Table 3.16. Total community parameters for AMBTOX Project Monitoring Stations (modified from Dauer & Rodi, 2004).

Station	Total Species	Individuals/ sq.m.	AFDW Biomass (g) Total	No Bivalves	B-IBI Value	Condition
MPN000.86	7	1,678	0.590	0.340	3.0	Good
MPN001.10	12	3,493	2.404	2.132	3.8	Good
MPN001.33	15	12,655	1.905	1.746	3.0	Good
MPN004.31	5	1,678	0.340	0.113	4.3	Good
MPN020.58	12	4,377	0.363	0.272	4.5	Good
MPN020.75	10	1,452	0.272	0.227	5.0	Good
MPN024.81	9	2,132	0.499	0.272	4.0	Good
PMK009.39	9	3,130	0.408	0.386	3.0	Good
PMK011.64	11	1,973	0.567	0.499	4.0	Good
PMK011.88	4	408	0.091	0.091	1.0	Bad
PMK012.00	5	454	0.181	0.181	4.6	Good
PMK013.06	9	1,769	0.227	0.204	5.0	Good
PMK020.31	7	1,157	0.159	0.159	4.5	Good
PMK033.04	9	1,497	1.202	1.179	5.0	Good

Table 3.17a. Benthic species sample abundance list with ash-free dry weight biomass (AFDW in mg) in the Mattaponi River (modified from Dauer & Rodi, 2004).

Taxon			MPN000.86		MPN001.10		MPN001.33		MPN004.31		MPN020.58		MPN020.75		MPN024.81	
Phylum	Class	Genus species	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW
Nemertea		*Nemertea* spp.					2	0.001								
Annelida	Polychaeta	*Heteromastus filiformis*			1	0.001										
Annelida	Polychaeta	*Hobsonia florida*					53	0.004								
Annelida	Polychaeta	*Marenzellaria viridis*	1	0.004	62	0.074	18	0.033			8	0.002	12	0.002	6	0.002
Annelida	Polychaeta	*Neanthes succinea*			3	0.001	6	0.001								
Annelida	Polychaeta	*Xenochironomus* sp.													3	0.001
Annelida	Oligochaeta	*Limnodrilus hoffmeisteri*									3	0.001			6	0.002
Annelida	Oligochaeta	*Limnodrilus* sp. juv.			5	0.001	3	0.001			11	0.001	17	0.001	44	0.002
Annelida	Oligochaeta	*Tubificoides heterochaetus*	34	0.001	12	0.001	260	0.003	59	0.001	4	0.001	3	0.001		
Mollusca	Bivalvia	*Boccardiella ligerica*					8	0.001								
Mollusca	Bivalvia	*Corbicula flumea*									127	0.002	6	0.001	5	0.002
Mollusca	Bivalvia	*Macoma balthica*	7	0.011	7	0.012	4	0.006	1	0.01						
Mollusca	Bivalvia	*Rangia cuneata*									4	0.002	1	0.001	1	0.008
Arthropoda	Isopoda	*Chiridotea almyra*			10	0.002					1	0.001	1	0.001		
Arthropoda	Isopoda	*Cyathura polita*	1	0.001	7	0.003	32	0.015			3	0.001	7	0.002	13	0.003
Arthropoda	Amphipoda	*Amerocuolodes* sp complex	1	0.001	2	0.001	3	0.001	5	0.001						
Arthropoda	Amphipoda	*Corophium lacustre*					5	0.001								
Arthropoda	Amphipoda	*Gammarus daiberi*			17	0.002	6	0.002	5	0.002	10	0.002	2	0.001	8	0.001
Arthropoda	Amphipoda	*Leptocheirus plumosus*	28	0.007	23	0.007	136	0.013	4	0.001						
Arthropoda	Amphipoda	*Melita nitida*	2	0.001	5	0.001	21	0.001			5	0.001				
Arthropoda	Decapoda	*Rhithropanopeus harrisii*					1	0.001								
Arthropoda	Insecta	*Cryptochironomus fulvus*									2	0.001	3	0.001		
Arthropoda	Insecta	*Tanytarsini* sp.									15	0.001	12	0.001	8	0.001
Totals			74	0.026	154	0.106	558	0.084	74	0.015	193	0.016	64	0.012	94	0.022

Table 3.17b. Benthic species sample abundance list with ash-free dry weight biomass (AFDW in mg) in the Pamunkey River (modified from Dauer & Rodi, 2004).

Taxon			PMK009.39		PMK011.64		PMK011.88		PMK012.00		PMK013.06		PMK020.31		PMK033.04	
Phylum	Class	Genus species	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW	Abund	AFDW
Annelida	Polychaeta	*Marenzellaria viridis*	2	0.007					2	0.001	5	0.002	10	0.001		
Annelida	Polychaeta	*Xenochironomus* sp.													6	0.005
Annelida	Oligochaeta	*Limnodrilus hoffmeisteri*													2	0.001
Annelida	Oligochaeta	*Limnodrilus* sp. juv.			3	0.001	3	0.001							7	0.001
Annelida	Oligochaeta	*Tubificoides heterochaetus*	77	0.001					3	0.001	42	0.001	25	0.001		
Mollusca	Bivalvia	*Boccardiella ligerica*	2	0.001	12	0.002										
Mollusca	Bivalvia	*Macoma balthica*			1	0.001										
Mollusca	Bivalvia	*Rangia cuneata*									6	0.001				
Mollusca	Bivalvia	Sphaeriidae spp.													20	0.001
Arthropoda	Isopoda	*Chiridotea almyra*							13	0.002			1	0.001		
Arthropoda	Isopoda	*Cyathura polita*	3	0.001	30	0.005			1	0.003	12	0.001	5	0.001	11	0.004
Arthropoda	Amphipoda	*Amerocuolodes* sp complex	1	0.001												
Arthropoda	Amphipoda	*Corophium lacustre*			3	0.001										
Arthropoda	Amphipoda	*Gammarus daiberi*	21	0.002	2	0.001	8	0.001					5	0.001		
Arthropoda	Amphipoda	*Leptocheirus plumosus*	23	0.003	4	0.001	4	0.001			1	0.001				
Arthropoda	Amphipoda	*Melita nitida*	8	0.001	8	0.001	3	0.001								
Arthropoda	Amphipoda	*Pristinella osborni*			6	0.001										
Arthropoda	Decapoda	*Rhithropanopeus harrisii*			6	0.01									1	0.028
Arthropoda	Insecta	*Chaoborus punctipennis*	1	0.001					1	0.001						
Arthropoda	Insecta	*Coelotanypus* spp.													2	0.001
Arthropoda	Insecta	*Cryptochironomus fulvus*											1	0.001		
Arthropoda	Insecta	*Hexagenia* spp.									1	0.001			13	0.011
Arthropoda	Insecta	*Pentaneura* spp.													4	0.001
Arthropoda	Insecta	*Procladius sublettei*									4	0.001				
Arthropoda	Insecta	*Tanytarsini* sp.			12	0.001					6	0.001	4	0.001		
Arthropoda	Insecta	*Trichoptera* sp.									1	0.001				
Totals			138	0.018	87	0.025	18	0.004	20	0.008	78	0.010	51	0.007	66	0.053

Table 3.18. Individual metric scores and calculated B-IBI for each station (modified from Dauer & Rodi, 2004).

Station	Shannon Index	Abundance	Biomass	Pollution Indicative Abundance	Pollution Sensitive Biomass	Pollution Sensitive Abundance	Carnivores/ Omnivores	Deep Deposit Feeders	Tolerance Score	Tanypodini to Chironomidae abundance ratio (%)	B-IBI Score
Mattaponi River											
MPN000.86	-	5	-	3	-	3	1	-	-	-	3.0
MPN001.10	3	3	3	5	5	-	-	-	-	-	3.8
MPN001.33	3	1	3	5	3	-	-	-	-	-	3.0
MPN004.31	-	5	-	-	-	5	-	3	-	-	4.3
MPN020.58	-	3	-	-	-	5	-	5	5	-	4.5
MPN020.75	-	5	-	-	-	5	-	5	5	-	5.0
MPN024.81	-	5	-	-	-	3	-	5	3	-	4.0
Pamunkey River											
PMK009.39	-	5	-	3	-	3	1	-	3	-	3.0
PMK011.64	-	5	-	5	-	1	5	-	3	5	4.0
PMK011.88	-	1	-	1	-	1	1	-	1	-	1.0
PMK012.00	-	5	-	5	-	5	5	-	3	-	4.6
PMK013.06	-	5	-	-	-	5	-	5	5	-	5.0
PMK020.31	-	3	-	-	-	5	-	5	5	-	4.5
PMK033.04	-	5	-	-	-	5	-	5	5	-	5.0

4.0 DISCUSSION

4.1 Sediment Quality Triad

Sediments of both rivers are sandy to sandy mud texture, although two or three occupied stations in each river have sediments with a silt-clay texture. The latter are the only stations where one might predict a substantial accumulation of contaminants.

The present study examined a study area extending up the Mattaponi and Pamunkey Rivers from their confluence to form the York River to locations 25 (Mattaponi) and 33 (Pamunkey) miles upstream. There is a single major industrial plant, a paper mile, located at the confluence of the two rivers. The plant has been operated at this location for over 85 years. While concern has existed regarding possible adverse impacts of this plant, no evidence has been produced to support the concern. It is worth noting, however, that an intensive characterization has not been performed in close proximity to the plant.

Sediments within the two river systems were analyzed at 7 randomly selected stations for heavy metals, PAHs, PCBs, a wide array of organophosphate and organochlorines pesticides and herbicides. The only exceedance of an ER-M for any chemical was observed at station MPN020.75 where the value was exceeded for Manganese. PAHs were not found at concentrations above the detection limit. Several organophosphate pesticides are tentatively or definitively identified, but never at substantial concentrations. Compounds identified included Carbophenothion, Deazinon, Disulfoton, Monocrotophos, Phosmet, TEPP, Thionazin, and Trichlornate. Several chlorinated pesticides were identified (b-BHC, Dibromochloropropane, Dieldrin, Ensodulfan Sulfate, g-BHC, Hexachlorobenzene, Hexachlorocyclopentadiente, Methoxychlor, and p,p'-DDD). The materials were not quantified in any case. Several PCB isomers were tentatively identified or verified, but the total concentrations were less than 125 ng/g. Detectable amounts of various herbicides were not observed. Even considered as an aggregate of chemicals, there is no basis for alleging a toxic impact.

This is consistent with the toxicological assessments of sediments from the same locations. There was no impact on the survival of any test species that was attributable to the presence of toxic chemicals. There was toxicity to *Ceriodaphnia* from sediment extracts at one station. That observation seems to result from sedimentary ammonia.

The B-IBI indices for all stations met or exceeded "goals" with the exception of one station in the Pamunkey River (PMK011.88). The only chemical present in high concentration was the common laboratory contaminant, bis [2-ethylhexyl] phthalate, but no corresponding toxic response was noted in any of the single species tests. Thus there is no evidence to support the notion that the low B-IBI at this station is attributable to chemical contamination. It is more likely that the condition relates to another stressor such as reduced oxygen or eutrophication, although there is no evidence to support this speculation.

4.2 Results of Previous Studies in the Mattaponi and Pamunkey Rivers

In 1995, Hall *et al.* (1998a) examined two stations located in the mouth of the Pamunkey River, one just upstream of the paper mill (off Berkley Street) and one just downstream of the paper mill (off 10th Street). In that study, water column toxicity was monitored as well as sediment toxicity. No aqueous toxicity was observed, though there was an exceedance of the US EPA marine chronic water quality criterion for lead. Sediment samples showed little or no toxicity to the battery of species test. Several organochlorine pesticides were measured, but at concentrations below those that produce adverse effects.

McGee *et al.* (2001) occupied a set of 5 stations, 3 distributed between Mt Folly and Brookshire in the York River just downstream of West Point, and two stations in the Mattaponi River, one off 2nd Street and one just north of the Lord Delaware Bridge. The latter station was in close proximity to station MPN001.33 of the present study. As with the 1995 study of Hall *et al.* (1998), there were no chemical measures that suggest any basis for concern, and in tests of sediment, there was no toxicity with a battery of species. The benthic community was degraded at three of the five stations and marginal at the station nearest the Lord Delaware Bridge. The condition of the benthic community was attributed to the high physical energy of the York River in this region. In addition, some locations in the vicinity are known to one of us (MHR) to be anaerobic as a result of wood chips from the paper mill operation that have accumulated in some locations. While one cannot verify the conditions at the stations occupied during the McGee *et al.* study, it seems likely that the community condition reflects general water quality conditions rather than specific toxicity consideration.

Neither previous study extended observations upstream from the City of West Point. However, the Hall *et al.* study provided some evidence of conditions in the lower Pamunkey River that was not sampled during the present study. Two stations in the McGee *et al.* study spanned the lower 1.3 mile stretch of the Mattaponi in which 4 stations were occupied in the present study. Chemical characterization and toxicity results in the two studies were clearly consistent. The community analyses however, were not consistent. In the McGee *et al.* study, the B-IBI value showed severe degradation at three stations (Y16, Y18 and Y21) and marginal degradation at Y22 near the Lord Delaware Bridge Station in which area the present study found a healthy benthic community. The index met the goal only at station Y17 (approximately 1.3 miles downstream of West Point). In contrast, two stations in the present study located between the Mattaponi stations of McGee *et al.* (Y21 and Y22) showed a healthy benthic community. These stations were located on the Mattaponi side of the river whereas the McGee station was on the shoreline of West Point where runoff from the city streets may have adversely affected the benthos.

Wright *et al.* (2002) produced a preliminary report for a study conducted in 2000 with stations in Maryland and Virginia. The Virginia stations included three in the Mattaponi River and 4 in the Pamunkey River. The study evaluated sites based on chemical analysis (Md and Va), sediment toxicity (Md and VA) and B-IBI (Md only).

With the exception of Mn, there were no exceedances of ER-M's for metals in sediment. PAH concentrations in sediment were low or non-detectable. The six chlorinated pesticides evaluated in fall 2000 sediment samples were non-detectable, but the detection limits are unknown. Pesticides were observed in spring 2001 water samples, notably the herbicide atrazine and the insecticide metalochlor. Atrazine is used in no-till production of corn and soy beans, and was observed only in the Mattaponi.

Sediments from two stations in the Pamunkey River produced significant toxicity to *Chironomus tentans* and this species had somewhat reduced survival at all stations in both rivers except the most upstream station in the Mattaponi when compared to a control sediment. Size increase for this species was depressed only at the most upstream station in the Pamunkey River. Sediments from the most downstream station in the Pamunkey River produced a significant reduction in survival of *Pimephales promelas* larvae compared to the control sediment, but sediments all stations in both rivers produced somewhat reduced survival. Size increase of fish larvae was depressed only by sediments from the most downstream station in the Mattaponi River. Sediment from all stations in both rivers produced no adverse effect on *Hyalella azteca* in either parameter. In a novel test using seed germination and final dry weight of *Vallisneria americana* as the endpoints, sediments from these two rivers had no effect on seed germination, but resulted in enhanced final dry weight compared to control sediment.

The Wright *et al.* (2002) report suggests no serious adverse chemical or toxicological conditions. Since the B-IBI was not determined during the Wright Virginia study, one leg of the characterization triad is missing.

A limited data set exists for metals (Table 4.1) and PAHs (Table 4.2) in sediments of these rivers and for metals (Table 4.3) and PCBs (Table 4.4) in fish tissues from these rivers. Sediment and fish samples were collected by the DEQ Tissue Monitoring Program and analyzed in the laboratory of Dr. Robert C. Hale at the Virginia Institute of Marine Science.

There were no exceedances of sediment quality guidelines for metals in the Mattaponi River. In the Pamunkey River, there were exceedances of the ER-L for Chromium (Station 8-PMK029.26), Nickel (Station 8-PMK006.36), and Mercury (Stations 8-PMK029.26, 8-PMK006.36, and 8-PMK032.00). The only exceedance of the ER-M was for Zinc at Station 8-PMK032.00. No exceedances of PAH sediment quality guidelines for PAH were observed in either river.

There were 10 exceedances of the DEQ Screening Value for mercury in tissue. In the Mattaponi, there were 3 exceedances in largemouth bass and one in channel catfish at mile 29 and mile 41. In the Pamunkey, 6 species exhibited exceedances for mercury in tissue: white perch at mile 6.36, channel catfish and largemouth bass at mile 32, and blue catfish, redbreast sunfish and spotted bass at mile 56.87. All exceedances in both rivers occurred in 2003.

PCB was measured at concentrations between 1 and 149 ng/g in fish from the Pamunkey River at four stations from mile 6 to mile 82 in 2003 and at three stations from mile 6 to mile 88 in 2000. With the exception of mile 41, fish from the Mattaponi also had concentrations in this range. One

fish in each river had a total PCB concentration exceeding 100 ng/g: at mile 41 in the Mattaponi in 2003 and at mile 6 in the Pamunkey in 2000.

The sample size for this data set is relatively small, with five or less species collected at each station and no species occurring in samples from all stations or years. Reconciling the metals and PCB data is difficult because the same species do not appear to have been analyzed at each station and date either because there were too few fish for metals and PCB analysts each to receive samples of each fish species or no sharing of tissue samples occurred. The relative cost for analyses of metals versus PCBs may also play a role in the seeming discrepancies, but insufficient information is available to us to differentiate these options.

4.3 Comparison to Results of James River Studies

In two recent studies (Roberts *et al.*, 2002; Roberts *et al.*, 2003), the oligohaline and tidal freshwater reach of the nearby James River were studied in the same three pronged manner as the present study. In contrast to the Mattaponi and Pamunkey Rivers, the James River has substantially more industrial development, with electric generation stations, municipal waste water treatment, a major shipping port, several petroleum transfer points, and a wide range of chemical industries, particularly in the 30+ miles from Hopewell to Richmond.

In the James River, as in the Mattaponi and Pamunkey Rivers, there was little evidence of chemical deterioration or toxicity of sediment. There were some locations in the James River in which the benthic community was degraded, unlike the present study, but the community condition was likely the result of the physical disruption of the river reach and general environmental degradation with reduced oxygen at the bottom much of the time.

4.4 Impacts from Hurricane Isabel

A major hurricane passed through the region just 10 days before sampling for chemical and toxicological analysis was initiated. Substantial rainfall was associated with the storm as well as high winds from which one might surmise that there was substantial wave action. The net effect might be to relocate sediments within the system or to dilute contaminated sediments with clean sediments, effects that could have modified both analytical and toxicological results.

Table 4.1 Bulk metal concentrations (µg/g dry weight) in sediment samples collected in the Mattaponi and Pamunkey Rivers over several years by DEQ's Fish Tissue & Sediment Monitoring Program

Station	Sample Date	Al	Sb	As	Cd	Cr	Cu	Pb	Hg	Ni	Se	Ag	Th	Zn
Mattaponi River														
8-MPN031.15	(6/6/1997)	7,000	< 0.5	1	0.36	16	5.3	6.4	0.05	0.33	< 0.5	< 0.02	0.58	41
Pamunkey River														
8-PMK029.23	(6/6/97)	*23,000*	0.5	7.5	0.52	*45*	*42*	45	*0.57*	2.5	0.5	0.1	0.3	232
8-PMK006.36	(7/27/2000)	13,000	< 0.5	< 0.5	0.29	34	*43*	24	*0.28*	*44*	< 0.5	< 0.02	< 0.3	95
8-PMK032.00	(5/31/2000)	9,600	< 0.5	< 0.5	0.9	35	*67*	34	*0.28*	15	< 0.5	0.3	< 0.3	**460**
8-PMK088.11	(8/3/2000)	8,700	< 0.5	< 0.5	0.12	20	32	8.5	0.056	7.5	< 0.5	< 0.02	< 0.3	52
ER-L[a]				8.2	1.2	81	34	46.7	0.15	20.9		1.7		271
ER-M[a]				70	9.6	370	270	218	0.71	51.6		3.7		410
ER-L[b]		14,000		13	0.7	39	41	55		24				110
ER-M[b]		58,000		50	3.9	270	190	99		45				550
TEC[c]				9.79	0.99	43.4	31.6	35.8	0.18	22.7				121
PEC[c]				33	4.98	111	149	128	1.06	48.6				459

Underlined and boldfaced values exceed the relevant ER-M or PEC
Italicized values exceed the relevant ER-L or TEC

[a] Long, E.R. *et al.* 1995.
[b] Ingersoll, C.G. *et al.* 1996.
[c] MacDonald, DD, CG Ingersoll and TA Berger. 2000

Table 4.2 Bulk PAH concentrations (ng/g, dry weight) in sediment samples collected by DEQ's Fish Tissue & Sediment Monitoring Program over several years in the Mattaponi and Pamunkey Rivers.

	Sediment Quality Guidelines						
	ER-L	**ER-M**	8-MPN031.15	8-PMK029.23	8-PMK006.36	8-PMK032.00	8-PMK088.11
Analyte			6/6/97	6/6/97	7/27/00	5/31/00	8/3/00
Low Molecular PAHs							
2-Methylnaphthalene	70	670	7.1	ND	1.3	1.6	ND
Acenaphthylene	44	160	ND	ND	ND	ND	ND
Acenaphthene	16	500	ND	ND	ND	ND	ND
Anthracene	85.3	1,100	ND	ND	ND	ND	1.9
Fluorene	19	540	ND	ND	ND	ND	1.3
Naphthalene (& compounds)	160	2,100	95.3	22.7	2.4	4.8	1.5
Phenanthrene (compounds)	240	1,500	71.7	195.9	2.5	1.4	5.8
Total LM PAHs	552	3,160	174.1	218.6	6.2	7.8	10.5
High Molecular PAHs							
Benzo[a]anthracene	261	1600	39.7	146.6	13.6	2.6	23.4
Benzo[a]fluorene			15.6	12.7	ND	ND	ND
Benzo[b]fluoranthene			ND	36.6	10.9	2.7	15.4
Benzo[k]fluoranthene			ND	ND	7.3	2.0	9.9
Benzo[j]fluoranthene			ND	10.2	ND	ND	ND
Benzo[ghi]fluoranthene			ND	6.2	ND	0.8	ND
Benzo[e]pyrene			39.6	31.8	6.5	6.2	7.6
Benzo[a]pyrene	430	1600	ND	11.7	4.1	1.5	5.9
Benzo[ghi]perylene			32.0	50.1	3.0	ND	2.9
Chrysene	384	2,800	ND	ND	20.2	3.7	24.3
Chrysene, trimethyltetrahydro-			145.0	340.2	ND	ND	ND
Dibenz[a,h]anthracene			17.3	23.4	1.1	ND	1.2
Fluoranthene	600	5,100	11.5	61.6	15.0	4.7	28.9
Indeno[1,2,3-cd]pyrene	63.4	260	ND	37.8	2.7	0.7	3.4
Perylene			71.9	406.3	198.0	30.3	57.6
Pyrene	665	2,600	11.0	35.3	13.0	4.4	22.9
Total HM PAHs	1,700	9,600	383.5	1210.5	295.3	59.6	203.4
Total PAHs	4,022	44,792	557.6	1429.1	301.5	67.4	213.9

Table 4.3 Metal concentrations (µg/g, wet weight basis) in fish tissue samples collected in the Mattaponi and Pamunkey Rivers during 2000 and 2003.

			Analyte (µg/g)					
Station	Collection Date	Fish Species	As	Cd	Cr	Hg	Pb	Se
		DEQ Screening Value	**0.072**	**11**	**32**	**0.3/0.5**	**NA**	**54**
Mattaponi River								
8-MPN008.91	8/4/03	Blue Catfish	<0.05	<0.01	<0.05	0.143	<0.1	<0.5
		Gizzard Shad	<0.05	<0.01	<0.05	0.023	<0.1	<0.5
		White Perch	<0.05	0.019	<0.05	0.160	<0.1	<0.5
8-MPN029.08	6/23/03	Channel Catfish	<0.05	<0.01	<0.05	0.142	<0.1	<0.5
		Largemouth Bass	<0.05	<0.01	<0.05	**0.896**	<0.1	<0.5
		Redbreast Sunfish	<0.05	0.013	<0.05	0.210	<0.1	<0.5
8-MPN041.41	8/21/03	Blue Catfish	<0.05	0.043	<0.05	0.077	<0.1	<0.5
		Gizzard Shad	<0.05	<0.01	<0.05	0.086	0.182	<0.5
		Channel Catfish	<0.05	0.064	<0.05	**0.376**	0.598	<0.5
		Largemouth Bass (1)	<0.05	<0.01	<0.05	**1.470**	0.452	<0.5
		Largemouth Bass (2)	<0.05	<0.01	<0.05	**0.577**	0.197	<0.5
		Striped Bass	<0.05	0.058	<0.05	0.144	<0.1	<0.5
Pamunkey River								
8-PMK006.36	7/27/00	Blue Crab	<0.05	0.032	<0.05	0.014	<0.1	<0.5
		Channel Catfish	<0.05	<0.01	<0.05	< 0.01	<0.1	<0.5
		Longnose Gar	<0.05	<0.01	<0.05	0.170	<0.1	<0.5
		White Perch	<0.05	<0.01	0.2	< 0.01	<0.1	<0.5
8-PMK006.36	8/27/03	Blue Crab	**0.085**	0.112	<0.05	0.081	<0.1	<0.5
		Croaker	<0.05	<0.01	<0.05	0.246	<0.1	<0.5
		Blue Catfish	<0.05	<0.01	<0.05	0.256	1.512	<0.5
		White Perch	<0.05	<0.01	<0.05	**0.350**	<0.1	<0.5
8-PMK032.0	5/31/00	Gizzard Shad	<0.05	<0.01	<0.05	<0.01	<0.1	<0.5
		Channel Catfish	<0.05	<0.01	<0.05	<0.01	<0.1	<0.5
		Largemouth Bass	<0.05	<0.01	<0.05	0.088	<0.1	<0.5
		White Perch	<0.05	<0.01	<0.05	<0.01	<0.1	<0.5
8-PMK032.0	9/17/03	Gizzard Shad	<0.05	<0.01	<0.05	0.072	<0.1	<0.5
		Channel Catfish (1)	<0.05	<0.01	0.075	0.063	<0.1	<0.5
		Channel Catfish (2)	<0.05	<0.01	<0.05	**0.483**	<0.1	<0.5
		Largemouth Bass	<0.05	<0.01	<0.05	**0.477**	<0.1	<0.5
8-PMK056.87	8/18/03	Blue Catfish	<0.05	<0.01	<0.05	**0.730**	0.15	<0.5
		Common Carp	<0.05	<0.01	<0.05	0.239	0.232	<0.5
		Redbreast Sunfish	<0.05	<0.01	<0.05	**0.367**	<0.1	<0.5
		Spotted Bass	<0.05	<0.01	<0.05	**0.303**	0.226	<0.5
8-PMK082.34	8/19/03	Common Carp	<0.05	<0.01	<0.05	0.226	<0.1	<0.5
		Channel Catfish	<0.05	<0.01	<0.05	0.100	0.145	<0.5
		Spotted Bass	<0.05	<0.01	<0.05	0.211	0.266	<0.5
8-PMK088.11	8/30/00	American Eel	<0.05	0.01	<0.05	0.011	<0.1	<0.5
		Channel Catfish	<0.05	<0.01	<0.05	<0.01	<0.1	<0.5
		Redbreast Sunfish	<0.05	<0.01	<0.05	<0.01	<0.1	<0.5

Table 4.4 Total PCB Concentrations (ng/g on a wet weight) in fish tissue collected in the Mattaponi and Pamunkey Rivers during 2000 and 2003 by DEQ's Fish Tissue & Sediment Monitoring Program.

Stream	River mile	Date	Species														
			Amer. Eel	Blue Cat-fish	Blue Crab	Blue -gill	Channel Catfish	Common Carp	Croaker	Gizzard Shad	Large-mouth Bass	Long-nose Gar	Redbreast Sunfish	Stripped Bass	Spotted Bass	White Perch	Yellow Perch
Mattaponi	8.91	8/04/2003		9.50						18.57						4.15	
	29.08	6/23/2003					28.91				3.93		22.58				
	41.41	8/21/2003		23.9			9.55			**169.82**	6.68 2.02			**61.32**			0.81
Pamunkey	6.36	7/27/2000			1.67		50.14					**149.42**				4.28	
		8/27/2003		6.66	3.08				5.12							10.14	
	32.00	5/31/2000					18.06			22.61	3.47					3.59	
		9/17/2003					37.87 23.7			4.79	0.31						
	56.87	8/18/2003		30.3				3.16		**51.66**			10.92		0.33		
	82.34	8/19/2003				1.17	11.40	8.95 40.84							0.99		
	88.11	8/3/2000	30.63				13.00						0.83				

Since the sampling of the benthic community predated the storm, there could have been no impact of the storm on the benthic community data. The community data are consistent with the low concentrations of analytes and low toxicity observed after the storm event, but it is not appropriate to conclude from this that there was no impact of the storm on the chemistry and toxicology analyses.

There is no evidence of major differences in chemistry among the several studies that have been accomplished previously and that described here. Similarly, there are no demonstrable differences in toxicological results before and after the storm. One has to temper any conclusion however by the passage of time between past and present studies and substantial inconsistencies in station locations among these studies. Only station Y22 of McGee *et al.* (2001) and station 8-MPN001.10 are closely located, and results from these two studies are in close agreement, suggesting that at this location at least, any impact of the hurricane was minimal.

There is no data from which to directly assess the immediate impact of the hurricane in 2003. Nevertheless, in using the 2003 data to characterize the area, potential impacts of the storm should not be discounted.

4.5 Sampling Design

As noted above, there were dramatic changes in the sampling design for this study compared to previous studies. In essence, the ability to gain insight into the variation in sediment within a 100 meter square area was sacrificed to allow more extensive sampling within the constraints of a limited budget and resources to perform toxicity tests.

One limitation of the procedures used is the methodology for rejecting a random station location on the basis of an assessment of sand content by texture as assessed by benthos specialists rather than objective sediment analysis of sand content. Such professional judgment does not have the resolution to reliably accept or reject stations through no fault of the benthos specialists. It is simply the nature of subjective determination.

A further limitation of the design is the assumption that if the sediment is coarse, pollutant analytes will be present at non-detectable concentrations and toxicological tests will yield no evidence of "toxicity." The assumption that pollutants will be present at non-detectable concentrations is reasonably well documented in the literature. However, the results of toxicological tests may reflect other environmental conditions than the presence of toxic materials, so the assumption that no evidence of "toxicity" is likely is not well founded. Further, the benthic community is not assessed if the station is occupied and deemed inappropriate for chemical and toxicological analysis. In the case of the B-IBI assessment, no assumption of the condition of the community can be made based on sediment texture since it is known that parameters other than toxic chemicals impact the health of communities.

Although this sampling design is biased toward soft sediments which are more likely to include toxic contaminants, it does allow for geographically more extensive sampling and for focusing available funds on samples with the greatest probability to detect contaminants and toxicity within a limited budget. Those stations rejected on the basis of sand content, can be characterized

as contaminant free and non-toxic, although one cannot draw conclusions about the benthic community with any degree of certitude.

By increasing the number of sites sampled, more information is gained regarding the health status of a stratum than is lost by compositing samples from within each sampling grid. The design will likely detect extreme hot spots that can then be examined in greater detail though more intense localized sampling.

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