Distribution and Biological Effects of Agricultural Chemicals and other Environmental Contaminants in the Sediments of Back Bay, Virginia

Virginia Field Office
U.S. Fish and Wildlife Service
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DISTRIBUTION AND BIOLOGICAL EFFECTS OF AGRICULTURAL CHEMICALS AND OTHER ENVIRONMENTAL CONTAMINANTS IN THE SEDIMENTS OF BACK BAY, VIRGINIA

U.S. Fish and Wildlife Service

Virginia Field Office

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EXECUTIVE SUMMARY

The Back Bay in Virginia is a sensitive ecological area in which the United States Fish and Wildlife Service maintains land holdings of approximately 3,238 ha (8,000 acres) and manages an additional 1,862 ha (4,600 acres) of water area in the bay. At one time, the bay provided extensive habitat for migratory waterfowl and supported an economically important, freshwater sport fishery. For the past several years, however, the bay has been in a period of decline in relation to these biological resources. Presumably, this decline has been the result of agricultural activities in the southern portion of the bay's watershed, as well as intensive urban development in the north. These activities have led to increased surface run-off into Back Bay, and as a result, the bay's water quality has been adversely impacted. Over the past two decades, once abundant populations of submerged aquatic vegetation (SAV), have virtually disappeared. Although there is no data to demonstrate cause and effect, based on scientific literature, it is hypothesized that the disappearance of SAV, which serves as a source of food and habitat for biota, has influenced the bay's decline of aquatic birds and fish populations as well.

In the Spring of 1991, a contaminant study was performed in Back Bay to determine if herbicides or other pesticides used in the watershed during the spring planting period have influenced the decline and continuing absence of SAV. Focusing on sediment-sorbed contaminants in this study, sediment samples were taken at all of the major tributaries leading into Back Bay, following the first major rain event after agricultural chemicals were applied. These sediment samples underwent chemical analysis for metals, pesticides, and various organics. Coupled with the chemical analyses, were a Microtox^{R} bioassay of sediment pore-water and a sediment bioassay using sago pondweed and an amphipod species.

The results of this study revealed that, with the exception of certain metals, contamination levels in Back Bay sediments were relatively low. Furthermore, sediment toxicity, as determined by the various bioassays employed, was also low, and could not be correlated with any sediment contaminants.

The study results are consistent with the hypothesis of previous investigators, concluding that SAV declines in Back Bay are primarily influenced by increased turbidity in the bay, rather than toxic effects of agricultural chemicals. This increased turbidity is largely influenced by urban and agricultural run-off, which adds a significant amount of suspended sediment to the bay each year. Future monitoring studies are being designed which will address and evaluate the impacts of this run-off on water quality in Back Bay.

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ABSTRACT: Back Bay is the northernmost extension of the Albemarle-Pamlico-Currituck Sound estuary. It is located entirely within the city limits of Virginia Beach, Virginia. Historically, Back Bay supported abundant waterfowl and freshwater fisheries. In recent years, however, dramatic declines have occurred in the submerged aquatic vegetation (SAV) populations within the bay, and concomitantly, populations of fish and birds have declined as well. Although declines in the fauna of Back Bay have generally been attributed to the loss of SAV, determining the cause of SAV decline itself has been difficult. Theories range from increased turbidity in the bay, caused by urban development in the northern portion of the bay's watershed and intensive agricultural activity in the southern portion, to inputs of phytotoxic compounds from a variety of sources, and a naturally occurring pattern of growth and decline in SAV populations.

This report describes a contaminant study conducted in Back Bay in the Spring of 1991. The purpose of this study was to perform a preliminary assessment of the impacts of commonly used agricultural chemicals on aquatic organisms in Back Bay. Sediment samples were taken from the major tributaries leading into Back Bay, chemically analyzed, and used in bioassays with a submerged macrophyte species, an amphipod species, and a photoluminescent bacteria. These studies revealed that although some contaminants in the Back Bay sediment were elevated (mainly metals), the bioassay test used indicated the toxicity associated with the sediments is minimal, and generally cannot be correlated with contaminant levels in the sediments.

Keywords: Environmental Contaminants, Water Quality, Metals, Pesticides, Polynuclear Aromatic Hydrocarbons, Bioassays, Sediments, Submerged Aquatic Vegetation, Microtox, Sago Pondweed, Amphipod, Back Bay

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TABLE OF CONTENTS

	Page
Executive Summary	i
Abstract	ii
Acknowledgements	iii
List of Tables	v
List of Figures	vi
List of Appendices	vi
Introduction	1
Materials and Methods	11
Field Sampling	11
Sediment Characterization	13
Chemical Analysis	13
Microtox Bioassay	16
Sago Pondweed Bioassay	16
Amphipod Bioassay	17
Statistical Analysis	19
Results	20
Sediment Characteristics	20
Chemicals in Sediments	20
Microtox Bioassays	20
Sago Pondweed Bioassays	30
Amphipod Bioassays	32
Discussion	37
Conclusions and Recommendations	40
Literature Cited	41
Appendices	43

LIST OF TABLES

		Page
Table 1.	Metal analyses of sediment performed at the Missouri Environmental Trace Substances Research Center, Columbia, Missouri	14
Table 2.	Chemical analyses of sediment performed at the Mississippi State Chemical Laboratory, Mississippi State University	15
Table 3.	Physical and chemical characteristics of sediment from the sampling stations in Back Bay	22
Table 4.	Relative values of site specific concentrations of metals in Back Bay sediments	23
Table 5.	Summary of Sago pondweed growth results from Back Bay sampling sites	31
Table 6.	Number of amphipods as adults, females with eggs or offspring in marsupium, and number of juveniles in sediment samples from each replicate	34
Table 7.	List of macroinvertebrate taxa in addition to *Hyalella azteca*, found in sediment at the end of the bioassay test, listed in order of relative abundance	36

LIST OF FIGURES

		Page
Figure 1.	General area map showing the location of Back Bay and the Poropotank River in relation to the Chesapeake Bay.	10
Figure 2.	Back Bay sampling stations.	12
Figure 3 (a-e).	Concentrations of metals in the sediments of Back Bay	24
Figure 4.	Results of Microtox[R] bioassay for Back Bay sediment pore water	29

LIST OF APPENDICES

		Page
Appendix 1.	Hydrolab[R] data.	A-1
Appendix 2.	Characteristics of Back Bay sediments.	A-2
Appendix 3.	Concentrations of organochlorines, polynuclear aromatic hydrocarbons, and chlorphenoxy acid herbicides in Back Bay sediments.	A-3
Appendix 4.	Concentrations of carbamate insecticides in the sediments of Back Bay.	A-4

INTRODUCTION

Back Bay National Wildlife Refuge (Refuge) was established in 1938 by President Franklin D. Roosevelt to provide the greater snow goose (Anser caerulescens atlantica) and other migratory waterfowl an unspoiled habitat and sanctuary within the North Atlantic Flyway. False Cape State Park and three Virginia Department of Game and Inland Fisheries Waterfowl Management Areas, located in Back Bay, provide additional habitat for migratory waterfowl. In addition to waterfowl, other aquatic birds and various animal species have been observed in the Back Bay region. In 1975, there were 258 avian species recorded in the bay watershed; 70 species are known to nest in the area (Department of Interior, 1975). Federally protected species such as the bald eagle, (Haliaetus leucocephalus) peregrine falcon, (Falco peregrinus) and piping plover (Charadrius melodus) are also found within the Back Bay watershed. Loggerhead turtles (Caretta caretta) nest throughout False Cape State Park's beach edge, and nutria (Myocaster coypus), as well as other mammals inhabit the area (Mann, 1984).

Back Bay is located in the southeast portion of Virginia Beach, Virginia, and is the northernmost extension of the Albemarle-Pamlico-Currituck Sound Estuary. Considered as a whole, this represents the second largest estuary in the United States. Back Bay itself covers an area of 101 square kilometers, with an average depth of 1.3 meters (Mann, 1984), and a maximum depth of 2.4 meters (Norman and Southwick, 1981). Because the bay is shallow, and lunar tides are negligible, circulation is predominately wind-driven (Mann, 1984). Winds are generally from the south in the summer and from the northeast in the winter. The strongest winds occurring in the bay are from the north and southeast during winter frontal passages (Swift et al., 1991). Using precipitation data (annual rainfall average is 114 centimeters) and

calculated runoff values, Mann (1984) determined the flushing time of the bay to be 0.92 years. Back Bay's receiving waters drain the southeastern quadrant of Virginia Beach. Included in this watershed is the nutrient-enriched Lake Tecumseh, which drains into Back Bay via Hell Point Creek and Black Gut. Back Bay discharges into Currituck Sound at the southern end of the bay, and the closest outlet to the Atlantic Ocean is approximately 97 kilometers south (Tursi, 1989).

The total area of the Back Bay watershed (including the bay) is 269 square kilometers (Mann, 1984), reaching as far north as Camp Pendleton, Virginia, and as far west as Princess Ann Road and Oceana Boulevard in Virginia Beach. On the eastern side, a barrier island separates the bay from the Atlantic Ocean. The Refuge lies at the northern edge of the bay where the marshland barrier narrows to 0.2 kilometers. At the southern end of the bay the barrier widens to 2.4 kilometers. Land within the watershed is predominantly wetlands, with marsh/swamp and scrub/shrub species dominating the diverse flora along the bay's perimeter (Mann, 1984). The soil in the watershed contains excess humus, and flooding is common (USDA, Soil Conservation Service, 1985). Although the potential habitat for hardwood trees and seed crops is poor, habitat potential, based on soil type, is good for wetland plant species (USDA and Soil Conservation, 1985). Despite the excess flooding and poor habitat for seed crops, much of the land has been converted to agricultural use (crops include corn, soybeans, and wheat). In order to keep the agricultural land in production, an extensive network of drainage ditches has been constructed in the farm fields. These ditches ultimately drain into eight principal creeks that discharge into the bay. The plant life in the ditches and creeks leading to the bay are very diverse in contrast to the lack of SAV in the bay.

Currituck Inlet once influenced the environmental parameters or habitat found in Back Bay. In the late 1700s, when this inlet was located at the southern edge of Back Bay, it provided a natural division between the two states of North Carolina and Virginia, thus Back Bay became a part of Virginia. As a result of storm events and tidal influence, this inlet slowly moved southward. Prior to the natural closing of Currituck Inlet in 1828, the bay directly received the ocean's saline water. After the Inlet closed, Back Bay became brackish or less saline (Mann, 1984). Salinity in the bay has fluctuated widely over time due to natural events such as geographical evolution and storm overwash.

Flora and fauna populations in the bay have fluctuated in relation to salinity. At the turn of the century, when the salinity of the bay was higher, the bay supported estuarine fauna and flora. As the bay decreased in salinity, estuarine fauna (e.g., shrimp, oysters, clams, and striped bass (*Morone saxatilis*)) were replaced by freshwater aquatic species (e.g., largemouth bass (*Micropertus salmoides*), bluegill (*Lepomis macrochirus*), and black crappie (*Pomoxis nigromaculatus*)). Likewise, submerged aquatic vegetation (SAV) species have varied due to altered salinity in the bay. Salt tolerant plants found prior to the closing of the inlet, such as eelgrass (*Zostera marina*) and widgeon grass (*Ruppia maritima*), were replaced by freshwater tolerant aquatic species such as sago pondweed (*Potamogeton pectinatus*) (Sincock, 1966). Salt-tolerant species have not dominated the SAV community since the bay became less saline, however, even freshwater species have fluctuated between high and low population densities.

It is not known whether the decline of SAV, waterfowl and fish are solely due to anthropogenic causes. There may be a natural, cyclic fluctuation of SAV populations in this fragile ecosystem. The earliest records of human disturbance were in the early 1920's, when the

Albemarle and Chesapeake (A & C) Canal and Corey's Ditch were dredged, allowing freshwater to enter the bay from the Elizabeth River. The marked decline in SAV, as well as a decline in the number of waterfowl, was blamed on the intrusion of this polluted water (Bourn, 1929). There have been resurgences of SAV in the bay, although the changes have been drastic and abrupt, as the SAV disappears from the bay almost as quickly as it appears (Mann, 1984). For instance, in 1965 SAV populations were almost nonexistent. A few years later a new species, Eurasian watermilfoil (Myriophyllum spicatum), appeared and was prolific, yet prior to this period it had not been documented in the bay. The watermilfoil grew rapidly, and by the mid-1970's it was so extensive, it was considered a nuisance, as it tangled in boat propellers. By 1986, the SAV disappeared again, and has not reappeared to date.

This estuarine system is shallow and wind driven, therefore, turbidity in the bay is cyclic and often elevated. Dredging canals, filling marshes, and stabilizing sand dunes have all contributed to the increased turbidity of the water in the bay. Excessive turbidity diminishes the light penetration needed for plant growth. Increased turbidity has been associated with decreased oxygen levels in the water and reductions of SAV populations (Carter et al. 1985). It was noted that prior to the 1960's, after periods of plant disturbance caused primarily by dredging, the SAV returned to the bay. After dredging and filling the Sandbridge Marshes in the early 1960's, the turbidity of Back Bay increased, and SAV populations decreased (Sincock, 1966; Davis and Brinson, 1983).

Laboratory studies have shown that adding salt water to sediments causes flocculation and increases water clarity (Mann, 1984). Storms that generated sea water overwash into Back Bay were found to produce increased biomass of SAV the following season. This occurred after

storms in 1936, 1951, 1955, and 1962 (Mann, 1984). Laboratory studies and examples of increased plant biomass following the introduction of salt water, suggested that increased salinity in Back Bay may increase SAV biomass in the bay. Based on this information, the city council of Virginia Beach decided to begin pumping salt water from the ocean into the bay.

The pumping began in 1965, with a goal of increasing Back Bay's salinity to 10 parts per thousand (ppt) (Norman and Southwick, 1987). Following the influx of salt water the SAV increased, not with native plants but with Eurasian watermilfoil. Clarity increased in the bay, although operations were interrupted several times. A fire then destroyed the pumping station, which interrupted the flow of sea water for 15 months (from May, 1977 to August, 1978). After the station was repaired operations continued, but mechanical problems arose early in the spring of 1979 and again in early 1980. These months of sporadic operation caused the salinity to vary dramatically (Norman and Southwick, 1981). Continuous pumping occurred from 1980 to 1985. During the 1980's, however, despite the salt water influx, SAV coverage declined throughout the bay. In 1985, a variable schedule of pumping was set up based on a recommendation from Mann (1984). This intermittent schedule continued for two years, during which the pumping did not decrease the turbidity or increase SAV biomass. In 1986, after 21 years of pumping salt water into the Bay, the water clarity was the lowest in years, according to records dating from 1959 (Norman and Southwick, 1987). No scientific correlation has been found between salinity and turbidity in the water in Back Bay. Ironically, Mann (1984) pointed out that when the pumping discontinued in 1977-78, an increase in water clarity was evident. Moreover, Norman and Southwick noted when salinity was low (in the mid-1970's), there was good water clarity and excellent fishing. These authors found a significant inverse correlation between salinity and

turbidity when salinity was greater than 3.0 ppt. They concluded there were additional factors affecting turbidity, in particular, wind. Davis and Brinson (1983) compiled a comprehensive study of the history of SAV in Currituck Sound and Back Bay and determined that although turbidity may be instrumental in the decline of SAV, there are other components involved. Even though the lack of statistical correlation between clarity and salt water was documented (Mann, 1984), pumping sea water into the bay continued through 1987. In response to a request by Virginia's Department of Game and Inland Fisheries (VDGIF), the city of Virginia Beach ultimately discontinued pumping after 22 years (Norman, 1988).

As mentioned earlier, the watershed surrounding the bay is largely agricultural. There are many drainage ditches interspersed among the fields, which empty into creeks, which in turn flow into the bay. It was suspected that residuals of fertilizers and pesticides could be carried in run-off through this type of system. The Virginia Water Control Board (VWCB) responded to this concern by sampling water from Back Bay at 17 stations, for two decades. Parameters analyzed included nitrite (NO_2), nitrate (NO_3), ammonia (NH_3), total Kjeldahl nitrogen (TKN), phosphorus (total and ortho), total suspended solids (TSS), total organic carbon (TOC), temperature, pH, conductivity, and dissolved oxygen.

In 1986, the VDGIF also started collecting monthly water samples in the mainstem of the bay, and the Back Bay Restoration Foundation (BBRF) sampled the bay's tributaries. Sampling by VDGIF has since been reduced to a quarterly basis, however, BBRF has continued to sample monthly. Although sampling has been relatively extensive during the past two

decades, problems with logistics, sampling and analytical procedures, and financing have resulted in an incomplete data set on Back Bay water quality.

Alden (1989) analyzed this extensive water quality data base by nonparametric trend analysis. There was not enough consistency in the data at the various stations to derive significant conclusions as to long-term trends in the water quality from the early 1970's to the late 1980's. Throughout the 16 year period, Hell Point Creek (HPC) was the only station with enough data to run the trend analysis for statistical significance. Data collections at the other stations revealed only qualitative trends due to the intermittent sampling. However, Alden (1989) did find significance in one of the 6 parameters that could be evaluated at Hell Point Creek: a decrease (7.4%) in ammonia concentrations. The data for three variables (TKN, NH_3, NO_2) were adequate for analysis at 8 sites on spatial and temporal patterns. Of the three variables analyzed statistically, TKN concentrations significantly increased from a mean of 1.14 mg/L to 1.97 mg/L. Elevated TKN concentrations may be related to organic-rich suspended solids in the bay. This correlates with a decrease in the primary productivity in the bay. Other parameters may have also changed, but the data collected does not allow for these statistical calculations. Spatial patterns revealed nutrient source areas were in tributary creeks. These areas contained elevated nitrogen and phosphorus concentrations, while elevated levels of organic-rich suspended solids were found in the main Bay. Both nitrogen and phosphorus concentrations repeatedly exceeded reference levels given by the State.

Pesticides were analyzed at 3 tributary stations in 1983 by the SWCB (Mann, 1984). Water samples were analyzed for 7 insecticides and 14 herbicides. Some herbicides were detected at 2 of the sites, but even

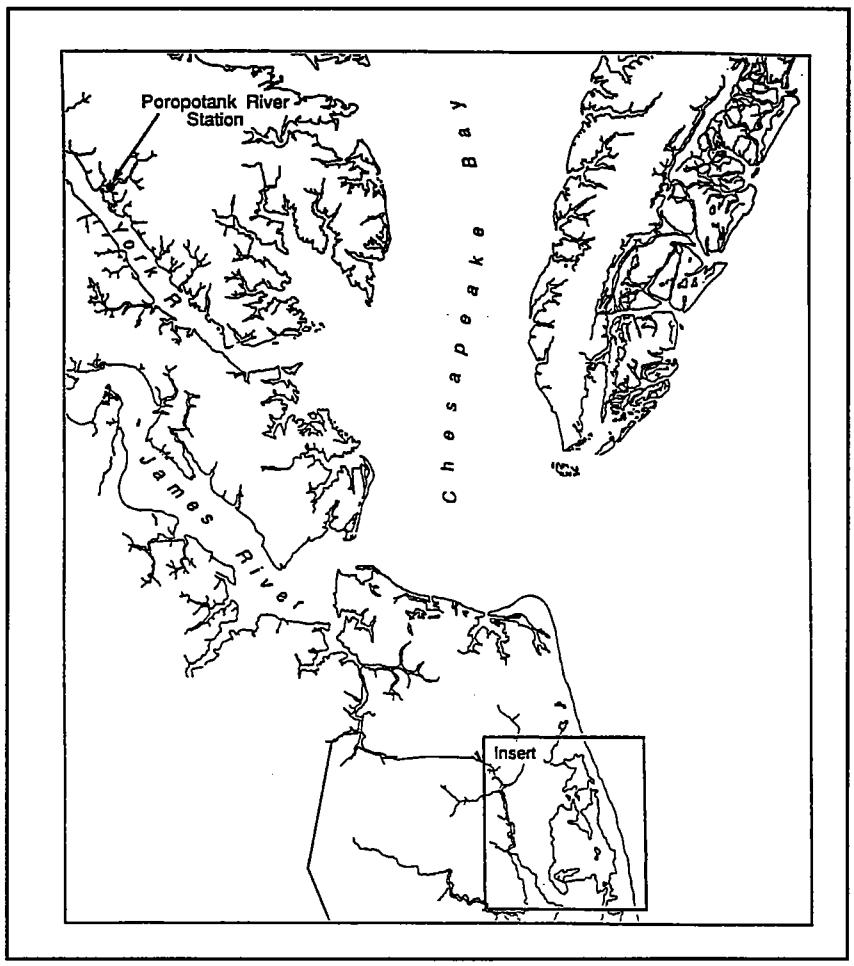
the highest concentration of herbicide (Alachlor, 0.81 µg/L) was considered below phytotoxic levels.

In an earlier unpublished report by Sincock (1966), metals and nutrients were analyzed in water samples. The results indicated that there was no evidence that industry or agriculture was having an adverse effect on the aquatic biota, although they did find elevated levels of copper, iodide, and chromate in the water. In the False Cape State Park Access Study (Department of Conservation and Economic Development, 1976), water was analyzed in 1959 and again in 1962. Salts of chromium were considered elevated, and mercury was found in higher concentrations compared to water samples taken elsewhere. The False Cape State Park Access Study also looked at metals in the sediments, and measured slightly elevated levels of lead (Department of Conservation and Economic Development, 1976). The Department of Conservation and Economic Development concluded that lead concentrations posed no threat to biota in the bay. These early reports on metal analyses are vague, and accuracy is questionable due to the sampling technique and the precision of analytical instruments used 17 years ago.

The U.S. Fish and Wildlife Service (Service) is a steward for natural resources and a major land owner in the Back Bay watershed. Declines in water quality and aquatic vegetation biomass have diminished the quality of habitat for aquatic birds and fish. The bay was once considered a "sportsman's paradise" for both waterfowl and sport fish species (Norman, 1988). In 1927, twenty-five hunting clubs surrounded the bay, while 30 years later there were less than four (Sincock, 1966). Waterfowl numbers throughout the Atlantic flyway have fluctuated, but the number of migratory birds in Back Bay has only declined (Settle and Schwab, 1991).

In this current study, an attempt has been made to quantify inputs of agricultural chemicals into Back Bay and assess their potential toxicity to biota. Since it is reasonable to assume that these and other chemicals can be washed into the bay during storm events, sampling was performed within 24-48 hours following the first significant rainfall subsequent to application of agricultural chemicals, during the spring planting period. During sampling, sediment grabs were taken at the mouths of several tributaries on the western side of Back Bay, as well as two sites in the mainstem of the bay, and one site on the eastern side. As a reference, sediment samples were taken in the Poropotank River, which is known to be relatively non-polluted (Figure 1).

Figure 1. General area map showing the location of Back Bay and the Poropotank River in relation to the Chesapeake Bay. Area labelled "insert" marks the Back Bay study area, which is detailed in Figure 2.



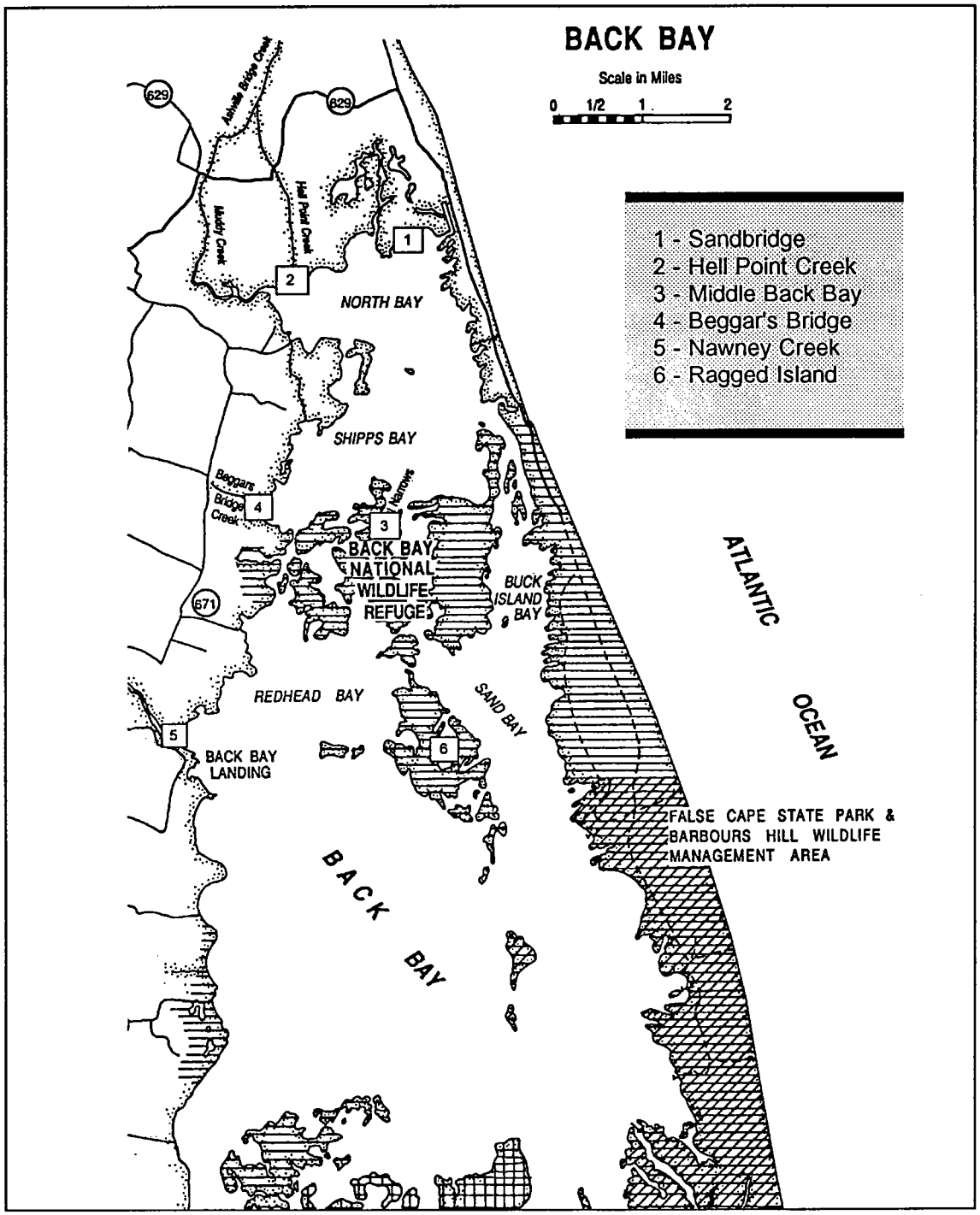
MATERIALS AND METHODS

Field Sampling

Sediment samples were collected from 6 sites in Back Bay: the mouth of Hell Point Creek; mouth of Beggar's Bridge Creek; mouth of Nawney's Creek; mouth of Sandbridge Canal; within Great Narrows (mid-Back Bay reference station), and within an embayment of Ragged Island (southern mid-Back Bay reference station). Sampling stations are shown in Figure 2. Sediment samples were collected by box corer (Wildco, Saginaw, Michigan) from April 29, 1991 to May 1, 1991, with the top 2-3 cm of sediment being skimmed off for use in this study. Because of the considerable distance between sampling sites, only two stations could be sampled per day.

Composite sediment samples (approximately 11.25 L per site) were sieved through a 500 µm sieve and refrigerated until used in chemical analysis or bioassays. The resultant sieved sediment (approximately 10 L per site) was stirred to homogenize and then apportioned into chemically-cleaned, 1 L glass containers. A portion of each sediment sample was brought back to the Service's Virginia Field Office for Microtox testing. Portions were also submitted to the U.S. Fish and Wildlife Service's Cooperative Fish and Wildlife Research Unit at North Carolina State University for use in the Sago Pondweed growth bioassay, and to the Virginia Institute of Marine Science for the amphipod (*Hyalella azteca*) bioassay. Small aliquots were provided to the Patuxent Analytical Control Facility, Patuxent Wildlife Research Center, Laurel, Maryland for chemical analysis. At each sampling site, water temperature, pH, specific conductivity, dissolved oxygen, and redox potential were measured at various depths using a Hydrolab^R probe (Datasonde 3, Hydrolab Corp., Austin, Texas). Hydrolab^R data are shown in Appendix A-1.

Figure 2. Back Bay sampling stations.



Sediment Characterization

Sediment grain size was determined by the wet sieve method for sand content and the pipet method for silt/clay size particles (Folk, 1980). Total volatile solids of the sediments were determined by weighing a volume of sediment before and after incineration (Clesceri, et al., 1989).

Chemical Analysis

Analysis of metals in sediments were performed at the University of Missouri Environmental Trace Substances Research Center, Columbia, Missouri. Metals analyzed and their detection limits are shown in Table 1. Carbamate analysis was performed at the USFWS Patuxent Analytical Control Facility, Laurel, Maryland. Analysis of sediments for organochlorines, polynuclear aromatic hydrocarbons and chlorphenoxy herbicides was performed at the Mississippi State Chemical Laboratory, Mississippi State University. These compounds are listed in Table 2. For quality control, samples were spiked with each element, analyzed, and the percent recovery was determined. Specific methodologies for each type of analysis are included in the data tables (see Appendices A-2 to A-5).

Table 1. Metal analyses of sediment performed at the Missouri Environmental Trace Substances Research Center, Columbia, Missouri.

Metal:	Detection Limit (ppm, dry weight):
Boron	2.0
Barium	0.1
Silver	2.0
Aluminum	3.0
Magnesium	4.0
Manganese	0.2
Copper	0.3
Chromium	1.0
Zinc	0.2
Selenium	20.0
Iron	1.0
Molybdenum	1.0
Arsenic	10.0
Cadmium	0.4
Lead	5.0
Strontium	0.1
Beryllium	0.1
Nickel	1.0
Thallium	6.0
Vanadium	0.4

Table 2. Chemical analyses of sediment performed at the Mississippi State Chemical Laboratory, Mississippi State University.

<u>Organochlorines</u>

- Hexachlorobenzene
- (α, Γ, ß, δ)-Benzenehexachloride
- Heptachlor Epoxide
- (α,Γ)-Chlordane
- Oxychlordane
- (cis, trans)-nonachlor
- PCBs (total)
- o,p'-DDD
- o,p'-DDE
- p,p'-DDD
- p,p'-DDE
- Endrin
- Mirex
- Atrazine
- Alachlor
- Metachlor
- Toxaphene

<u>Polynuclear Aromatic Hydrocarbons (PAHs)</u>

- Anthracene
- Fluoranthrene
- Fluorene
- 1,2-Benzanthracene
- Benzo(b)fluoranthrene
- Benzo(k)fluoranthrene
- Benzo(e)pyrene
- Benzo(a)pyrene
- Benzo(g,h,i)perylene
- Chrysene
- 1,2,5,6-Dibenzanthracene
- Napthalene
- Phenanthrene
- Pyrene

<u>Chlorphenoxy Herbicides</u>

- Dicamba
- Dichlorprop
- 2,4-D
- 2,4-DB
- 2,4,5-T
- Silvex

Microtox[R] Bioassay

An aliquot (approximately 30 mL) of pore water was extracted from sediment samples for subsequent use in the Microtox[R] bioassay using a technique described by Winger (1990). Sediments were considered toxic if they resulted in an EC_{50} ("effective concentration", or the pore water concentration capable of producing a sublethal effect, in this case reduced bacterial photoluminescence, in 50 percent of the population sampled) of less than 100%, and if the upper confidence interval around the EC_{50} was less than 100%.

Sago Pondweed Bioassay

Sediments were placed in clean, 50 mL glass jars that had been rinsed in 10% chlorine bleach and allowed to air dry. The 50 mL jar was filled to two-thirds capacity with the sediment. The sediment was then topped with clean quartz sand (approximately 0.5 to 1.0 cm).

One sago pondweed explant was placed into each jar containing sediments. Sago pondweed was obtained from monoclonal cultures maintained by Steve Ailstock, Anne Arundel Community College, Maryland. Clonal cultures were of a uniform age, and were screened for size uniformity (0.5 to 1.1 g).

The sediment samples with plants were placed individually into 3.8 L glass jars (cleaned and rinsed with 10% chlorine bleach), filled with 3.5 L of reconstituted, moderately hard freshwater (Table 1). These jars were positioned under full spectrum fluorescent lighting (approximately 130 µEinsteins) operating on a 16 hour light/8 hour dark cycle. Aeration of each test chamber was provided by microbore tubing

connected to an air pump operating to produce about 20 pounds of pressure. This resulted in a gentle flow of air to each chamber. The test period for all plants was 26 days.

Sediment samples were available from six potentially contaminated sites and from one reference site (Poropotank River). Nine replicates were used per site. At the time of planting, each plant was gently blotted dry and weighed (initial fresh weight). The remainder of the data was collected at the end of the study. Fresh weights (blotted dry weights), percent change in fresh weight (100*{[W1-W0]/W0}), and oven-dried weights (24h @ 50°C) were measured. Internode and maximum leaf lengths, as well as the number of rhizome tips were also determined.

In order to determine the efficacy of the sago pondweed bioassay, it was necessary to spike certain sediment samples with a known quantity of an herbicide. Since atrazine was initially believed to have the greatest potential for contaminating Back Bay sediments, formulation grade atrazine (Atrazine 4L, Universal Coop., Inc.) was added to a subsample of the reference (Poropotank River) sediment. Sufficient atrazine was added to give a final concentration of approximately 36 ppm in moist sediment.

Amphipod Bioassay

Amphipod bioassays were performed in a series of 22 L aquaria. Each sediment was tested in triplicate. A 1-2 cm layer of sediment was placed in the bottom of each aquarium and overlain with 12 L of freshwater. During set up of the aquaria, triplicate subsamples of sediment samples from each site were taken for grain-size analysis and total organic content.

After a 1 hour settlement period, 100 amphipods (Hyalella azteca) were added to each aquarium. Test animals were purchased from Chesapeake Cultures, Inc. in Gloucester, Virginia. The test animals utilized in these assays were juveniles of uniform age and size.

Water used in the test was dechlorinated tapwater filtered to 1 µm. During the exposure period, test animals were fed twice weekly, as described by Nebeker, et al. (1984). Rabbit food (Purina[R]) was ground with a mortar and pestle and the resultant powder was passed through a 250 µm mesh screen. A portion of this powder (200 mg) was wetted by shaking with 100 mL of dilution water and added to each aquarium. The tanks were examined daily for dead animals and signs of abnormal behavior.

Temperature, dissolved oxygen concentration and pH were measured three times weekly (on Days 0, 3, 6, 8, 10, 14, 17, 20, 22, 24, 27, and 28). Temperature was measured with a stem thermometer. Dissolved oxygen was determined with a YSI Model 57 Oxygen Meter. The pH was measured with an Orion EA920 pH/Ion Meter with a combination pH electrode. Ammonia was measured on Days 0 and 24 using an Orion EA290A pH/Ion Meter with an ammonia gas sensing electrode.

After 28 days, the contents of each aquarium were passed through a 202 µm sieve and the remaining debris, sediment and amphipods rinsed into a glass jar. Replicates from most stations required two sample jars to retain the material. The contents of each jar were preserved in buffered formaldehyde with rose bengal. The stain is selectively absorbed by biota, and thereby facilitates the process of picking amphipods from the sample. All amphipods and other macroinvertebrates were picked from each sample under a dissecting microscope. The adult and juvenile amphipods in each sample were enumerated. In addition,

other macroinvertebrates found were preserved in small vials for later identification. These volunteer organisms, presumably from the original sediment, were not counted.

Statistical Analysis

For the sago pondweed bioassay, one way analysis of variance (ANOVA) was used to test for significant differences in growth characteristics among sediment sampling sites. In all cases, $P \leq 0.05$ was interpreted as being statistically significant.

RESULTS

Sediment Characteristics

The sediments from all stations contained a relatively small percentage of sand and were dominated by clay-sized particles (Table 3). Sandbridge sediment contained the most sand (13.3%). Great Narrows and Nawney's Creek sediment contained 9.3 and 9.7% sand, respectively, and all other stations contained less than 7% sand. The reference stations contained 33% to 69% clay-sized particles, whereas sediments from all other stations contained between 33 and 54% clay-sized particles. The volatile solids content of the sediment was high but uniform at all stations (8 to 17% by weight).

Chemical Analysis

Results of analyses performed on the sediment samples are listed in Appendices A-2 through A-5. With the exception of some metals, concentrations of all analytes were either extremely low or non-detectable. While certain metal concentrations (i.e., aluminum, iron, and magnesium) were measured at elevated concentrations, no toxicological guidelines for interpreting concentrations of these metals in sediment currently exist. Thus, it is difficult to evaluate the significance of the chemical data collected. Relative concentrations of metals at the various sampling sites are shown in Table 4. Absolute concentrations of various metals are shown in Figures 3a through 3e.

Microtox® Bioassay

Toxicity was measured in three of the six sediment samples (Figure 4). Some toxicity was measured in other samples, but had wide confidence intervals that included 100%. These were retested with the 100% bioassay and all were found to have minimal toxicity (confirming the

earlier results and interpretations). Beggar's Bridge sediments appeared to be the most toxic of all sites sampled with a mean EC_{50} of 29%.

Table 3. Physical and chemical characteristics of sediment from sampling stations in Back Bay.

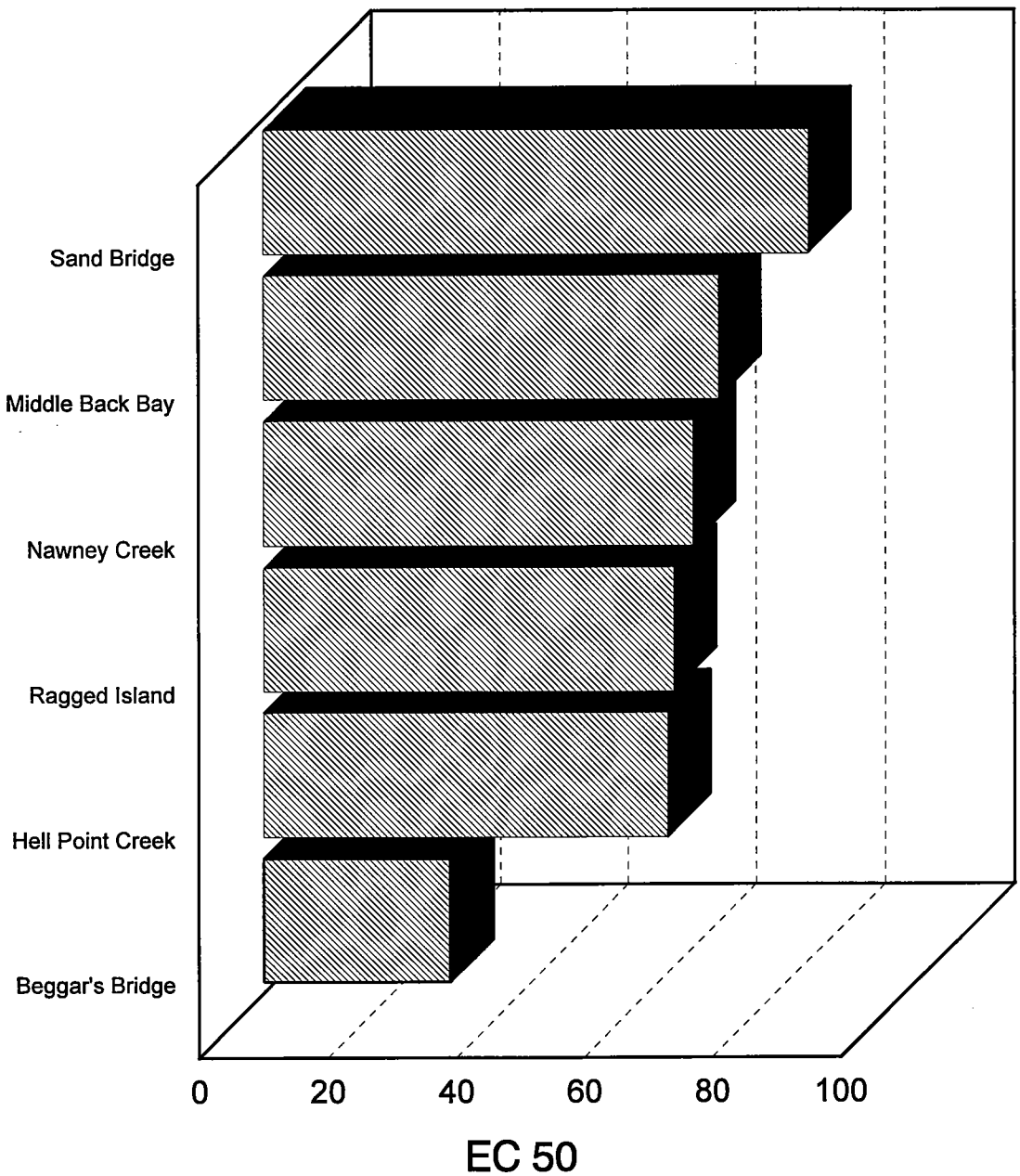
Station	Replicate	%Sand	%Clay	%Silt	%Volatile Solids
Poropotank River	1	6.3	25.4	68.3	12.0
	2	6.5	25.6	67.9	12.0
	3	6.3	24.4	69.3	12.0
Mean		6.4	25.1	68.5	12.0
Ragged Island	1	6.7	61.7	31.6	8.0
	2	6.8	60.5	32.7	8.0
	3	6.7	59.0	34.3	8.0
Mean		6.7	60.4	32.9	8.0
Nawney's Creek	1	9.6	46.7	43.7	12.0
	2	9.8	47.1	43.1	12.0
	3	9.6	46.4	44.0	12.0
Mean		9.7	46.4	43.6	12.0
Sandbridge Canal	1	13.8	54.4	31.8	10.0
	2	13.5	52.2	34.3	10.0
	3	12.6	54.1	33.3	10.0
Mean		13.3	53.6	33.1	10.0
Great Narrows	1	9.7	53.5	36.8	9.0
	2	9.3	53.1	37.6	8.0
	3	8.8	53.5	37.7	9.0
Mean		9.3	53.4	37.4	8.7
Beggar's Bridge	1	5.9	44.7	49.4	17.0
	2	6.9	48.4	44.7	17.0
	3	5.1	45.3	49.6	17.0
Mean		6.0	46.1	47.9	17.0
Hell Point Creek	1	1.9	41.5	56.6	14.0
	2	3.0	44.0	53.0	13.0
	3	2.7	44.6	52.7	13.0
Mean		2.5	43.4	54.1	13.3

Table 4. Relative values of site specific concentrations of metals in Back Bay sediments.

METAL	RELATIVE CONCENTRATION
ALUMINUM:	PKR > HPC > BBR > NCR > MBB > RIR > SDB
ARSENIC:	PKR > BBR > HPC > NCR > MBB > RIR = SDB
BARIUM:	HPC > PKR > BBR > NCR > MBB > RIR > SDB
BERYLLIUM:	PKR > BBR > HPC > NCR > MBB > RIR = SDB
BORON:	PKR > BBR > MBB > RIR > HPC = NCR > SDB
CADMIUM:	PKR = BBR = HPC = NCR = MBB > RIR = SDB
CHROMIUM:	PKR > NCR > HPC > MBB > RIR > SDB > BBR
COPPER:	BBR > PKR > NCR > HPC > SDB > MBB > RIR
IRON:	PKR > BBR > HPC > NCR > MBB > SDB > RIR
MAGNESIUM:	PKR > BBR > NCR > HPC > MBB > RIR > SDB
MANGANESE:	PKR > HPC > BBR > NCR > MBB > RIR > SDB
MOLYBDENUM:	BBR > HPC = NCR > PKR = MBB > RIR = SDB
NICKEL:	PKR > HPC > NCR > MBB > RIR > SDB > BBR
LEAD:	HPC > NCR > BBR > PKR > MBB > SDB > RIR
SELENIUM:	PKR > BBR > NCR > HPC > MBB > RIR > SDB
STRONTIUM:	NCR > PKR > HPC > MBB > BBR > RIR = SDB
SILVER:	BBR = HPC = NCR > PKR > MBB > RIR > SDB
ZINC:	NCR > HPC > MBB > BBR > SDB > RIR

CODES: PKR = Poropotank River, BBR = Beggar's Bridge, HPC = Hell Point Creek, NCR = Nawney Creek, MBB = Middle of Back Bay, RIR = Ragged Island, SDB = Sandbridge

Figure 4. Results of Microtox[R] bioassay for Back Bay sediment pore water. Note: Bars represent EC_{50} values. Low EC_{50} values correspond to high toxicity.



Sago Pondweed Bioassay

Growth characteristics of plants grown in sediments from Back Bay are summarized in Table 5. Fresh weights of plants on the day the experiment was initiated did not differ significantly ($p \leq 0.05$) among sites, and appeared uniformly green and healthy. Fresh weights of plants at the termination of the study showed average increases of 385 to 528% over initial plant weights.

Biomass production, as determined by fresh plant weights and the percent increase in plant weights, did not differ significantly among sediment collection sites. Dry weights of plants grown in Poropotank River sediment was significantly greater than those grown in the sediments from Sandbridge, Hell Point Creek, Beggar's Bridge and Nawney's Creek.

The number of propagative rhizome tips in the plants grown in Poropotank River sediment were significantly greater than the number of tops on plants grown in either Sandbridge or Nawney's Creek sediments. Leaf length for plants grown in sediments from Nawney's Creek were significantly greater than plants grown in Hell Point Creek, Beggar's Bridge, Ragged Island and Poropotank River sediments. There was no statistically significant difference among sites in terms of internode lengths. Sago pondweed growth results are summarized in Table 5.

In the comparison of reference samples that were not spiked and those spiked with atrazine, initial plant weights among groups did not differ significantly. After 26 days of growth, both sediments with and without atrazine added, produced plants that appeared uniformly green and in good health. Plants grown in the atrazine-treated sediment accumulated less biomass, as demonstrated by lower fresh weights, smaller percent biomass increase compared to initial weights, and lower

Table 5. Summary of sago pondweed growth results for Back Bay sampling sites. Sago pondweed growth is compared to growth on a reference sediment (Poropotank River). In the table "No" indicates that there was no significant difference compared to the reference sediment. "Yes" indicates there was a significant difference.

SAMPLING SITE	FINAL FRESH WEIGHT (g)	FINAL DRY WEIGHT (g)	% WEIGHT CHANGE	INTERNODE LENGTH (cm)	# RHIZOME TIPS	LEAF LENGTH
Sandbridge	No	Yes	No	No	Yes	No
Hell Point Cr.	No	Yes	No	No	No	No
Beggar's Brdg.	No	Yes	No	No	No	No
Great Narrows	No	No	No	No	No	No
Nawney's Cr.	No	Yes	No	No	Yes	Yes
Ragged Is.	No	No	No	No	No	No

oven-dried weights (Table 5). The number of rhizome tips and the internode length was significantly lower in the atrazine-treated sediments. However, leaf length was significantly greater for plants grown in the atrazine-treated sediment compared to the reference sediment.

Amphipod Bioassay

The number of adults recovered from each treatment replicate was between 75 and 106 (Table 6). Survival of the parental generation was high, with only a single replicate at one station yielding less than 80 of the 100 individuals introduced. There was no evidence of toxicity in the various samples, based on survival rates. The number of adults bearing eggs was also determined for each sample during the picking process. This measure of response was extremely variable, so no statistically sound conclusions could be drawn.

The number of offspring in each treatment was variable among replicates, even after log(N+1) transformation of the data (Table 6). The geometric mean number of offspring at Nawney's Creek was much higher than that at all other stations (approximately 100/station vs. 20-40/station). Only a minor depression of offspring production was measured in sediments from sampling stations compared to the reference sites (Poropotank River and Ragged Island).

Various other macroinvertebrates were found in the sediment samples from each station (Table 7). Removal of these animals was not quantitative, but the taxa are listed in order of relative abundance in the samples. Universally present were oligochaetes, tendippids, and harpacticoids. In addition to tendippids and odonatid nymphs, there were numerous empty tubes of the types formed by these insects in some samples. Sediment samples from Nawney's Creek contained the fewest non-amphipod specimens.

This may reflect inadequate picking of the sample rather than actual low abundance. The sediments from the Poropotank River contained species characteristic of oligohaline locations in addition to the freshwater species.

Table 6. Number of amphipods as adults, females with eggs, or offspring in marsupium, and number of juveniles in sediment samples from each replicate.

Location/ Replicate	Adults	# Females with Eggs	% Adults with Eggs	Juveniles	Offspring
Poropotank River					
A	75	11	14.7	43	0.57
B	89	33	37.1	6	0.07
C	83	43	51.8	62	0.75
Mean	82.3	29.0	34.5	25.9*	0.46
Ragged Island					
A	90	33	36.7	26	0.29
B	101	30	29.7	28	0.28
C	98	44	44.9	22	0.22
Mean	96.3	35.7	37.1	25.2	0.26
Nawney's Creek					
A	94	34	36.2	152	1.62
B	100	34	34.0	82	0.82
C	92	37	40.2	126	1.37
Mean	95.3	35.0	36.8	116.3	1.27
Sandbridge					
A	106	15	14.2	38	0.36
B	92	19	20.7	36	0.39
C	97	28	28.9	98	1.01
Mean	98.3	20.7	21.2	51.3	0.59
Great Narrows					
A	92	27	29.3	92	1.00
B	102	34	33.3	13	0.13
C	96	43	44.8	26	1.01
Mean	96.7	34.7	35.8	31.8	1.40

Table 6. (continued)

Location/ Replicate	Adults	# Females with Eggs	% Adults with Eggs	Juveniles	Offspring
Beggar's Bridge					
A	94	25	26.6	26	0.28
B	83	2	2.4	14	0.17
C	99	18	18.2	31	0.27
Mean	92.0	15.0	15.7	22.5	0.26
Hell Point Creek					
A	97	15	15.5	41	0.42
B	93	22	23.7	40	0.43
C	89	48	53.9	12	0.13
Mean	93.0	28.3	31.0	27.2	0.33

* mean number of juveniles calculated as the geometric mean (antilog(mean(log(N+1))-1. All other mean are arithmetic means

Table 7. List of macroinvertebrate taxa, in addition to *Hyalella azteca*, found in sediment samples at the end of the bioassay test, listed in order of relative abundance in replicate samples.

Poropotank River:	oligochaetes tendippids pelecypods gastropods (two species) harpacticoids polychaetes ostracods
Nawney's Creek:	oligochaetes tendippids (+ empty tubes) ostracods daphnids
Great Narrows:	oligochaetes nematodes
Hell Point Creek:	oligochaetes tendippids (+ empty tubes) harpacticoids ostracods
Ragged Island:	oligochaetes tendippids harpacticoids daphnids
Sandbridge:	oligochaetes tendippids harpacticoids ostracods
Beggar's Bridge:	oligochaetes harpacticoids nematodes odonate nymphs

DISCUSSION

Based on bioassay measurements of reproduction and survival in the benthic amphipod, Hyalella azteca during this study, the data did not indicate Back Bay sediments were toxic. The parent generation of amphipods exhibited strong survival rates during the test and production of progeny occurred in animals exposed to all sediments.

In this study, the number of females in individual exposure groups was not determined. Assuming half the adults were females (i.e., sex ratio was 1:1), the number of females with eggs ranged from 10 to 100%. The lowest proportion of oviparous females was observed in a population exposed to Beggar's Bridge sediment. However, there was no evidence of reduced offspring production in this replicate.

The high production of offspring in populations exposed to sediment from Nawney's Creek cannot be explained based on available data. The sediment characteristics at this site were average. The organic content of the sediment was not considered to be elevated, so food availability was presumably similar to other sediments tested. The number of oviparous adults was within a normal range at the end of the exposure.

These data demonstrate that the sediments from all stations are not exerting toxic effects to Hyalella. These results may be due to insufficient amounts of pesticides entering the system to have a demonstrable toxic effect. In addition, the time between spraying, rainfall and sediment collection, may have been inappropriate to detect what is believed to be an ephemeral event. If the time was insufficient for significant transport and accumulation of pesticides in the sediments at the moths of the creeks, this would have influenced the

pesticide residue concentration in the test sediment samples. If the time was too long, the pesticides may have had time to undergo a chemical transformation before sampling.

The non-amphipod species of macroinvertebrates present in the samples were probably in the sediments at the start of the test. Amphipod cultures were free of other organisms except ostracods, and perhaps harpacticoid copepods. Therefore, most species observed could not have come from the cultures. Reference sediment from the Poropotank River included several organisms not found in other sediments. Several species in this sediment were clearly of estuarine origin. This is consistent with the collection location. The oligochaetes, tendippids and harpacticoids are taxa that one would expect to find at any of the locations sampled.

There were few differences measured among plants grown in sediments collected at the various sites in Back Bay. Larger oven dried weights for plants grown in the reference sediment, compared to sediments from Sandbridge, Hell Point Creek, Beggar's Bridge and Nawney's Creek, are difficult to explain due to the similarity of the fresh weight data among sites. However, differences in mineral composition among sediments could result in mineral accumulation on plant surfaces via evapotranspiration. There may have been less variability in oven-dried plant weights if these plants had been rinsed in a weak acid to remove mineral deposits prior to being placed in a drying oven.

Although atrazine was believed to be the primary pesticide influencing the growth rate of SAV in Back Bay, the atrazine-spiked sediments did not demonstrate significant decreases in growth rates of the sago pond weed in the bioassay tests. This data suggests that once atrazine is

sorbed to sediment particles it becomes relatively unavailable to the biota. This may explain why the other bioassays were unable to measure significant differences among sites.

CONCLUSIONS AND RECOMMENDATIONS

The results of this study indicate that toxicity to biota in Back Bay, associated with sediment contamination, is minimal. However, given the ephemeral nature of many of the chemicals used in agricultural practices, this result was not entirely unexpected. As mentioned earlier, it is possible that these pesticides could have chemically broken down prior to the rain event monitored, or the pesticides could have been flushed out of the system entirely during heavy rains and never accumulated in the sediments of Back Bay. Lastly, the pesticide atrazine, which was the primary chemical of concern, may simply be unavailable to biota once it is sorbed to sediment particles. In summary, it seems reasonable at this time to conclude that sediment-associated toxicity is not a major threat to SAV populations in Back Bay.

Since direct toxicity of agricultural chemicals may be ruled out as a causative factor in the decline of SAV in Back Bay, the question still remains as to what is actually causing this decline. Numerous studies in the past have pointed to excessive turbidity in the bay caused by human activities in the watershed. The U.S. Fish and Wildlife Service is currently conducting a comprehensive storm water monitoring plan which will allow us to assess the relative impacts of both agricultural and urban contributions to this turbidity. Further, it is anticipated that this storm water study will also allow the Service to assess the efficacy of various best management practices reducing inputs of topsoil and nutrients into the bay.

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APPENDICES

APPENDIX 1
Hydrolab[R] Data

	SAMPLING SITE						
PARAMETER	SDB	HPC	BBR	MBB	NCR	RIR	PKR
TEMP (°C)	23.8	25.4	27.3	21.5	22.4	22.0	22.6
pH	7.4	7.4	6.8	7.8	6.6	7.6	7.3
SALINITY (PPT)	0	0	0	0.2	0.2	0.3	4.3
D.O. (% SAT.)	102.1	103.5	105.3	105.8	74.3	103.7	82.9
D.O. (mg/L)	8.6	8.5	8.3	9.1	6.4	9.0	7.0
REDOX (VOLTS)	0.38	0.37	0.37	0.34	0.38	0.35	0.37

Hydrolab data for sampling sites used in Back Bay.

APPENDIX 2
Sediment Characteristics

ANALYTICAL REPORT (6-2)
Soil/Sediment Parameters - CATALOG: 5070009

ıb Name: ETSR 10/15/91 P.O.#: 85800-1-1447

; TVS Method Code (A):

; TOC Method Code (B): 006 018

; SAND/SILT/CLAY Method Code (C):

ımple ımber	(A) Percent TVS	(B) Percent TOC	(C) Particle Size % Sand	% Silt	% Clay	Lab Sample Number
RSEDOA	-	7.9	-	-	-	1051347
CSEDOA	-	4.6	-	-	-	1051348
CSEDIA	-	6.2	-	-	-	1051350
BSEDOA	-	4.4	-	-	-	1051351
RSEDOA	-	6.	-	-	-	1051353
RSEDOA	-	3.9	-	-	-	1051355
BSEDOA	-	5.1	-	-	-	1051356

ANALYTICAL REPORT (6-1)
Weight, % Moisture, % Lipid - CATALOG: 5070009

Lab Name: ETSR 10/15/91 P.O.#: 85800-1-1447

% Moisture Method Code (A): 006 005

% Lipid Method Code (B):

Sample Number	Sample Matrix	Sample Weight (g)	(A) Percent Moisture	(B) Percent Lipid	Lab Sample Number
BBRSEDOA	Sediments	234.50	82.	-	1051347
FSCSEDOA	Sediments	261.60	77.4	-	1051348
IPCSEDIA	Sediments	145.90	79.	-	1051350
MBBSEDOA	Sediments	251.70	73.7	-	1051351
NCRSEDOA	Sediments	243.80	79.3	-	1051353
RIRSEDOA	Sediments	263.90	69.3	-	1051355
SDBSEDOA	Sediments	234.70	68.8	-	1051356

APPENDIX 3
Metal Concentrations in Back Bay Sediments

APPENDIX 4

Concentrations of Organochlorines, Polynuclear Aromatic Hydrocarbons, and chlorphenoxy acid herbicides in Back Bay sediments

MISSISSIPPI STATE UNIVERSITY
MISSISSIPPI STATE CHEMICAL LABORATORY
BOX CR
MISS. STATE, MS 39762
REPORT FORM
USDI/FWS

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 85800-1-1448

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

ORGANOCHLORINES

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	BBRSEDOA	FSCSEDOA	HPCSEDOA	MBBSEDOA	NCRSEDOA	RIRSEDOA	SDBSEDOA
LAB #	810014	810015	810016	810017	810018	810019	810020
MATRIX	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment
COMPOUND							
HCB	ND*	ND	ND	ND	ND	ND	ND
α-BHC	ND	ND	ND	ND	ND	ND	ND
γ-BHC	ND	ND	ND	ND	ND	ND	ND
β-BHC	ND	ND	ND	ND	ND	ND	ND
δ-BHC	ND	ND	ND	ND	ND	ND	ND
Oxychlordane	ND	ND	ND	ND	ND	ND	ND
Hept. Epox.	ND	ND	ND	ND	ND	ND	ND
γ-Chlordane	ND	ND	ND	ND	ND	ND	ND
t-Nonachlor	ND	ND	ND	ND	ND	ND	ND
Toxaphene	ND	ND	ND	ND	ND	ND	ND
PCB's (total)	ND	ND	ND	ND	ND	ND	ND
o, p'-DDE	ND	ND	ND	ND	ND	ND	ND
α-Chlordane	ND	ND	ND	ND	ND	ND	ND
p, p'-DDE	ND	ND	ND	ND	ND	ND	ND
Dieldrin	ND	ND	ND	ND	ND	ND	ND
o, p'-DDD	ND	ND	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND
cis-nonachlor	ND	ND	ND	ND	ND	ND	ND
o, p'-DDT	ND	ND	ND	ND	ND	ND	ND
p, p'-DDD	ND	ND	ND	ND	ND	ND	ND
p, p'-DDT	ND	ND	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	ND	ND	ND
OTHER:							
WEIGHT (g)	334	251	240	325	249	339	336
MOISTURE (%)	83.0	75.2	79.4	73.2	81.0	71.6	70.6
LIPID (%)	-	-	-	-	-	-	-

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Etc. 0.05 for Toxaphene and PCBs.
For Water, LLD= 0.005 ppm for OCs, Tox , PCBs.
*ND = None Detected
**Spike = ppm for
***NS = Not Spiked
= Confirmed by GC/Mass Spectrometry

Larry Lane
Signature

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 85800-1-1448

MISSISSIPPI STATE UNIVERSITY
MISSISSIPPI STATE CHEMICAL LABORATORY
BOX CR
MISS. STATE, MS 39762
REPORT FORM
USDI/FWS

ORGANOCHLORINES

Date P.O. Recd	04/15/91
Date Spls Recd	05/14/91
Queue Date	05/14/91

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	Blank	Matrix Blank	Spike**	% Recovery			
LAB #	810021	for	810022				
MATRIX	Reagent	Sediment	Sediment				
COMPOUND							
HCB	ND*	ND	0.030	75			
α-BHC	ND	ND	NS***				
γ-BHC	ND	ND	0.041	103			
β-BHC	ND	ND	0.042	105			
δ-BHC	ND	ND	NS				
Oxychlordane	ND	ND	0.037	93			
Hept. Epox.	ND	ND	0.040	100			
γ-Chlordane	ND	ND	NS				
t-Nonachlor	ND	ND	0.038	95			
Toxaphene	ND	ND	NS				
PCB's (total)	ND	ND	NS				
o, p'-DDE	ND	ND	0.042	105			
α-Chlordane	ND	ND	0.040	100			
p, p'-DDE	ND	ND	0.040	100			
Dieldrin	ND	ND	0.035	88			
o, p'-DDD	ND	ND	NS				
Endrin	ND	ND	0.038	95			
cis-nonachlor	ND	ND	0.039	98			
o, p'-DDT	ND	ND	0.041	103			
p, p'-DDD	ND	ND	0.042	105			
p, p'-DDT	ND	ND	0.041	103			
Mirex	ND	0.01	0.038	95			
OTHER:							
WEIGHT (g)	-	-	-				
MOISTURE (%)	-	50.0	50.0				
LIPID (%)	-	-	-				

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Etc. 0.05 for Toxaphene and PCBs.
For Water, LLD= 0.005 ppm for OCs, Tox , PCBs.
*ND = None Detected
**Spike = 0.040 ppm for Sediment.
***NS = Not Spiked
= Confirmed by GC/Mass Spectrometry

Larry Lane
Signature

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 85800-1-1448

MISSISSIPPI STATE UNIVERSITY
MISSISSIPPI STATE CHEMICAL LABORATORY
BOX CR
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REPORT FORM
USDI/FWS

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

ORGANOCHLORINES (SUPPLEMENTAL)

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	BBRSEDOA	FSCSEDOA	HPCSEDOA	MBBSEDOA	NCRSEDOA	RIRSEDOA	SDBSEDOA
LAB #	810014	810015	810016	810017	810018	810019	810020
MATRIX	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment
COMPOUND							
Atrazine	ND*	ND	ND	ND	ND	ND	ND
Alachlor	ND	ND	ND	ND	ND	ND	ND
Metalochlor	ND	ND	ND	ND	ND	ND	ND
OTHER:							
WEIGHT (g)	334	251	240	325	249	339	336
MOISTURE (%)	83.0	75.2	79.4	73.2	81.0	71.6	70.6
LIPID (%)	-	-	-	-	-	-	-

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Etc. 0.05 for Toxaphene and PCB
For Water, LLD= 0.005 ppm for OCs, Tox , PCBs.
**Spike = ppm for
= Confirmed by GC/Mass Spectrometry
*ND = None Detected
***NS = Not Spiked

Larry Lane
Signature

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REPORT FORM
USDI/FWS

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 858000-1-1448

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

POLYNUCLEAR AROMATIC HYDROCARBONS

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	BEGGARS BRIDGE BBRSEDOA	ARTIFICIAL SEDIMENT FSCSEDOA	HELL POINT CREEK HPCSEDOA	MID-BACK BAY MBBSEDOA	NANNEY CREEK NCRSEDOA	RAGGED ISLAND RIRSEDOA	SANDBRIDGE SDBSEDOA
LAB #	810014	810015	810016	810017	810018	810019	810020
MATRIX	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment
COMPOUND							
napthalene	ND*	ND	ND	ND	ND	ND	ND
fluorene	ND	ND	ND	ND	ND	ND	ND
phenanthrene	ND	0.03	0.01	ND	0.01	ND	0.01
anthracene	ND	ND	ND	ND	ND	ND	ND
fluoranthrene	ND	0.03	0.01	0.01	0.02	0.01	ND
pyrene	ND	0.04	0.01	0.01	0.01	ND	ND
1,2-benzanthracene	ND	0.01	ND	ND	0.01	ND	ND
chrysene	0.01	0.01	ND	ND	ND	ND	ND
benzo(b)fluoranthrene	ND	0.01	0.01	ND	0.01	ND	ND
benzo(k)fluoranthrene	ND	ND	ND	ND	ND	ND	ND
benzo(e)pyrene	ND	0.01	ND	ND	0.01	ND	ND
benzo(a)pyrene	ND	0.01	ND	ND	ND	ND	ND
1,2,5,6-dibenzanthracene	ND	ND	ND	ND	ND	ND	ND
benzo(g,h,i)perylene	ND	ND	ND	ND	ND	ND	ND
WEIGHT (g)	334	251	240	325	249	339	336
MOISTURE (%)	83.0	75.2	79.4	73.2	81.0	71.6	70.6
LIPID (%)	-	-	-	-	-	-	-

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Sediment, etc.
LLD = 0.005 ppm for Water
*ND = None Detected
**Spike = ____ ppm for _____
***NS = Not Spiked
* = Confirmed by GC/Mass Spectrometry

Larry Lane
Signature

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BOX CR
MISSISSIPPI STATE, MS 39762

REPORT FORM
USDI/FWS

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 858000-1-1448

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

POLYNUCLEAR AROMATIC HYDROCARBONS

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	Blank	Matrix Blank	Spike**	% Recovery			
LAB #	810021	for	810022				
MATRIX	Reagent	Sediment	Sediment				
COMPOUND							
napthalene	ND*	ND	0.058	58			
fluorene	ND	ND	0.085	85			
phenanthrene	ND	ND	0.094	94			
anthracene	ND	ND	0.097	97			
fluoranthrene	ND	ND	0.11	110			
pyrene	ND	ND	0.092	92			
1,2-benzanthracene	ND	ND	0.084	84			
chrysene	ND	ND	0.084	84			
benzo(b)fluoranthrene	ND	ND	0.085	85			
benzo(k)fluoranthrene	ND	ND	0.072	72			
benzo(e)pyrene	ND	ND	0.082	82			
benzo(a)pyrene	ND	ND	0.089	89			
1,2,5,6-dibenzanthracene	ND	ND	0.059	59			
benzo(g,h,i)perylene	ND	ND	0.067	67			
WEIGHT (g)	-	-	-				
MOISTURE (%)	-	50.0	50.0				
LIPID (%)	-	-	-				

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Sediment, etc.
LLD = 0.005 ppm for Water
*ND = None Detected
**Spike = 0.10 ppm for Sediment.
***NS = Not Spiked
= Confirmed by GC/Mass Spectrometry

Larry Lane
Signature

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SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 85800-1-1448

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

ORGANOCHLORINES (SUPPLEMENTAL)

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	Blank	Matrix Blank	Spike**	% Recovery			
LAB #	810021	for	810022				
MATRIX	Reagent	Sediment	Sediment				
COMPOUND							
Atrazine	ND*	ND	0.10	100			
Alachlor	ND	ND	0.10	100			
Metalochlor	ND	ND	0.10	100			
OTHER:							
WEIGHT (g)	-	-	-				
MOISTURE (%)	-	50.0	50.0				
LIPID (%)	-	-	-				

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Etc. 0.05 for Toxaphene and PCB
For Water, LLD= 0.005 ppm for OCs, Tox , PCBs.
**Spike = 0.10 ppm for Sediment.
= Confirmed by GC/Mass Spectrometry
*ND = None Detected
***NS = Not Spiked

Larry Lane
Signature

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BOX CR
MISSISSIPPI STATE, MS 39762
REPORT FORM
USDI/FWS

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 85800-1-1448

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

CHLOROPHENOXY ACID HERBICIDES

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	BBRSEDOA	FSCSEDOA	HPCSEDOA	MBBSEDOA	NCRSEDOA	RIRSEDOA	SDBSEDOA
LAB #	810014	810015	810016	810017	810018	810019	810020
MATRIX	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment	Soil/ Sediment
COMPOUND							
Dicamba	ND*	ND	ND	ND	ND	ND	ND
Dichlorprop	ND	ND	ND	ND	ND	ND	ND
2,4-D	ND	ND	ND	ND	ND	ND	ND
Silvex	ND	ND	ND	ND	ND	ND	ND
2,4,5-T	ND	ND	ND	ND	ND	ND	ND
2,4-DB	ND	ND	ND	ND	ND	ND	ND
OTHER:							
WEIGHT (g)	334	251	240	325	249	339	336
MOISTURE (%)	83.0	75.2	79.4	73.2	81.0	71.6	70.6
LIPID (%)	-	-	-	-	-	-	-

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Etc. 0.05 for Toxaphene and PCBs
For Water, LLD= 0.005 ppm for OCs, Tox , PCBs.
**Spike = ppm for
= Confirmed by GC/Mass Spectrometry
*ND = None Detected
***NS = Not Spiked

Larry Lane
Signature

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MISSISSIPPI STATE CHEMICAL LABORATORY
BOX CR
MISSISSIPPI STATE, MS 39762
REPORT FORM
USDI/FWS

SAMPLE TYPE: Soil/ Sediment

CAT NO. 5070005
REG.ID #: 5104
ORDER NO. 85800-1-1448

Date P.O. Recd 04/15/91
Date Spls Recd 05/14/91
Queue Date 05/14/91

CHLOROPHENOXY ACID HERBICIDES

PARTS PER MILLION AS RECEIVED (WET WT)

FWS #	Blank	Matrix Blank	Spike**	% Recovery			
LAB #	810021	for	810022				
MATRIX	Reagent	Sediment	Sediment				
COMPOUND							
Dicamba	ND*	ND	0.096	96			
Dichlorprop	ND	ND	0.081	81			
2,4-D	ND	ND	0.084	84			
Silvex	ND	ND	0.092	92			
2,4,5-T	ND	ND	0.078	78			
2,4-DB	ND	ND	0.10	100			
OTHER:							
WEIGHT (g)	-	-	-				
MOISTURE (%)	-	50.0	50.0				
LIPID (%)	-	-	-				

Lower Level of Detection = 0.01 ppm for Tissue, Soil, Etc. 0.05 for Toxaphene and PCBs
For Water, LLD= 0.005 ppm for OCs, Tox , PCBs.
**Spike = 0.10 ppm for Sediment.
= Confirmed by GC/Mass Spectrometry
*ND = None Detected
***NS = Not Spiked

Larry Lane
Signature

UNKNOWN COMPONENTS - PAH FRACTION

(RRT) - RETENTION TIME RELATIVE TO PHENANTHRENE
(PPM) - PARTS PRE MILLION BASED ON PHENANTHRENE RESPONSE FACTOR

Catalog: 5070005
Reg.ID #: 5104
Order: 85800-1-1448

RECALC
TITLE: BBRSEDOA 16:43 23 MAY 91

CHANNEL NO: 3 SAMPLE: 45037 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
1		0.14	26.586	36170	1.34	VV
TOTALS:		0.14		36170		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND

RECALC
TITLE: FSCSEDOA 18:00 23 MAY 91

CHANNEL NO: 3 SAMPLE: 45038 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
TOTALS:		0.00		0		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND
NO PEAKS

RECALC
TITLE: HPCSEDOA 19:15 23 MAY 91

CHANNEL NO: 3 SAMPLE: 45039 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
TOTALS:		0.00		0		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND
NO PEAKS

RECALC
TITLE: MBBSEDOA 20:35 23 MAY 91

CHANNEL NO: 3 SAMPLE: 45040 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
1		0.21	34.229	54756	1.73	BV
TOTALS:		0.21		54756		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND

RECALC
TITLE:

NCRSEDOA

21:53 23 MAY 91

CHANNEL NO: 3 SAMPLE: 45041 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
1		0.20	28.796	52888	1.45	BV
TOTALS:		0.20		52888		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND

RECALC
TITLE:

RIRSEDOA

23:11 23 MAY 91

CHANNEL NO: 3 SAMPLE: 45042 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
TOTALS:		0.00		0		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND
NO PEAKS

RECALC
TITLE:

SDB SEDOA

0:28 24 MAY 91

CHANNEL NO: 3 SAMPLE: 45043 PAH METHOD: PAH

PEAK NO	PEAK NAME	RESULT PPM	TIME (MIN)	AREA COUNTS	RRT	SEP CODE
TOTALS:		0.00		0		

DIVISOR: 25.0000 MULTIPLIER: 1.00000

ERRORS:
REL RETEN PEAK NOT FOUND
NO PEAKS

Method 8. Organochlorine Pesticides, Aliphatic and Polynuclear Aromatic Hydrocarbons, and Chlorophenoxy Acid Herbicides in Soil and Sediment

1. Weigh 20 g soil into a PRQ centrifuge bottle. (Add 10 ml PRQ H_2O to dry samples) Adjust pH to ≤ 2 with PRQ 12N sulfuric aid (about 1 ml). Add 50 ml acetone and shake 6 times over a one and one-half hour period (about every 15 mins.). Add 50 ml of a 1:1 petroleum ether/ ethyl ether mixture and repeat shaking. Centrifuge and decant liquid into a 500 ml separatory funnel containing 200 ml PRQ water. Re-extract soil by shaking one minute with 50 ml 1:1 PE:EtoEt (may need to add 10 ml H_2O & adjust to pH ≤ 2), then centrifuge and decant liquid into sep. funnel.
2. Using PRQ 6N KOH (5 ml), adjust contents of sep. funnel to pH ≥ 12. Shake vigorously 2 min, then allow to stand 30 min. with intermittent shaking. Drain water layer and reserve ether layer. Re-extract H_2O layer with 100 ml 1:1 PE:EtoEt. Cap and reserve combined ether extracts.(This contains organochlorine pesticides, aliphatic and polynuclear aromatic hydrocarbons.)
3. Adjust aqueous layer to pH ≤ 2 using 3 ml of PRQ 12 N sulfuric acid and extract with 100 ml 1:1 PE:EtoEt. Reserve this extract and re-extract H_2O with 100 ml 1:1 PE:EtoEt. Combine extracts (these extracts contain chlorophenoxy acid herbicides).
4. Concentrate acid and basic extracts with Kuderna-Danish evaporators and reduce volume to adequate size for column clean-up.
5. Column Clean-up:

   * BASIC FRACTION (N/P and Organochlorine pesticides, Aliphatic and Polynuclear aromatic hydrocarbons) - adjust sample extract to exact volume and remove an appropriate aliquot for column clean-up techniques specific to analyte; for pesticides use Mini-florisil (described in Method 2), for hydrocarbons use 1% deactivated silica

gel (described in Method 4).

* ACID FRACTION (Chlorophenoxy acid herbicides) -

Derivitization: Reduce sample volume to approximately 0.5ml and ethylate using diazoethane (15 min.). Exchange to hexane (N-EVAP) and reduce volume to 0.2ml.

Column clean-up: Place 2.0g of 1% deactivated silica gel in a 7mm i.d. chromatography column (#22 Kontes). Top with 1cm Na_2SO_4 and prewet column with 10ml hexane. Collect sample eluents in three fractions as follows:

Fraction A: add sample and rinse container with two 0.5ml washes of 20% benzene in hexane. Elute with 9ml of the same solution.(Contains PCP.)

Fraction B: add 10ml 40% benzene in hexane. Add 10ml 60% benzene in hexane.(Contains Dalapon, PNP, Silvex, Dinoseb, portion of Dicamba.)

Fraction C: add 10ml 80% benzene in hexane. Add 10ml 100% benzene.(Contains remaining Dicamba, Dichlorprop, 2,4-D, 2,4,5-T, 2,4-DB, Bentazon, Blazer.)

[Reference for column clean-up for acid herbicides:
Shafik, T. A.,H. C. Sullivan, H. R. Enos, 1973." Multiresidue Procedure for Halo- and Nitrophenols. Measurement of Exposure to Biodegradable Pesticides Yielding These Compounds as Metabolites." J. Agr. Food Chem. 21:295-298.]

Elution Profiles for Florisil, Silica Gel and Silicic Acid Column Separations

A. Florisil Column:

1. <u>Fraction I</u> (6% ethyl ether containing 2% ethanol, 94% petroleum ether)

   HCB, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, oxychlordane, heptachlor epoxide, gamma-chlordane, trans-nonachlor, toxaphene, PCB's, o,p'-DDE, alpha-Chlordane, p,p'-DDE, p,p'-DDT, cis-nonachlor, o,p'-DDT, p,p'-DDD, p,p'-DDT, mirex, dicofol, endosulfan I (Split with FII).

2. <u>Fraction II</u> (15% ethyl ether containing 2% ethanol, 85% petroleum ether)

   dieldrin, endrin, dacthal, endosulfan I (split with FI), endosulfan II (split with FIII), endosulfan sulfate (split with FIII).

3. <u>Fraction III</u> (50% ethyl ether containing 2% ethanol, 50% petroleum ether)

   endosulfan II (split with FII), endosulfan sulfate (split with FII), malathion.

B. Florisil Mini-Column:

1. Fraction I (12 ml hexane followed by 12 ml 1% methanol in hexane)

   HCB, gamma-BHC (25%), alpha-BHC (splits with FII), trans-nonachlor, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD (splits with FII), o,p'-DDT, p,p'-DDT, mirex, cis-nonachlor, cis-chlordane, trans-chlordane, PCB's, Photomirex and derivatives.

2. Fraction II (24 ml 1% methanol in hexane)

   gamma BHC (75%), beta-BHC, alpha-BHC (splits with FI), delta-BHC, oxychlordane, heptachlor epoxide, toxaphene, dicofol, dacthal, endosulfan I, endosulfan II, endosulfan sulfate, octachlorostyrene, Kepone (with additional 12mls 1% methanol in hexane).

C. Silica Gel:

1. SG Fraction I (100 ml petroleum ether)

   n-dodecane, n-tridecane, n-tetradecane, ocylcyclohexane, n-pentadecane, nonycyclohexane, n-hexadecane, n-heptadecane, pristane, n-octadecane, phytane, n-nonadecane, n-eicosane.

2. SG Fraction II (100 ml 40% methylene chloride in petroleum ether followed by 50 ml methylene chloride)

   napthalene, fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, 1,2-benzanthracene, chrysene, benzo [b] fluoranthrene, benzo [k] fluoranthrene, benzo [e] pyrene, benzo [a] pyrene, 1,2:5,6-dibenzanthracene, benzo

[g,h,i] perylene.

D. Silicic Acid:

1. <u>SA Fraction I</u> (20 ml petroleum ether)

   HCB, mirex

2. <u>SA Fraction II</u> (100ml petroleum ether)

   PCB's, p,p'-DDE (splits with SA III)

3. <u>SA Fraction III</u> (20 ml mixed solvent: 1% acetonitrile, 80% methylene chloride, 19% hexane)

   alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, oxychlordane, heptachlor epoxide, gamma-chlordane, trans-chlordane, toxaphene, o,p'-DDE, alpha-chlordane, p,p'-DDE (splits with SAII), o,p'-DDT, cis-nonachlor, o,p'-DDT, p,p'-DDD, p,p'-DDT, dicofol.

APPENDIX 5

Concentrations of Carbamate Insecticides in the Sediments of Back Bay

Figure 3a. Concentrations of metals in the sediments of back Bay (ppm dry wt.)

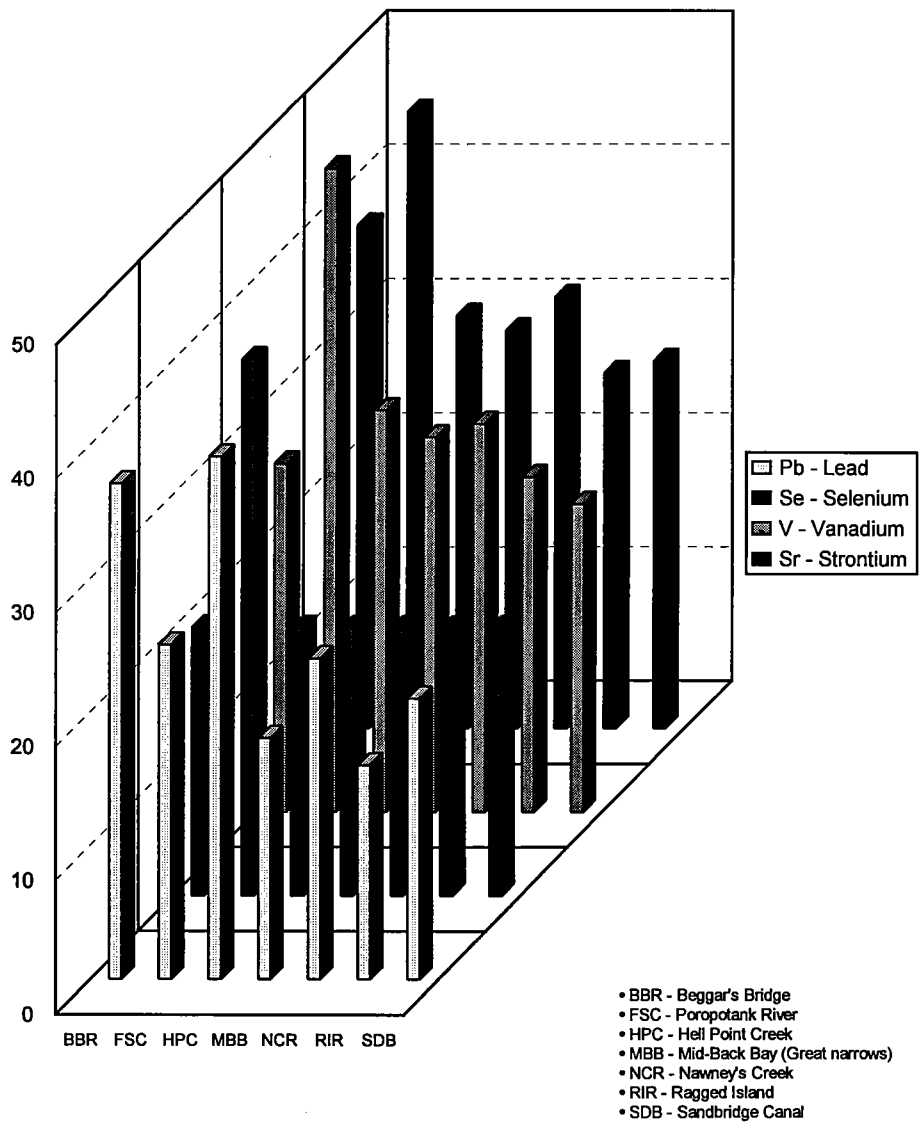


Figure 3b. Concentrations of metals in the sediments of Back Bay (ppm dry wt.)

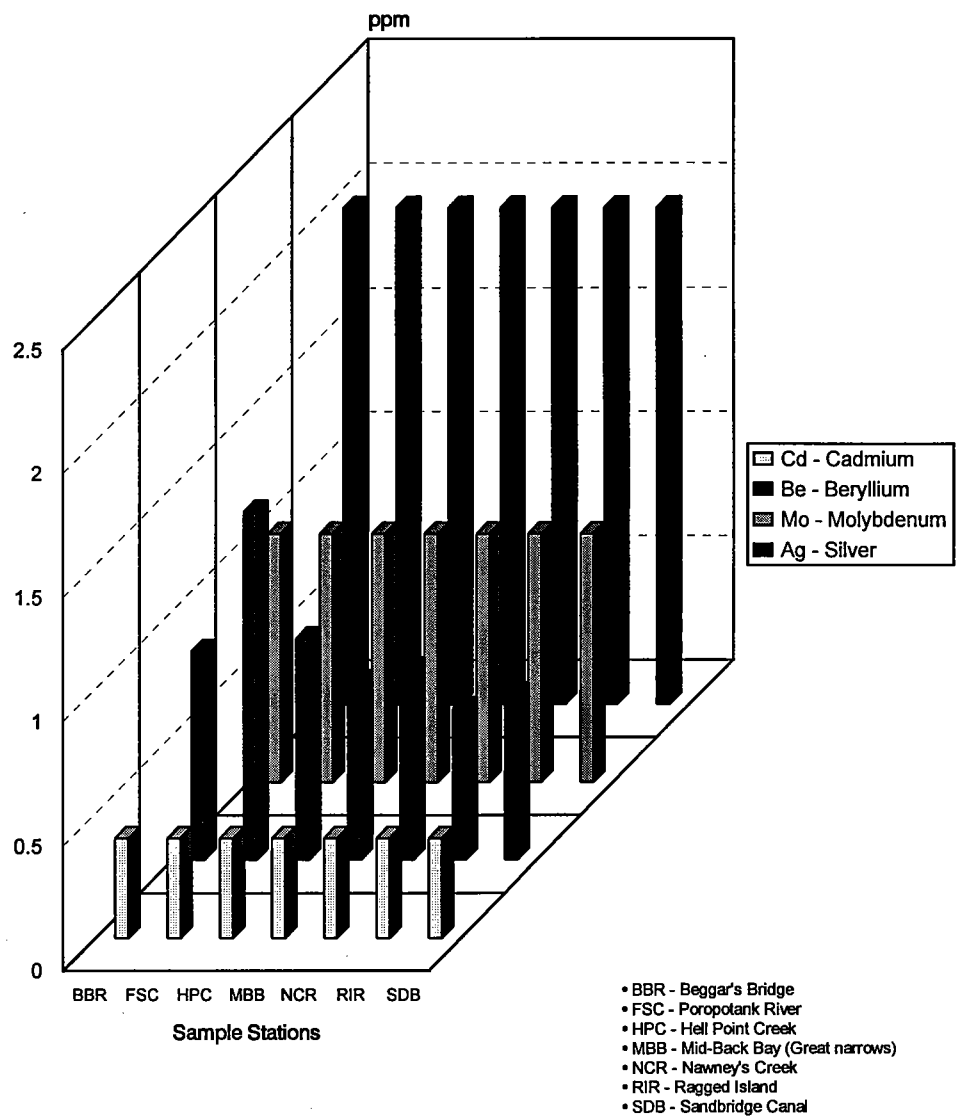


Figure 3c. Concentrations of metals in the sediments of Back Bay (ppm dry wt.)

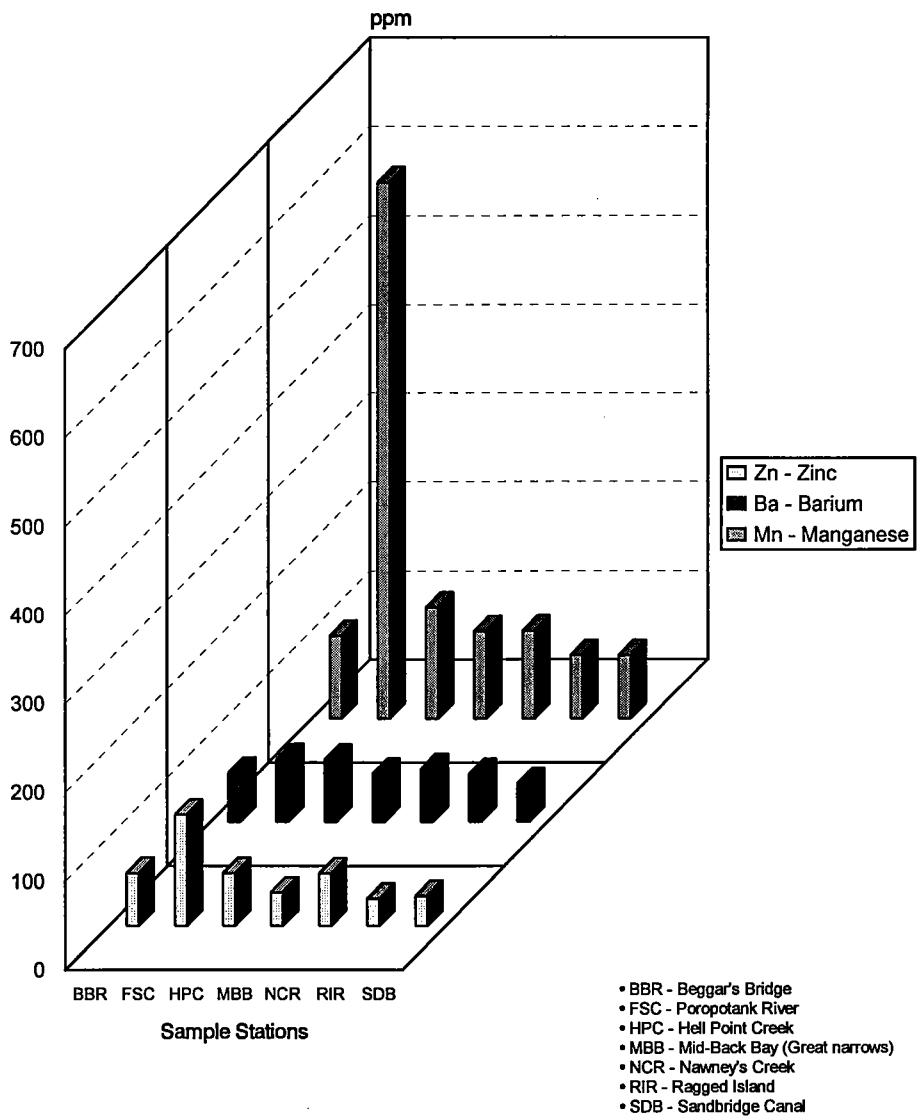


Figure 3d. Concentrations of metals in the sediments of Back Bay (ppm dry wt.)

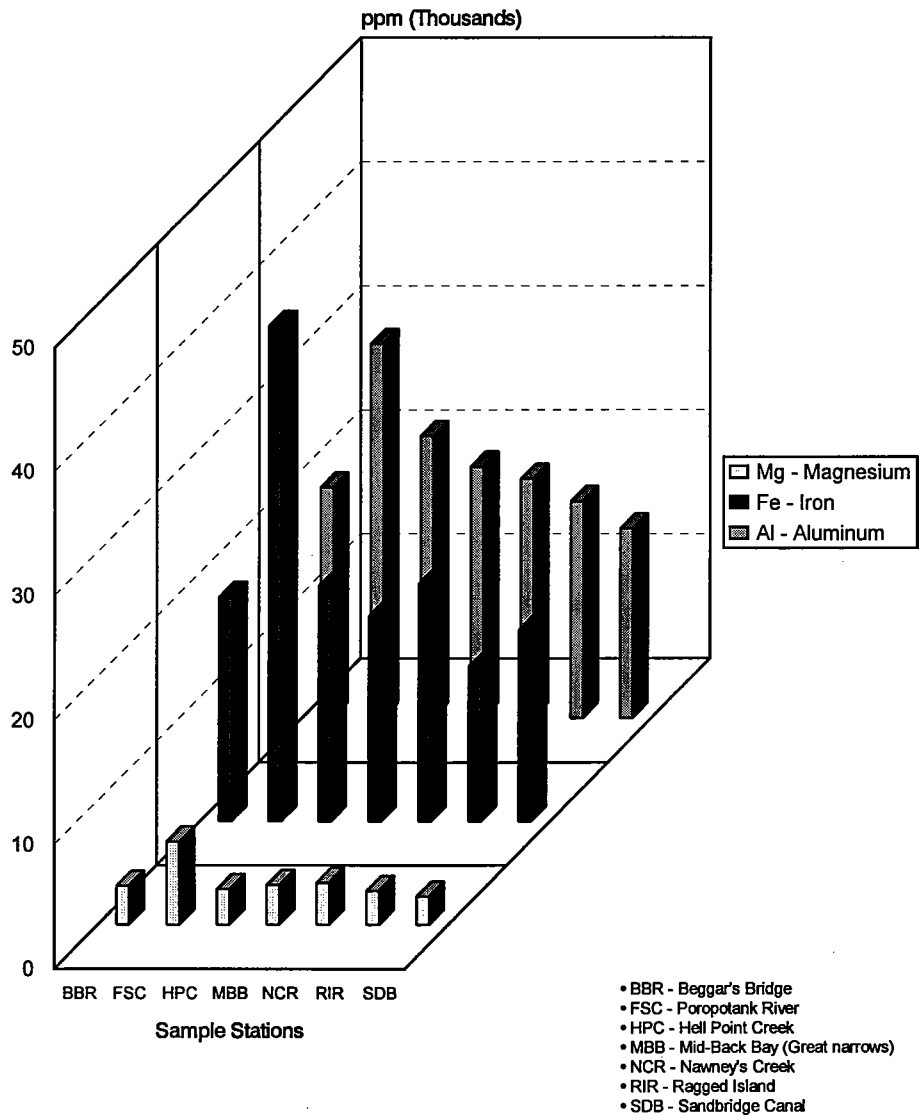
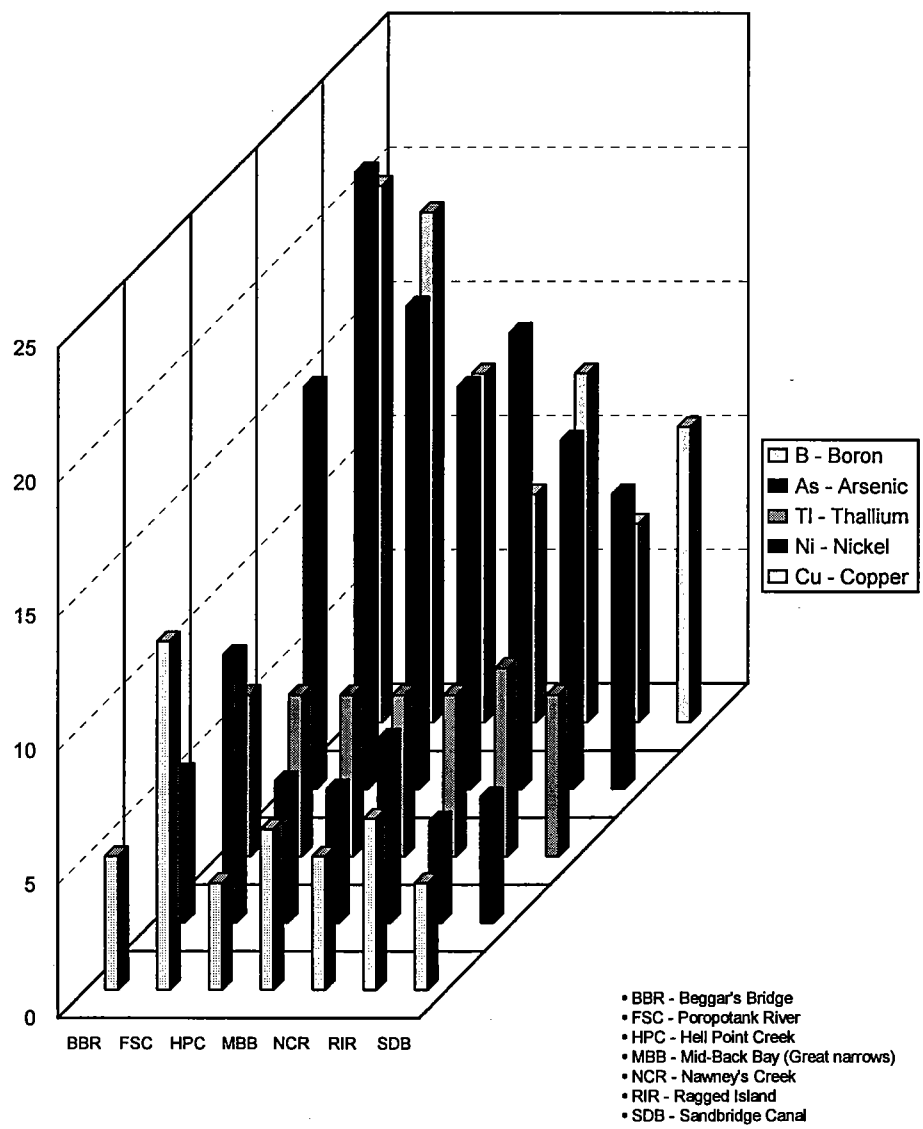


Figure 3e. Concentrations of metals in the sediments of back Bay (ppm dry wt.)



APPENDIX 1
Hydrolab[R] Data

	SAMPLING SITE						
PARAMETER	**SDB**	**HPC**	**BBR**	**MBB**	**NCR**	**RIR**	**PKR**
TEMP (°C)	23.8	25.4	27.3	21.5	22.4	22.0	22.6
pH	7.4	7.4	6.8	7.8	6.6	7.6	7.3
SALINITY (PPT)	0	0	0	0.2	0.2	0.3	4.3
D.O. (% SAT.)	102.1	103.5	105.3	105.8	74.3	103.7	82.9
D.O. (mg/L)	8.6	8.5	8.3	9.1	6.4	9.0	7.0
REDOX (VOLTS)	0.38	0.37	0.37	0.34	0.38	0.35	0.37

Hydrolab data for sampling sites used in Back Bay.