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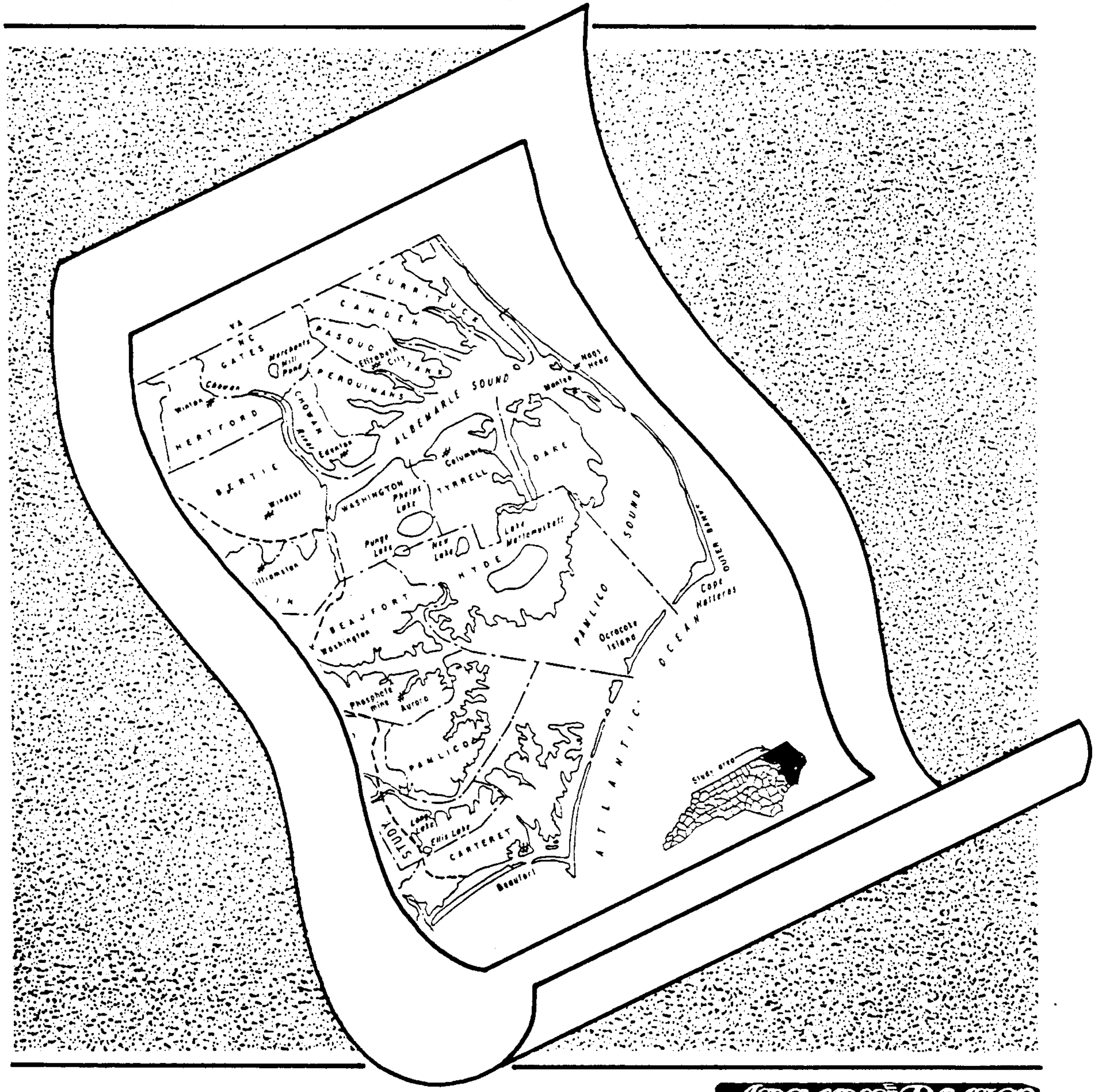
HEAVY METAL POLLUTANTS IN ORGANIC-RICH MUDS OF THE PAMLICO RIVER ESTUARINE SYSTEM: THEIR CONCENTRATION, DISTRIBUTION, AND EFFECTS UPON BENTHIC ENVIRONMENTS AND WATER QUALITY

ALBEMARLE - PAMLICO ESTUARINE STUDY



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HEAVY METAL POLLUTANTS IN ORGANIC-RICH MUDS OF THE PAMLICO RIVER ESTUARINE SYSTEM: THEIR CONCENTRATION, DISTRIBUTION, AND EFFECTS UPON BENTHIC ENVIRONMENTS AND WATER QUALITY

FINAL REPORT: THE PAMLICO RIVER

DECEMBER 20, 1989

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SUMMARY

Status of the Pamlico River Estuarine System

Discharge of apparently low concentrations of heavy metals from both natural and anthropogenic point and non-point sources into these estuarine environments dominated by organic-rich muds leads to potential pollution problems. High adsorption capabilities of clay minerals coupled with high chemical reactivity of organic matter, continuously strip trace metals from the water column. Resuspension of mud sediments by storms, biological processes and man, further concentrate metals within bottom sediments. Thus, the cumulative effect of large wastewater and runoff discharge volumes with low metal concentrations over long time periods can lead to significant metal enrichment. Toxic metals are then potentially available for further concentration and movement through the food chain by abundant filter and detritus feeding organisms living within organic-rich mud environments.

Analyses of major, minor, and trace elements within the organic-rich muds cored at 153 stations within the Pamlico River estuarine system document specific lateral and vertical distribution and concentration of metals within the basin and define environmental conditions favoring heavy metal enrichment. Anthropogenic sources are believed to be largely responsible for heavy metal enrichment within the Pamlico River estuarine system. Sediments in the vicinity of known point source discharges are enriched in specific metals by factors up to 14 times as compared to sediments in other portions of the Pamlico River. Surface sediments have been enriched up to and occasionally in excess of 100 times the elemental concentrations occurring in sediments deeper in the cores.

Ten areas of concern have been delineated in the Pamlico River estuarine system (Fig. 1). These areas have surface sediments that are enriched in one or more of the critical elements and include the eight EPA priority pollutant metals (As, Cr, Cd, Cu, Ni, Pb, Zn, and Hg) and other important trace elements (Co, Mn, Mo, Ti, V, F, and the nutrient element P). Enrichment is determined by comparing the concentration for each critical element to the trimmed mean for surface samples in the estuarine system. Areas containing one or more sample sites with critical elements that are at least 2 times enriched over the trimmed mean are defined as areas of concern. Table 1 summarizes the areas of concern and the elements enriched within each area.

Some portions of the Pamlico River estuarine system have little to no significant enrichment of metals within the surface sediments. Most notable of these are the vast portions of the outer Pamlico and outer Pungo Rivers, the upper portion of Chocowinity Bay, Durham Creek, outer Tranters Creek, Mixon Creek, and Blounts Creek; the latter two areas had only a single sample analyzed. Bath Creek, characterized by scattered rural development, is slightly enriched over the preceeding unpolluted areas; however, no elements were enriched significantly enough to be considered an area of concern. Upper Chocowinity Bay has the lowest concentration of metals within the entire Pamlico River estuarine system with no present or known historic wastewater discharges, wide vegetation zones around the perimeter, and very minimal development. Upper Chocowinity Bay is considered to be among the most pristine of environments within this estuarine system.

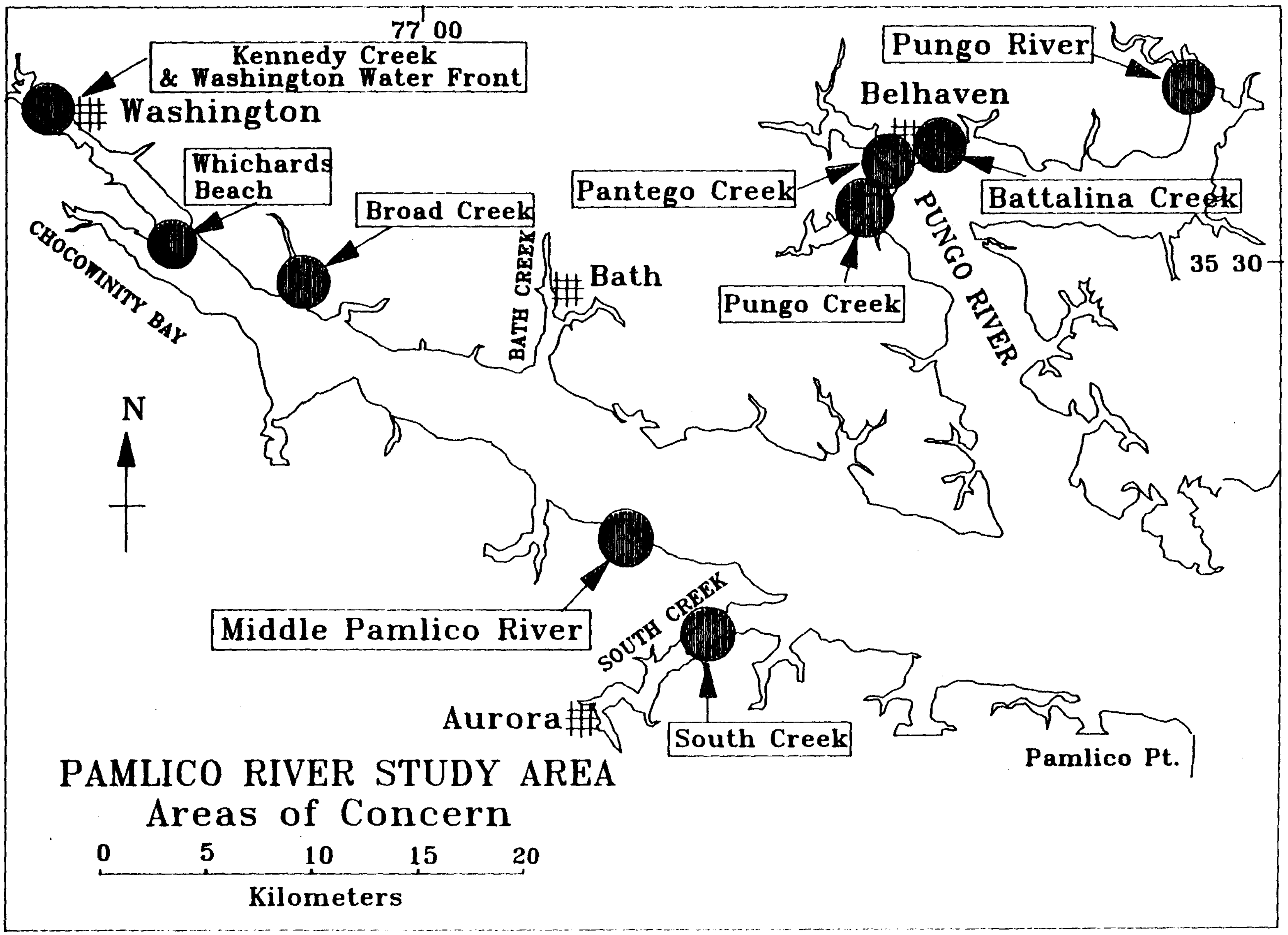


FIGURE 1. AREAS OF CONCERN for toxic metal pollution with the Pamlico River estuarine system

TABLE 1. <u>Areas of Concern</u> within the Pamlico River estuarine system including the enriched elements and maximum enrichment factor for each area. Enrichment factor = X trimmed mean for the Pamlico River.

AREAS OF CONCERN	ENRICHED ELEMENTS	MAXIMUM ENRICHMENT FACTORS, RESPECTIVELY
Kennedy Creek	Hg, P, Zn, Cu, Cr, Ni, Cd, Co, As, V, Pb, Al, Ca	14, 7, 6, 6, 6, 5 5, 3, 3, 3, 2 3, 2
Middle Pamlico River	Cd, Mo, As, Mn, V, Ti Ca, P, Na, K, F	5, 5, 3, 3, 3, 2 34, 3, 3, 2, NC
Washington Waterfront	Pb, Mn, Mo, Co, Hg, Zn	4, 4, 3, 2, 2, 2
South Creek	Cd, Mo, As K, Na	5, 2, 2 2, 2
Battalina Creek	Cu, Ni, Cd, Mo, Zn Na	5, 3, 3, 3, 3 2
Inner Pungo River	Ni, Mn, Ti Mg, Ca, K, Na	3, 3, 2 3, 3, 2, 2
Broad Creek	Cu, Pb, Hg	14, 2, 2
Lower Pantego Creek	Ni, Co	5, 2
Whichards Beach	Cu, P	3, 2
Pungo Creek	Ni	2

Table 2 shows concentrations of metals and the nutrient element phosphorus in surface sediments for the following areas: 1) trimmed mean concentrations for the entire Pamlico River estuarine system; 2) Kennedy Creek, the most polluted portion of the estuary; and 3) Chocowinity Bay, an unpolluted portion of the estuary.

Low metal concentrations within Chocowinity Bay surface sediments are similar to concentrations occurring in subsurface samples throughout the Pamlico system. When evaluating only the mud sediments, there are very poor and irregular correlations between metal enrichment and % clay or % organic matter within the samples. This suggests that there is a fairly constant natural background of metals with low concentrations. On the other hand, there is a strong correlation between metal enrichment and known anthropogenic sources. Consequently, the subsurface samples are interpreted to represent the natural background during pre-industrialization conditions. If this is the case, the pre-man situation within the entire Pamlico River estuarine system would have had similar metal concentrations to the surface sediments within Chocowinity Bay. This suggests that anthropogenic activity has approximately doubled the average background concentration of all toxicant metals within the surface sediments throughout most of the Pamlico River system (Table 2). Thus, within areas such as Kennedy Creek that are characterized by increased municipal and industrial activities, <u>concentrations of toxicant metals have been enriched by factors up to 14 times that of pre-man concentrations</u>.

TABLE 2. Heavy metal concentrations (in ug/g) in organic-rich muds of the most- and least-polluted portions of the Pamlico River estuarine system. Pamlico is the trimmed mean for the whole system, Kennedy Creek is the most polluted and Chocowinity Bay is the least polluted portion of the system.

EPA PRIORITY POLLUTANTS	PAMLICO	KENNEDY CREEK		CHOCOWINITY BAY	
	AVE.	AVE.	RANGE	AVE.	RANGE
Arsenic	12.8	21.2	5.8- 35.4	7.8	3.6- 12.6
Cadmium	0.36	0.85	0.3- 1.7	0.18	0.0- 0.4
Chromium	10.5	27.3	5.9- 58.8	4.6	2.5- 8.3
Copper	13.6	51.5	17.6- 84.4	6.4	3.5- 9.8
Nickel	2.7	8.4	1.5- 13.3	1.0	0.1- 2.1
Lead	35.9	68.5	29.8- 86.9	21.7	11.9- 40.9
Zinc	77.0	377.9	151.2- 490.3	35.6	17.1- 56.6
Mercury	0.09	0.44	0.16- 1.3	0.06	0.03- 0.08
Phosphorus	804.7	3369.5	644.3-5821.4	464.6	217.3- 707.3

Figure 2 compares the concentrations of six metal pollutants occurring within four areas within the Pamlico River estuarine system, each with different degrees of urbanization and industrialization. Chocowinity and Blounts Bays are relatively pristine areas without point sources and only minor nonpoint sources of local pollutants; however, both areas are presently being considered as sites for major development. Bath Creek is an old, very small rural community with low-density residential homes and scattered small-scale agriculture and appears to be only moderately affected by anthropogenic influences. Washington is a small city characterized by the highest levels of development within the Pamlico River estuarine system: extensive paved areas with storm sewers, a moderate number of major industrial facilities, a municipal waste treatment plant, and numerous historic industrial facilities and waste disposal sites. Consequently, the estuarine area around Washington reflects a high level of anthropogenic influence. Figure 2 clearly shows the direct relationship between metal pollutants in the estuarine sediment system and increased urban and industrial development.

Comparison with Other Estuarine Areas

It is important to compare the higher metal concentrations found in the Pamlico River estuarine system with other similar estuarine environments. A large data set for heavy metals in sediments was reported in 1987 as part of the National Status and Trends Program (NSTP), conducted by NOAA. Figures 3 through 5 compare the Pamlico data with NSTP results for specific marine and estuarine regions of the Atlantic Coast.

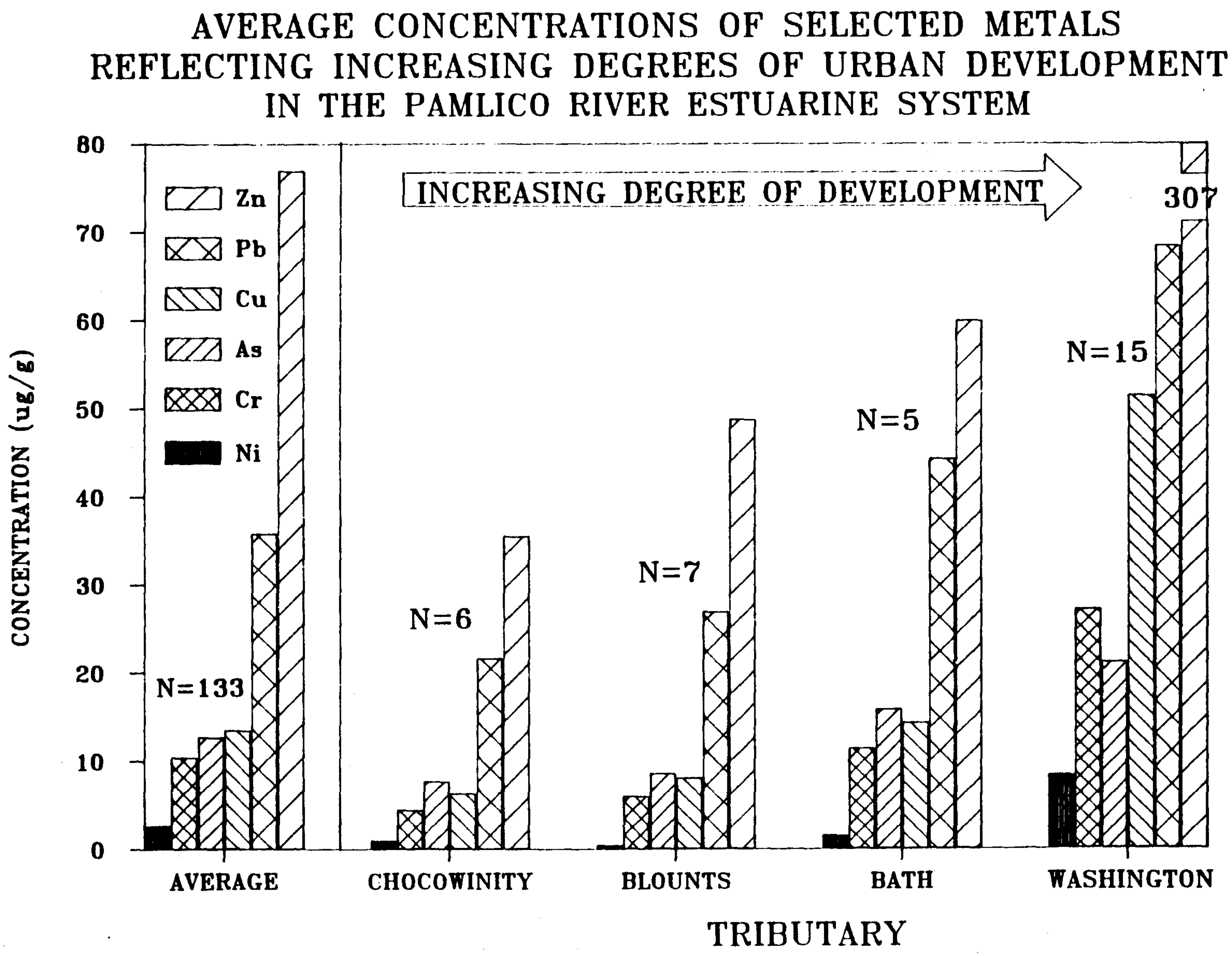


FIGURE 2. Relationship of metal pollution in the Pamlico River estuarine system to increased urban and industrial development

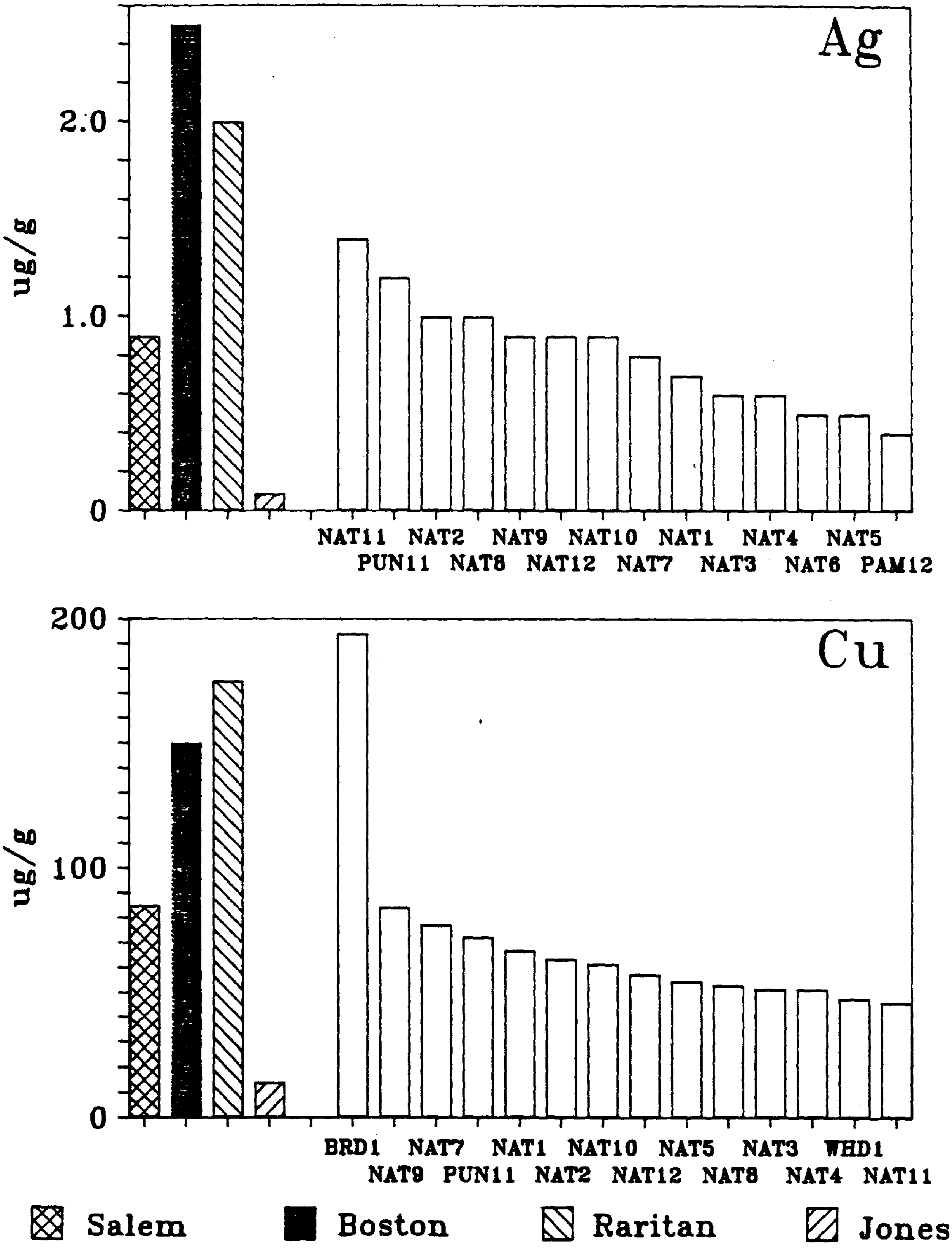


FIGURE 3. Comparison of silver and copper concentrations in the most polluted samples from the Pamlico River estuarine system with other Atlantic coast estuarine sites analyzed by NOAA's National Status and Trends Program (1987)

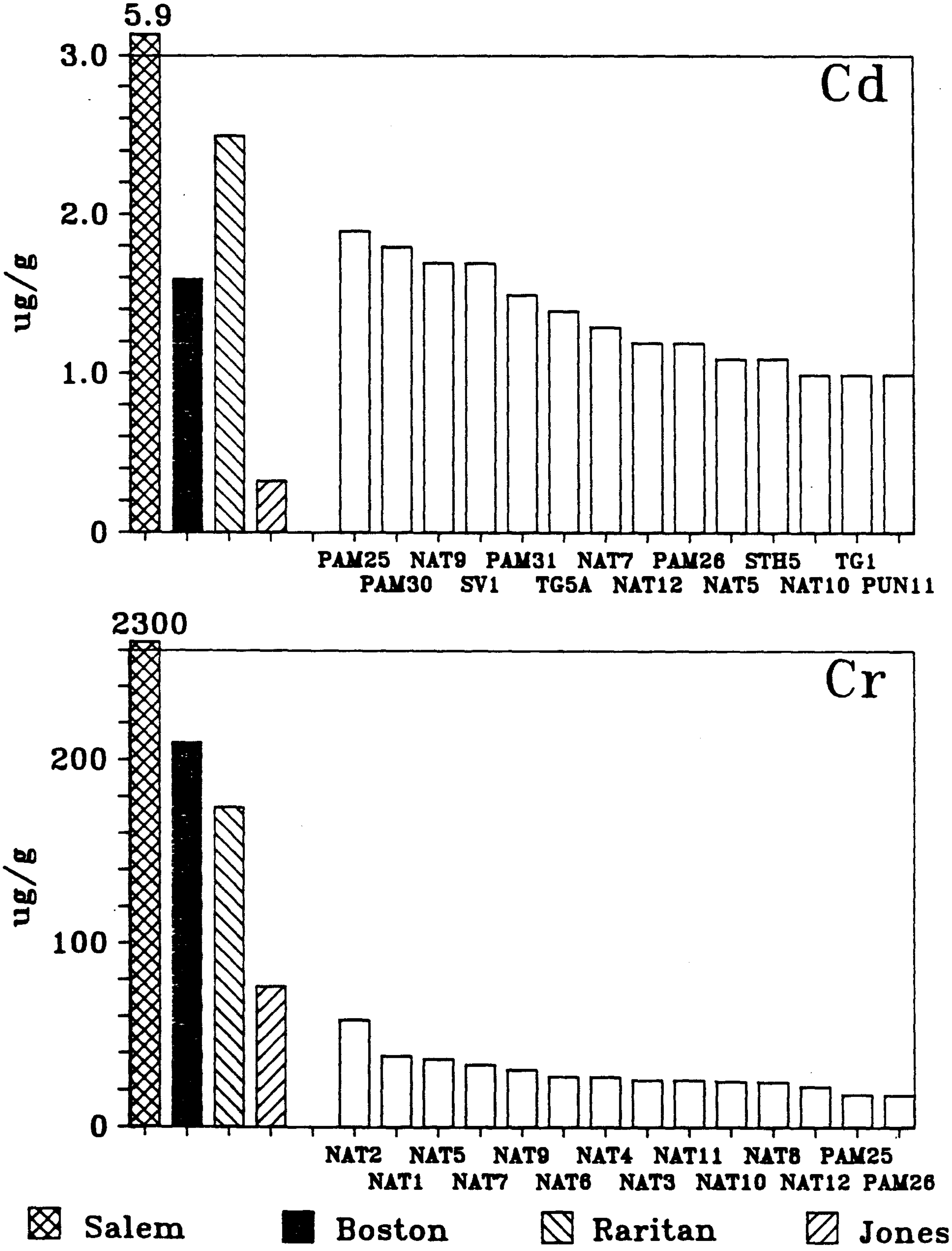


FIGURE 4. Comparison of cadmium and chromium concentrations in the most polluted samples from the Pamlico River estuarine system with other Atlantic coast estuarine sites analyzed by NOAA's National Status and Trends Program (1987)

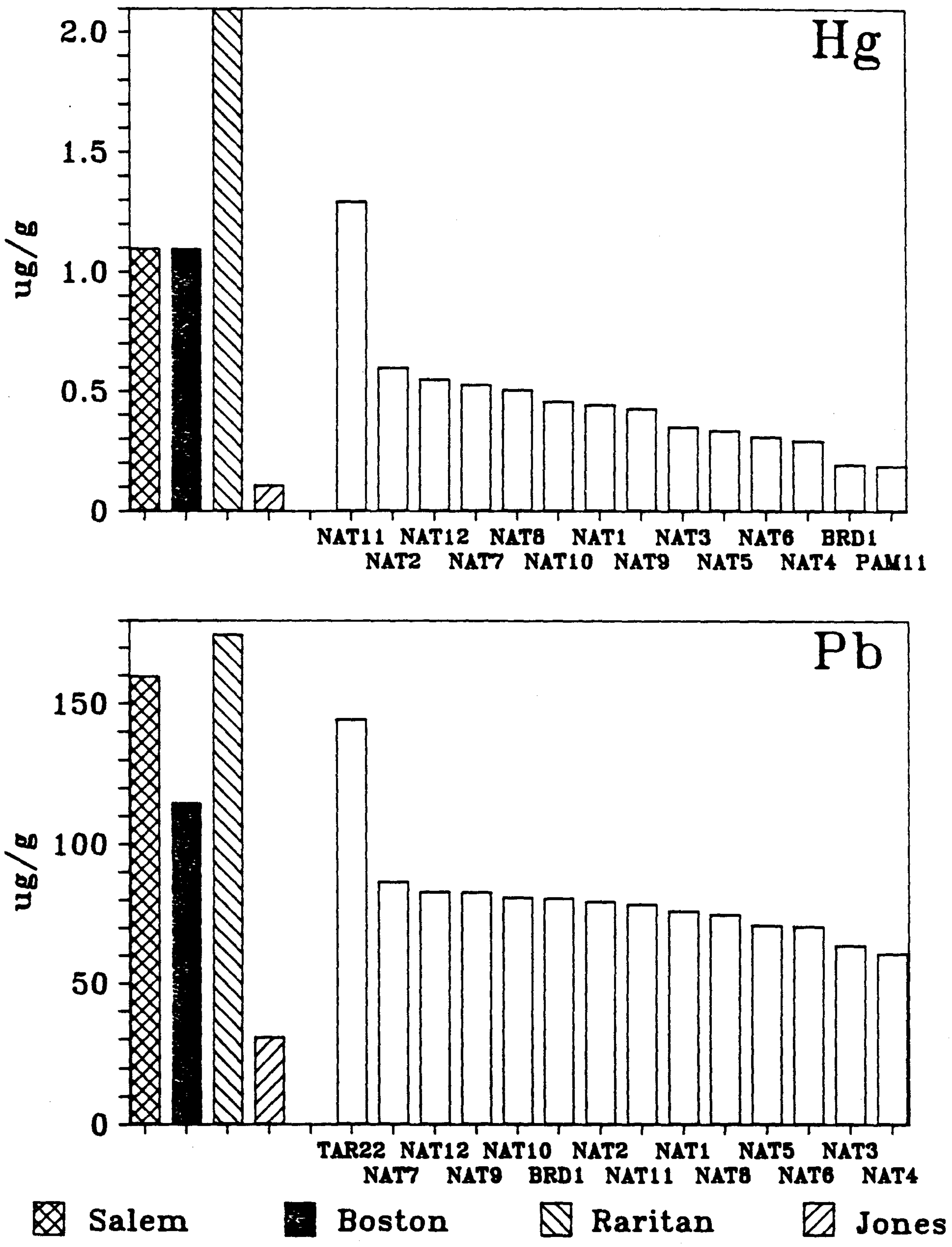


FIGURE 5. Comparison of mercury and lead concentrations in the most polluted samples from the Pamlico River estuarine system with other Atlantic coast estuarine sites analyzed by NOAA's National Status and Trends Program (1987)

Comparisons illustrated in Figures 3 through 5 consider the 15 surface samples that contain the highest concentrations of heavy metal pollutants in the Pamlico River estuarine system. These individual samples are compared with the average of three composite samples obtained by NSTP (1987) utilizing total sediment digestion techniques. The NSTP samples include Salem and Boston Harbors, Mass.; Raritan Bay, New Jersey; and Jones Bay, N.C. Samples from the first three areas generally contained the highest concentrations of the respective metals for the entire U.S. coastal regions studied. Jones Bay, located on the western side of Pamlico Sound near the mouth of the Pamlico River, represents an area that has minimal influence from anthropogenic sources and contained among the lowest concentrations of heavy metals within the NSTP sites.

Several points should be kept in mind when comparing the Pamlico River results to the NSTP data. The NSTP sites were deliberately located away from known anthropogenic point sources and dump sites in order to represent accumulations from multiple sources. Consequently, site-specific samples from each region should produce a wide range of numbers that could be significantly higher and lower than the values presented in Figures 3 through 5. Also, NSTP analyses were based upon total digestions, whereas analyses for the present study are based upon partial extraction techniques. Table 3 compares data obtained by Moore (in prep.) on three NSTP samples, obtained from NOAA, for Jones Bay and 30 samples for the Pamlico River utilizing both partial extraction and total digestion procedures on all samples. This comparison suggests that analytical numbers within this report are very conservative and on the low side of total elemental analyses such as the NSTP data, by the amount indicated in the column titled 'percent recovered by partial extraction' (Table 3).

Figures 3 through 5 indicate that the most enriched samples from the Pamlico have comparable concentrations to the averages from some of the most polluted regions of coastal U.S. Noteworthy among the Pamlico samples are the following:

1. High concentrations of most metals occur in all samples from Kennedy Creek (NAT1 through NAT12);
2. Cadmium concentrations in samples from the middle Pamlico River (PAM25, PAM26, PAM30, PAM31, TG1, and SV1) and South Creek (STH5), adjacent to an active phosphate mining operation, are very high.
3. Samples near municipal treatment outfalls at Washington (NAT samples in Kennedy Creek) and Belhaven (PUN11) are particularly enriched in cadmium, silver, and copper;
4. One sample near a marina railway in Broad Creek (BRD1) is extremely enriched in copper; and
5. One sample in the lower Tar River off Washington (TAR22) is extremely enriched in lead.

Chromium values in the Pamlico samples appear anomalously low (Fig. 4); however, the light leach extraction procedure utilized recovered between 20% to 25% of total chromium present (Table 3). Consequently, actual chromium values may be from four to five times higher than those shown in Figure 4 and thus, are actually quite comparable to levels within the polluted harbors.

TABLE 3. Comparison of elemental concentrations in 30 sediment samples from the Pamlico River estuary with 3 samples obtained from NOAA for Jones Bay (NSTP, 1987). Data from both Jones Bay and Pamlico River listed below, except total digestion data on Jones Bay samples (*) which are from NSTP (1987), were analyzed on the same equipment utilized in the present study and compare the partial extraction procedure (2N nitric acid) utilized within this report with a total digestion procedure (H_2O_2, HNO_3, and HF) as utilized in the NSTP (1987) study. The data in this table were obtained from an ongoing study concerning the "Partitioning of Heavy Metals in Sediments of the Pamlico River Estuary, North Carolina" by Richard Moore (in prep.).

	PAMLICO RIVER MEAN (ug/g)			JONES BAY MEAN (ug/g)		
ELEMENT	PARTIAL EXTRACTION	TOTAL DIGESTION	% REC BY PART EXTR	PARTIAL EXTRACTION	*TOTAL DIGESTION	% REC BY PART EXTR
CRITICAL TRACE ELEMENTS:						
Be	0.8	1.6	50	0.5	1.5	33
Cd	0.9	1.7	53	1.5	2.5	60
Co	5.8	18.9	31	5.2	15.0	35
Cr	25.3	72.2	35	12.9	66.2	19
Cu	29.8	38.2	78	46.1	66.4	69
Li	5.5	35.2	16	10.6	39.1	27
Mn	120.4	194.0	62	167.8	358.3	47
Mo	0.8	2.6	31	3.7	6.9	53
Ni	6.6	15.1	44	10.3	15.2	68
Pb	47.2	66.9	71	161.0	177.9	91
Ti	38.2	4,365.8	< 1	106.1	3,209.5	3
V	24.2	86.4	28	27.9	85.9	32
Zn	201.3	233.8	86	261.5	313.7	83
MAJOR ELEMENTS:						
Al	11,431.2	64,006.0	18	3,928.7	51,294.3	8
Fe	13,153.1	32,338.7	41	16,640.9	37,322.9	45
K	570.7	5,750.8	10	1,624.7	14,049.9	12
Mg	2,228.8	4,040.2	55	4,950.9	9,291.5	53
Na	3,609.2	5,216.3	69	9,825.7	14,348.4	68
Si	1,967.3	189,699.0	1	1,473.1	154,412.0	1

CONCLUSIONS

1. Anthropogenic sources are at least partly responsible for elemental enrichment within the Pamlico River estuarine system and includes all eight of the EPA "priority pollutant metals" (As, Cd, Cr, Cu, Pb, Hg, Ni, Zn), other critical trace elements (Co, F, Mo, Mn, P, Ti, V), and major elements (Al, Ca, K, Mg, Na).

2. Point source discharges within the Pamlico River estuarine system that appear to be contributing significant concentrations of pollutant elements include the following permitted discharges: two city sewage outfalls, several large and small industrial discharges, two marina sites, and one major mining facility.

3. Nonpoint source discharges within the Pamlico River estuarine system that appear to be contributing significant concentrations of pollutant elements include historic waste dump sites and industrial facilities, urban runoff, agricultural drainage systems, and boat channels.

4. Sediments in the vicinity of known point source discharges are enriched (up to 14 times) in As, Cd, Cr, Cu, F, Hg, Ni, P, Pb, and Zn compared to sediments in other portions of the Pamlico River estuarine system.

5. Surface sediments have significantly higher concentrations (up to 100 times and greater) of As, Cd, Cr, Cu, F, Hg, Ni, P, Pb, and Zn than sediments deeper in the cores. This zone contains a very large and important community of benthic organisms.

6. Surface enrichment of heavy metals may be related to the presence of a sediment surface floc layer of variable thickness. This floc layer is thought to be composed primarily of bacteria, benthic organisms, and organic detritus.

7. Sewage outfalls and agricultural drainage systems appear to be supplying abnormally high levels of organic-matter to the tributary creeks with associated high levels of phosphorus.

8. The strong vertical up-core gradients of phosphorus concentration in all cores suggests that these organic-rich muds may be an important source of nutrients to the estuarine waters.

9. Ten regions of the Pamlico River estuarine system are defined as areas of concern based on the enrichment of one or more critical trace elements by a factor of two times the trimmed mean for the Pamlico system. These include the following regions: Kennedy Creek, Washington waterfront, middle Pamlico River adjacent to the phosphate mining operation, South Creek, Battalina and Pantego Creek adjacent to Belhaven, inner Pungo River and Pungo Creek agricultural areas, and the marina areas at Broad Creek and Whichards Beach.

10. The outer Pamlico River, outer Pungo River, upper Chocowinity Bay, Durham Creek, outer Tranters Creek, Mixon Creek, Blounts Creek, and Bath Creek are areas in which the elemental enrichments are either slightly above, equal to, or below the trimmed mean for the Pamlico River system.

INTRODUCTION

There is little doubt that the North Carolina estuarine environment is now indelibly marked by products of human activity. Concerns about possible deleterious effects of this impingement of man on the well-being of this critical ecosystem bring renewed importance to the problems of the fate of anthropogenic chemical species within the estuarine environment. This is becoming critical in the Pamlico River estuarine system; mans activities contribute ever increasing amounts of suspended sediment and trace metals resulting in the potential for increased bioavailability of specific toxic elements whose previous occurrences and distributions were limited.

Low concentrations of toxic heavy metals in discharge waters or in estuarine water columns are not indications that the estuaries are free from contamination. Due to rapid changes in estuarine water chemistry, high adsorption characteristics of omnipresent inorganic clay minerals, and the chemical processes associated with metal complexing and organic matter, many trace metals are often enriched in the sediments at levels that are orders of magnitude above acceptable water level concentrations. Enrichment of trace metals continues as storms, biological processes, and man routinely resuspend the mud sediments into the water column. Consequently, the cumulative effect of large discharge volumes over long time periods allows for continuous interaction with the inorganic and organic sediment components; this becomes a critical factor in long-term bioavailability of trace metals. Thus, trace metals become increasingly more available to the food chain through time by the abundant filter and detritus feeding organisms living within the organic-rich mud environments.

The site specific and regional baseline data obtained for the Pamlico River estuarine system is critical and should help to determine the causal relationships between sediment pollution by critical toxic metals, water quality, and the resultant health of the biological components of the estuary (i.e. shellfish, finfish, etc.) and ultimately man. Only when these causal relationships are understood can effective management plans be developed to optimize the estuarine resources and minimize the detrimental impacts of increasing concentrations of sediments and metal pollutants resulting from rapid urbanization, industrialization, and chemical agriculture occurring within North Carolina's estuarine system. The National Academy of Sciences (1974) in a study on "Geochemistry and the Environment" concluded that finding realistic, workable means to mediate conflicts between human uses clearly depends upon understanding the complex interactions between heavy metals resulting from human activities and natural systems.

OBJECTIVES

The major objective and subobjectives for the technical project entitled "Heavy Metal Pollutants in Organic-Rich Muds of the Pamlico River Estuarine System: Their Concentration, Distribution, and Effects Upon Benthic Environments and Water Quality" are to:

Determine concentrations and distributions of heavy metal and phosphorus pollutants associated with organic-rich-mud within the Pamlico River estuarine system in order to:

a) Establish present pollutant levels around a series of known point and nonpoint sources,

b) Identify specific "hotspots" or "areas of concern" within the estuarine system,

c) Define a basinwide framework for determining migration paths of pollutants through time, and

d) Determine the pre-man or "natural background" levels of pollutants and establish the changing impact through time resulting from agriculture, urbanization, and industrialization.

This report represents the preliminary results from year one of a three year project. Each year will consider one of the main estuarine systems (i.e., the Pamlico River, Neuse River, and Albemarle Sound estuaries, respectively). This long term study will develop critical baseline information essential for generating a management plan concerning toxic metal pollution within the estuarine system and for addressing the following all important question:

> What are the inter-relationships between sediment/water column and sediment/organism interactions and resultant chronic effects of heavy metal pollutants upon the North Carolina estuarine system?

TRACE ELEMENTS

Trace Elements and Health

Heavy metals and other elements are normal constituents of most ecosystems. Natural concentrations, however, are being supplemented and the normal ratios among them are being altered by the activities of man, sometimes at an alarming rate. The dual role of many trace elements in biological systems (i.e., some acting as required nutrients within a restricted concentration range and all acting as potentially toxic contaminants at some level) is a well documented fact (Crounse et al., 1983a, 1983b).

Many factors affect the availability, transport, and concentration of metals into and through the natural coastal system. Ultimately, some of these metals get into the food chain and influence the well-being of many organisms, including man. Small excesses of specific metals in the food chain, when present over long periods of time, may have measurable health effects on organisms (Nat. Academy of Sciences, 1974). Increases that can be tolerated depend largely on the natural background levels and subsequent rates and amounts of increased concentrations resulting from urbanization and agricultural and industrial development. Trace elements can enter the aquatic food chain in many ways including direct incorporation from soluble aqueous phases, ingestion and digestion of water and sediment, or by the transport across gill membranes, to name a few.

Accessibility of an element in the abiotic environment for incorporation into the biosphere is referred to as "bioavailability". Because of the magnitude of the concentrations encountered in sedimentary environments, the intimacy with which most benthic organisms are in contact with this environment, and the fact that many of these benthic organisms form the base of important food chains, bioavailability constitutes an important consideration. The bioavailability of any given element depends on a host of factors, sometimes too numerous and complex to model. Principal among these factors are 1) the feeding habits, stage in the life cycle, and age and health of the particular organism in question; 2) the chemical form and manner in which a particular element is incorporated into the sediments; and 3) the physical and chemical conditions of the environment at the time of incorporation (e.g., temperature, salinity, Eh, pH, etc.).

Many studies document the direct and indirect effects of anomalous levels of heavy metals on organisms. For example, mercury, cadmium, arsenic, and lead are toxic to man and to other living things in virtually all chemical forms. In most cases threshold limits for long-term, toxic effects are poorly known, but they often tend to accumulate in the body (Sandstead et al., 1974). Mercury for example, "has long been recognized as one of the more toxic metals" (DEM, 1983). EPA (1980) states that "mercury and its various compounds have no known metabolic function and their presence in the cells of organisms represents some contamination from either natural or anthropogenic sources." On the other hand, chromium and zinc are trace elements known to be essential to animal and human health and additions to the environment may actually be beneficial; in these situations, deficiency is the major health concern (Mertz et al., 1974; Sandstead et al, 1974). In a third category are such elements as selenium, copper, and molybdenum which are both essential nutrient elements, but will cause severe health problems with either deficiencies or excesses (Davis et al., 1974; Oldfield et al., 1974).

Thirteen metals have specific restrictions in drinking water. Federal standards (EPA, 1986) include 8 heavy metals in their primary restrictions which have critical health effects (As=50, Ba=1,000, Cd=10, Cr=50, Pb=50, Hg=2, Se=10, and Ag=50, all in ug/L). Five other elements are listed in the EPA list for secondary restrictions, which are less critical to health (Cl=250,000, Cu=1,000, Fe=300, Mn=50, and Zn=5,000, all in ug/L).

Trace Elements in the Estuarine Environment

The transient nature of estuarine water column characteristics and the dilution factors frequently engineered into point source discharges often maintain trace metal concentrations in water below "safe" or even detectable limits. On the other hand, the sedimentary regime is much less transitory with regard to both the medium as well as the organisms inhabiting it. Furthermore, heavy metals can become incorporated into sediments by several different mechanisms and they can be partitioned among a variety of sedimentary phases:

1) Dissolved in interstitial pore waters;
2) Adsorbed or chelated by organic matter (often occurring as surface coatings);
3) Adsorbed or occluded with oxy-hydroxy precipitates of iron or manganese (occurring as discreet particles or surface coatings);
4) Precipitated as distinct metal salts (e.g., hydroxydes, sulfides, carbonates, etc.) or other mineral species;
5) Adsorbed or occluded in carbonates of inorganic origin (calcite, aragonite, etc.) or of biogenic origin (shell hash);
6) Adsorbed at ion exchange or adsorption sites of mineral grains;
7) Bound at interlayer sites of clay minerals; and
8) Incorporated into the crystalline lattice of minerals.

As a result of these important concentrating mechanisms, benthic sediments are often envisioned as the ultimate sink for much of the soluble and nearly all particulate matter entering aquatic environments. Consequently, heavy metal concentrations in sediment are often orders of magnitude greater than those in the overlying waters, even for unpolluted systems (Wolfe and Rice, 1972).

The partition of many elements between solution and suspended particles in fresh water undergoes drastic changes during estuarine mixing in response to major changes in pH, ionic strength, solution composition, salinity, etc. (Li et al., 1984). During estuarine mixing, some elements form strong complexes with humic acids and are coagulated into particles (Sholkovitz, 1978; Sholkovitz and Copland, 1981). Other heavy metals are scavenged from the water column by the fine-grained, suspended clay components (Turekian, 1971). Aller (1980) demonstrated extensive scavenging of reactive elements dissolved in the overlying water column by fine-grained estuarine bottom sediments within time scales of days. Turekian (1971) demonstrated that many heavy metals are maintained at low levels within the estuarine water column as a result of scavenging action of suspended particles. Consequently, Turekian et al. (1980) found that estuarine bottom sediments are "strongly impacted by the trace-metal injections from industry" and that "the primary mode of transportation to the estuarine zone is via particles".

It has been well established that fine-grained sediments represent the largest reservoir for heavy metals within an estuarine system (Renfro, 1973). This reservoir, which occurs both in suspension and as bottom sediment, obviously has the potential of conveying large quantitites of anthropogenically derived metals to estuarine biota, particularly filter and detritus feeding macrofauna. In efforts to assess the relative importance of bioaccumulation of heavy metals by estuarine organisms, Cross and Sunda (1978) and Jenne and Luoma (1975) concluded that the "utility of continuing to conduct bioaccumulation and toxicity experiments based solely on total dissolved concentrations in the water must be severely questioned." Knowledge of the concentrations, chemical form, and bioavailability of metals in the sediment and organic matter reservoirs is essential before the consequences of metal additions, both in terms of bioaccumulation and toxicity, can be predicted (Cross and Sunda, 1978).

Turekian et al. (1980) concluded that "a strong correlation exists between high metal concentrations in all components of the coastal system (water, sediment, and organisms) and the proximity of polluted fresh-water stream and sewer discharges." They demonstrated a direct correlation between increasing heavy metal concentration with decreasing grain size in the estuarine sediments. Aller (1980) found that fine grained sediments were more efficient scavenging agents and that during mixing they exchanged low-activity for high-activity elements within the overlying water column. Thus, from the standpoint of particle interaction with geochemically reactive elements in the water column, a source of heavy metals and a fine-grained sediment are extremely important.

The horizontal dispersal during deposition and vertical redistribution after deposition result from storm and current processes affecting particles suspended in the water column, and physical and biological mixing of particles in the sediment column. Turekian et al. (1980) found strong horizontal distribution patterns of specific heavy metals which they believe demonstrates that complete homogenization does not proceed fast enough to obliterate the point sources of metals.

Tidal and storm resuspension of the organic-rich muds that floor the bottom of a large portion of the Albemarle-Pamlico estuarine system, are important for sedimentological, biological, and geochemical processes. The physical stability and resuspension of bottom muds are important to water transparency and hence photosynthesis (Rhoads et al., 1978). Resuspended material often contains microbial coatings which are important food resources for both zooplankton and benthic organisms (Rhoads et al., 1975; Tenore, 1977) and estuarine chemical processes associated with adsorption and desorption of heavy metals and radionuclides (Benninger, 1976; Aller and Cochran, 1976; and Turekian, 1977; Aller, 1980; Li et al., 1984).

Sediment transport and resuspension within estuarine water bodies are often tied directly to major storm events. Storm processes that affect coastal sedimentation include storm surges, wave action, and flooding resulting from heavy rainfall (Hayes, 1978). Single storms can cause more erosion, bottom resuspension, and deposition in estuaries within a few hours than would occur in decades under normal conditions. During these same storm periods, there is a maximum contribution of heavy metals and other pollutants to the estuarine systems, in consort with maximum turbidity levels for absorption and removal to the bottom sediment regime. For example, urban runoff and industrial waste is often processed through sewage-treatment plants. However, during periods of high discharge, treatment plants are often bypassed and unprocessed effluent is discharged directly into the rivers, resulting in enrichment of the sediment surrounding the outfall in organic carbon and heavy metals (Turekian et al., 1980) as demonstrated for sewage outfalls in Long Island Sound.

Potential Sources of Trace Element Pollutants

The Albemarle-Pamlico estuarine system acts as a large settling basin for sediments, organic matter, heavy metals, and other pollutants resulting from agriculture, urbanization, and industrialization within the drainage basin (Copeland et al., 1983, 1984). For example, Harned (1980) sampled Neuse River water at two stations repeatedly between 1974-77. The river water contained the following ranges of values of dissolved heavy metals in ug/L: As = 0 to 50, Cd = 0 to 50, Co = 0 to 100, Cu = 2 to 70, Fe = 90 to 950, Pb = 0 to 500, Mn = 20 to 2200, Hg = 0 to 2.2, Se = 0 to 12, and Zn = 0 to 1400. Heavy metal concentrations at two stations were above the EPA (1986) domestic raw water supply criteria levels as follows: iron (28% and 39% of the time), manganese (100% and 88% of the time), cadmium (22% and 17% of the time), selenium (15% and 25% of the time), and lead (25% and 20% of the time).

Below the Pamlico River Estuary is one of the largest phosphate deposits in the world; on the banks of the Pamlico River is one of the world's largest phosphate mines and associated chemical facilities. The phosphate ore contains a large number of trace elements, some of which occur in very high concentrations (Table 4). During chemical dissolution of the phosphate for production of chemical fertilizer products, these trace elements are released. The subsequent flow path and residence of most of these elements is very poorly understood. Some elements remain with the fertilizer products, some end up in the vast wastepiles of phosphogypsum, and some will be discharged into the estuary with the sixty million gallons of wastewater per day (Appendix I). However, the discharge permits do not have limits nor do they require monitoring for the EPA "priority pollutant metals". Consequently, even though the wastewater probably meets required discharge standards most of the time, the massive volumes that contain low concentrations of metals are discharged over long periods of time with continous adsorption and concentration by organic-rich muds within the estuarine system.

TABLE 4. Average composition of hand-picked phosphate concentrate composite from various units of the Miocene Pungo River Formation in North Carolina. This composite sample includes a mixture of 60% intraclasts, 30% pellets, and 10% skeletal grains (from Ellington, 1984). Uranium value (*) is from Indorf (1982) and the second uranium and rare earth values are from Dolfi (1983).

Major Element	Mean Conc.	Trace Element	Mean Conc.
CaO	47.97%	Mo	121 ppm
P_2O_5	29.25%	Zn	113 ppm
SiO_2	5.56%	Cr	101 ppm
F_2	3.50%	Cu	26 ppm
Na_2O	1.41%	As	24 ppm
MgO	.64%	Pb	23 ppm
Fe_2O_3	.72%	Ni	20 ppm
Al_2O_3	.59%	V	18 ppm
K_2O	.16%	Se	8 ppm
TiO_2	.08%	Cd	7 ppm
MnO	.005%	Co	6 ppm
		*U	92 ppm
		U	57 ppm
		Ce	64 ppm
		La	30 ppm
		Nd	23 ppm
		Sm	5 ppm
		Yb	2 ppm

Human (metabolic) waste products often have high concentrations of phosphorus and various metals such as zinc (1,000 ppm), lead and copper (400 to 500 ppm each) (Horvath, 1972). Without industrial waste, the raw municipal wastewater often contains concentrations of many heavy metals that are lower than the EPA drinking water standards (Crites et al., 1979). However, sewage sludge contains high metal contents including Fe = 9,800 to 11,000 ppm, Zn = 4,300 to 7,690 ppm, Cr = 2,100 to 3,200 ppm, Cu = 1,200 to 2,100, Ni = 790 to 1,200, Pb = 650 to 1,100, and Cd = 290 to 520 ppm (Regan and Peters, 1970, 1972). Actual concentrations for any sewage treatment plant are extremely variable and depend upon the amount and composition of industrial waste that is treated. During breakdowns and periods of storms and high rainfall runoff, all effluent is often discharged directly into the environment.

The major source of lead in the environment is from the combustion of lead-containing fuel, most of which either ends up in the atmosphere or falls on or near roads. Lead is removed from the atmosphere by rain and is washed off the roadways, parking lots, and commercial and industrial sites by rainwater. Much of this lead is insoluble and is quickly removed from the water by sediment adsorbtion. Carr et al. (1983) found stormwater runoff from seven storms in three different urban settings had the following range of concentrations of dissolved heavy metals: (Hg = <0.3 to 5, As = <5 to 90, Pb = 250 to 64,600, Zn = 130 to 37,600, Fe = 6,1302 to 970,000, Cu = 100 to 20,100, Ni = 30 to 5,900, Cr = 25 to 8,470, and Cd = <10 to 950 ug/L).

There is an increased use of heavy metal pesticides with the decline in chlorinated hydrocarbon pesticides through the years (Nat. Acad. of Sci., 1974). In 1970 there were 96 pesticides commercially available that had heavy metal bases including Li, Cr, Pb, Cd, Zn, Se, Cu, F, and I. The National Academy of Science concluded that "knowledge of toxicity levels at relatively low-level long-term dosages for many of these pesticides are completely lacking. Furthermore, the ultimate depository in nature for many of these elements is at present unknown."

Based on limited available data, Gale and Adams (1984) concluded that peat mining activity in North Carolina and subsequent land use changes will significantly increase effluxes of trace metals. Various peat mining EIS studies have demonstrated mercury concentrations are consistently high in examined sediments (0.01 to 1.0 ppm) from drainage canals and the Pungo River. Nine percent of 368 water samples obtained with the Ambient Water Monitoring Program (AWMP) within the Washington regional office of NRCD from 1979 through 1981 contained detectable mercury (DEM, 1983). However, "at this point in time, little information exists to address the critical question of the impacts of such increases in drainage waters on biota of the receiving estuarine systems" (Gale and Adams, 1984). They believe that determining the potential for impacts is a critical research need and "if impacts do occur, they are not likely to be the result of a single material, such as mercury or Alachlor, but rather the result of the cumulative effects of a variety of trace metals, pesticides, and other substances." The banks of North Carolina's estuaries contain other major industrial plants such as pulp and paper mills, metal plating operations, textile mills and synthetic fiber plants with large, and potentially heavy metal-rich wastewater discharges. In addition, there are numerous smaller industrial operations with potential localized or cumulative impacts resulting from point source discharges.

A totally unknown contributor, and potentially one of the most important, are the many historic waste disposal sites and industrial sites scattered through the marshes and lowlands within the estuarine area. Both the locations and the chemicals dispensed into these waste facilities and dump sites are very poorly known. Since these facilities generally predate the time of environmental awareness, their past and present potential impact upon the estuarine system is also very poorly known, but it could be overwhelmingly significant.

Point and Nonpoint Source Discharges

The Division of Environmental Management's (DEM) Focus database contains information on location, size and discharge characteristics of all permitted National Pollution Discharge Elimination Standard (NPDES) discharge facilities in the Tar-Pamlico River drainage basin. Each permitted industrial and municipal discharge is plotted on maps of the lower Tar River and the Pamlico River and listed in decreasing order of design flow in Appendix 1.

As of this writing, there are 133 permitted non-municipal and 30 permitted municipal discharges within the entire Tar-Pamlico drainage basin. These represent a design flow of 74.3432 and 44.953 million gallons per day, respectively and are listed by decreasing discharge volume in Appendix I.3. Note that only a very few of the permitted discharges are required to monitor parameters of metels or organic compounds. This is the sole source for limited information that does exist from monitoring data gathered to fulfill individual permit requirements about the chemical content of effluent from specific discharges.

Little is known about nonpoint source discharges into the Tar-Pamlico River drainage systems. Sources of nonpoint discharges are extremely varied in space, time, volume, and chemical composition and include agricultural and urban runoff, peat mining and timbering, groundwater discharge associated with historic waste dump sites and landfills, land and shoreline erosion, and atmospheric fall out.

UTILIZATION OF EXISTING DATABASES

Data were retrieved from the EPA STORET Database System for the entire Tar-Pamlico drainage basin. This database contains information from monitoring sites for the Ambient Water Monitoring Program administered jointly by the NC DEM and US EPA. Measured monthly, data at each site consists of chemical and physical parameters for water samples including heavy metals. The NC DEM's FOCUS Database was accessed to obtain a listing of all permitted waste-water discharge points within the Tar-Pamlico drainage basin. This listing gives information on location, design flow specifications, and name of permittee.

In 1987, a North Carolina state agency (Rader et al.) concluded that heavy metals were not a problem in the Pamlico River estuary. This conclusion was based primarily on water analysis data obtained by various agencies supplying information to the data bases listed above. The main basis for their heavy metal conclusion was that most analyses were below detection limits. Only copper and zinc were detected with any frequency, out of a group of metals that included Pb, Hg, Ni, and Cr.

Table 5 compares detection limits for five heavy metals reported for rivers and estuaries in N.C. (Barker et al, 1986) compared to concentrations for the Mississippi River (Shiller and Boyle, 1987). Detection limits for these five metals are significantly higher than ambient concentrations in the Mississippi, a river probably heavily influenced by anthropogenic input of heavy metals. It is apparent from this table that methods used routinely by many labs studying North Carolina waters are not adequate for determining ambient trace metal concentrations. Cadmium for example, may be 500 times higher in concentration compared to background or non-polluted waters; however, this would not be detected using some of the presently available techniques. Since trace metals required for proper nutrition can become toxic when concentrations are from 40 to 200 times greater than "normal" levels (Forstner and Wittman, 1983), toxic levels of heavy metals may occur but probably are not detected in river and estuarine waters. These considerations, combined with Table 5, illustrate the fallacy that a problem does not exist because water samples are below detection.

Also, when metals can be accurately measured within the water colum, their concentrations are often too low to cause direct toxic conditions (Staples et al., 1985, in press). However, such anlayses do not address the potential concentration and toxicity of metals that might occur within the associated sediments. Due to rapid changes in estuarine water chemistry, high adsorption characteristics of omnipresent inorganic clay minerals, and the chemical processes associated with metal complexing and organic matter, many pollutants become enriched in the sediments to levels that are orders of magnitude above acceptable water concentrations. For example, "of sixty-five classes of toxic pollutants for which EPA has issued water quality criteria, two-thirds of those classes have constituents that will bind to sediments" (Gilford and Zeller, 1987). Enrichment of trace metals continues through time as storms, biological processes, and man routinely resuspend the mud sediments into the water column. Consequently, the cumulative effect of large discharge volumes over long time periods with continuous interaction with inorganic and organic sediment components is a critical factor on long-term concentrations and potential bioavailability of trace metals. Thus, trace metals may become increasingly more available to the food chain through time by abundant filter and detritus feeding organisms living within the organic-rich mud environments. Kimerle (1987) concluded that some chemicals tend to strongly partition to sediments becoming sinks that "are acutely and chronically toxic to aquatic organisms". Gilford and Zeller (1987) have found that polluted sediments have impacted benthic organisms in areas where water column criteria were not violated.

TABLE 5. Comparison between detection limits for trace metal samples from North Carolina rivers (Barker et al., 1986) and average metal concentrations in the Mississippi River (Shiller and Boyle, 1987). > X = amount detection limits used for N.C. rivers are above average of Mississippi values.

ELEMENT	MISS RANGE nmol/kg	MISS AVE nmol/kg	NC DETECT LIMITS nmol/kg	> X
Cu	18.3 -30.9	22.7	160	7
Ni	20.5 -26.2	23.4	890	38
Zn	1.7 - 4.2	3.2	154	48
Cr	.4 - 2.8	1.6	470	294
Cd	.08- .2	0.13	80	615

Thus, analysis of the estuarine mud sediments represents a much easier and more reliable approach to determining the health of estuarine water quality for several reasons.

First, concentrations of critical toxic heavy metals are considerably enriched in the sediments compared to their dilute character within the water column; therefore they can be analyzed for and monitored with much more reliable results.

Second, the sediments represent a synthesis reflecting long-term assimilation that smooths out the extreme variability associated with collecting water samples; therefore they can readily pinpoint problem areas associated with various types of heavy metal sources.

Third, heavy metal analyses of organic-rich muds can be applied relatively cheaply and quickly to define potential problem areas; such problem areas often have a high potential of being enriched in other chemical components that may cause more serious water quality problems (i.e. organic toxins, many of which are difficult and costly to analyze for).

FIELD SAMPLING METHODLOLOGY

Delineation of Study Area

The study area extends from the mouth of the Tar River, 3 miles west of Washington, east to Pamlico Point at the mouth of the Pamlico River and north in the Pungo River to the Alligator River Canal and the US-264 bridge near Leechville (Fig. 6). Most major lateral tributary creeks on the main rivers were also included within the study area (Table 6).

TABLE 6. Location of sediment samples collected in the Pamlico River estuarine system for subsequent sediment and elemental analysis.

SAMPLE AREAS	CORE NAME	NUMBER OF SITES OCCUPIED	NUMBER OF SUBSAMPLES
TAR RIVER SYSTEM		42	83
Mouth of the Tar River	TAR	24	45
Tranters Creek	TRA	3	6
Kennedy Creek	NAT	15	32
PAMLICO RIVER SYSTEM		86	209
Inner Pamlico River	PAM	17	127
Middle Pamlico River	PAM	29	
Outer Pamlico River	PAM	5	
Chocowinity Bay	PAM	6	14
Whichards Creek	WHD	2	5
Broad Creek	BRD	7	14
Blounts Creek	BLT	1	2
Bath Creek	BTH	4	8
Mixon Creek	MXN	1	2
Durham Creek	DHM	3	7
South Creek	STH	11	30
PUNGO RIVER SYSTEM		25	52
Inner Pungo River	PUN	13	27
Outer Pungo River	PUN	4	8
Pantego Creek	PTG	6	13
Pungo Creek	PUN	2	4
	TOTALS	153 SITES	344 SUBSAMPLES

Development of Base Maps

Digital base maps were generated for the entire Pamlico and Pungo River estuarine system to plot pre-existing data and data generated by this study. The base maps were developed from National Ocean Service 1:40,000 and 1:80,000 scale nautical charts and from U.S. Geological Survey 7.5 minute quadrangle maps. A LORAN-C map was produced for location of most sampling

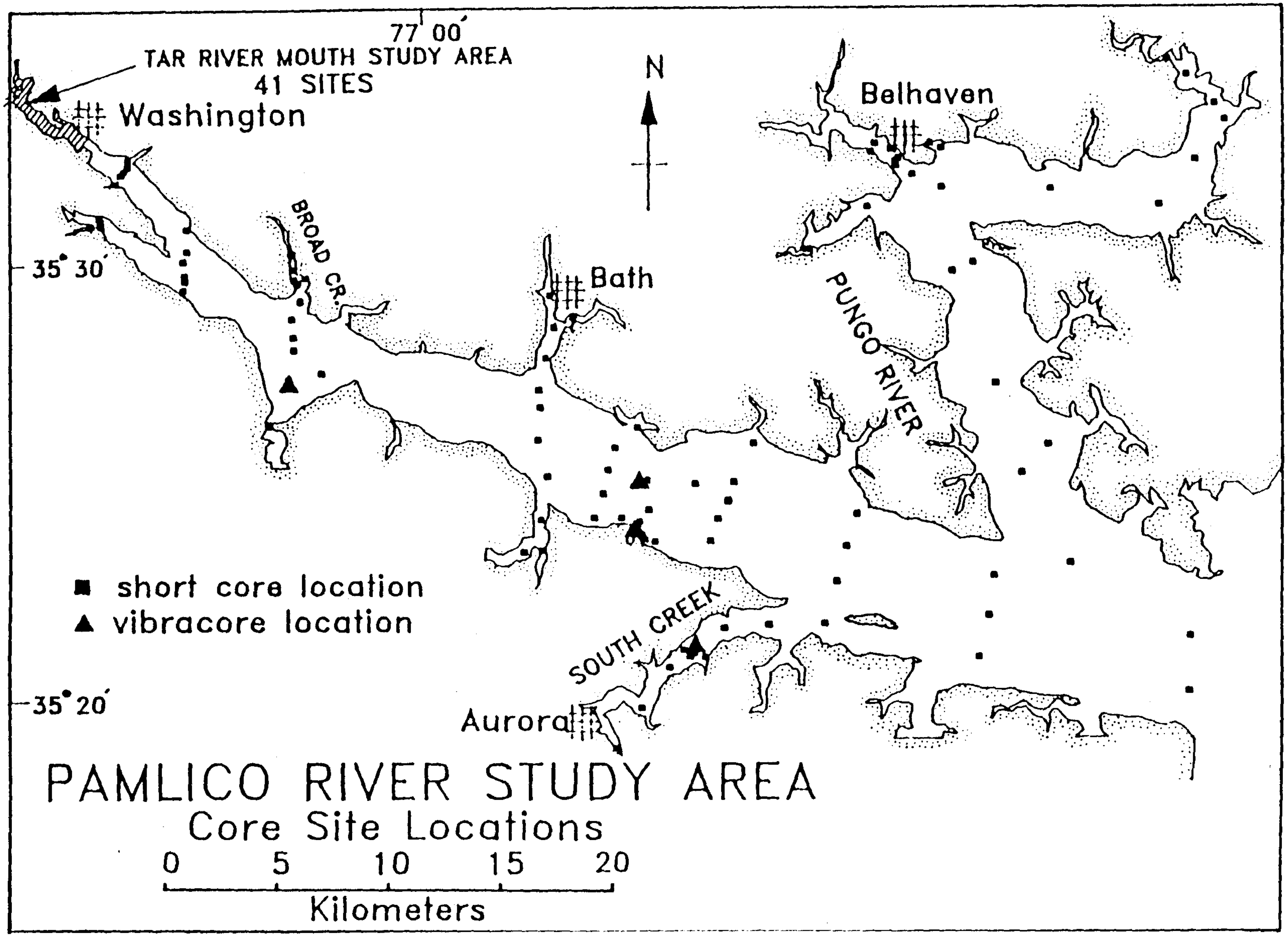


FIGURE 6. Location map of the Pamlico River estuarine system study area showing the location of diver-obtained short core and deep vibracore sediment samples

sites in the field. The LORAN-C map was produced by making repeated observations at known points to correct for ground-wave distortion throughout the study area; coordinates were calculated and plotted on maps. Core site positions were located utilizing LORAN-C coordinates that were plotted on the corrected LORAN-C map to obtain latitude and longitude coordinates. In areas where LORAN-C signals were unobtainable, compass bearings taken on available landmarks were used for navigational positioning.

Acquisition of samples

A regional sampling grid of 153 core sites in the Pamlico River estuarine system (Fig. 6) was developed based upon information from the published literature, unpublished maps and data from previous research programs, and the DEM Focus database. One core was obtained at each core site; these sites were located (Fig. 6) in areas that were 1) proximal to known point sources such as municipal and industrial discharges, 2) adjacent to non-point discharge sources such as marinas, urban runoff, and agricultural areas, and 3) areas that were assumed not to be influenced by human activity. Table 6 summarizes the number of core sites within the creeks and rivers of the Pamlico River estuarine system. Appendix II presents core hole location data for all samples acquired within the Pamlico River estuarine system for the present study.

Samples were obtained during the summer of 1988 aboard the R/V NITRO, a 34 foot, diesel powered, converted navy personnel boat belonging to the ECU Department of Geology. The following sample and field data were collected at each of the 153 core sites: a) station number; b) location (Loran C coordinates or compass bearings and descriptive landmarks); c) weather conditions; d) hydrographic conditions including water depth, visibility, salinity (surface and bottom), and temperature (surface and bottom); d) bottom sediment characteristics including a description, a core with assigned number, and core length. Sediment cores were obtained by divers using either SCUBA, surface supplied air, or by free diving. Sediment and bottom characteristics at each site were described by the diver.

Diver-obtained sediment cores at the 153 sample sites range from 20 cm up to 3.2 meters in length and reflect the following types of core samples: a) areas that have high levels of man-influenced point and nonpoint discharges; b) areas that have limited man-influenced discharge points; and c) deep cores that contain sediment that is pre-anthropogenic and below the man-influenced surface sediment. The last two sample types provide "background" values for metals in the estuarine system while the first type will be utilized to define the type and levels of heavy metal pollutants in the organic-rich estuarine muds. These latter areas include several types of point source industrial and municipal sites such as sewage treatment plants, waste dump sites, mines, and chemical plants; and nonpoint source sites associated with marinas, and agricultural and urban runoff.

Diver-obtained cores were taken by hand-forcing a 9 centimeter diameter, clear polybuterate pipe into the sediment to a depth of .25 to 1.00 meters. Ends of the core pipe and included sediment were covered with plastic caps and the core pipe withdrawn. As soon as the core was aboard the boat, it was measured, trimmed, sealed, labeled, and stored vertically for transport to the laboratory. In the lab the cores were frozen in a vertical position and freezer-stored until they could be subsampled.

Three deeper cores (3 to 4 meters in length) were taken at selected locations (Fig 5). These 9 centimeter PVC cores were obtained using a portable vibracore system mounted on the boat. These long cores were utilized to determine the pre-anthropogenic sediment characteristics and to determine rates and changing patterns of sedimentation within the estuarine system through time.

LABORATORY METHODOLOGY

Sediment Sub-Sampling Procedures

Analytical procedures were developed in accordance with the Quality Assurance/Quality Control Report submitted when the project was accepted for funding in June 1987. All procedures associated with sample preparation and storage were done in a trace-element clean manner for avoidance of sample contamination. Sub-sampling involved production of two sets of uniform and homogenous samples for the following purposes. The first sample set was used for the sedimentological lab analyses and is discussed in this section. The second sample set was prepared for chemical analyses and will be discussed in the next section entitled Chemical Analytical Procedures. All remaining sample material from both the sedimentological and chemical analyses have been archived for future reference and subsequent analyses. Following sub-sampling, the remaining core material was not saved due to lack of storage facilities.

For sub-sampling (Fig. 7), each core was allowed to thaw around the core liner until the solid sample could be extruded from the core liner. Cores were extruded horizontally into individual trays and allowed to completely thaw; pore waters were kept with the sediment as thawing occurred. The lithologic characteristics of each core were described. Two to four sub-samples of 10 cm thickness were obtained at vertical intervals down the core. Sampled intervals for every core included a surface sample containing the top ten cm of sediment and a bottom interval containing the lowermost 10 cm. If the core was longer than 30 cm, one or two additional 10 cm samples were obtained between the surface and bottom samples depending upon the core length and lithologic variability. Samples from each interval were homogenized and divided into two splits for sedimentologic and chemical analyses.

A total of 153 cores have been described and subsampled. This resulted in 344 subsamples distributed regionally as outlined in Table 6 and were analyzed as follows (Fig. 7):

a. Core and Sediment Description
b. Sediment Composition (% water, % organic, and % inorganic)
c. Grain Size Analysis (% sand, % silt, and % clay)
d. Chemical Analysis (Table 7)
    ICAPES (quantitative for 22 elements; Table 7)
    AA Spectrophotometry (quantitative for mercury; Table 7)
    Electrometric determination of fluorine based on specific ion electrode measurements (quantitative; Table 7)
    EDXRF (qualitative and semi-quantitative for 30 elements; Table 8).

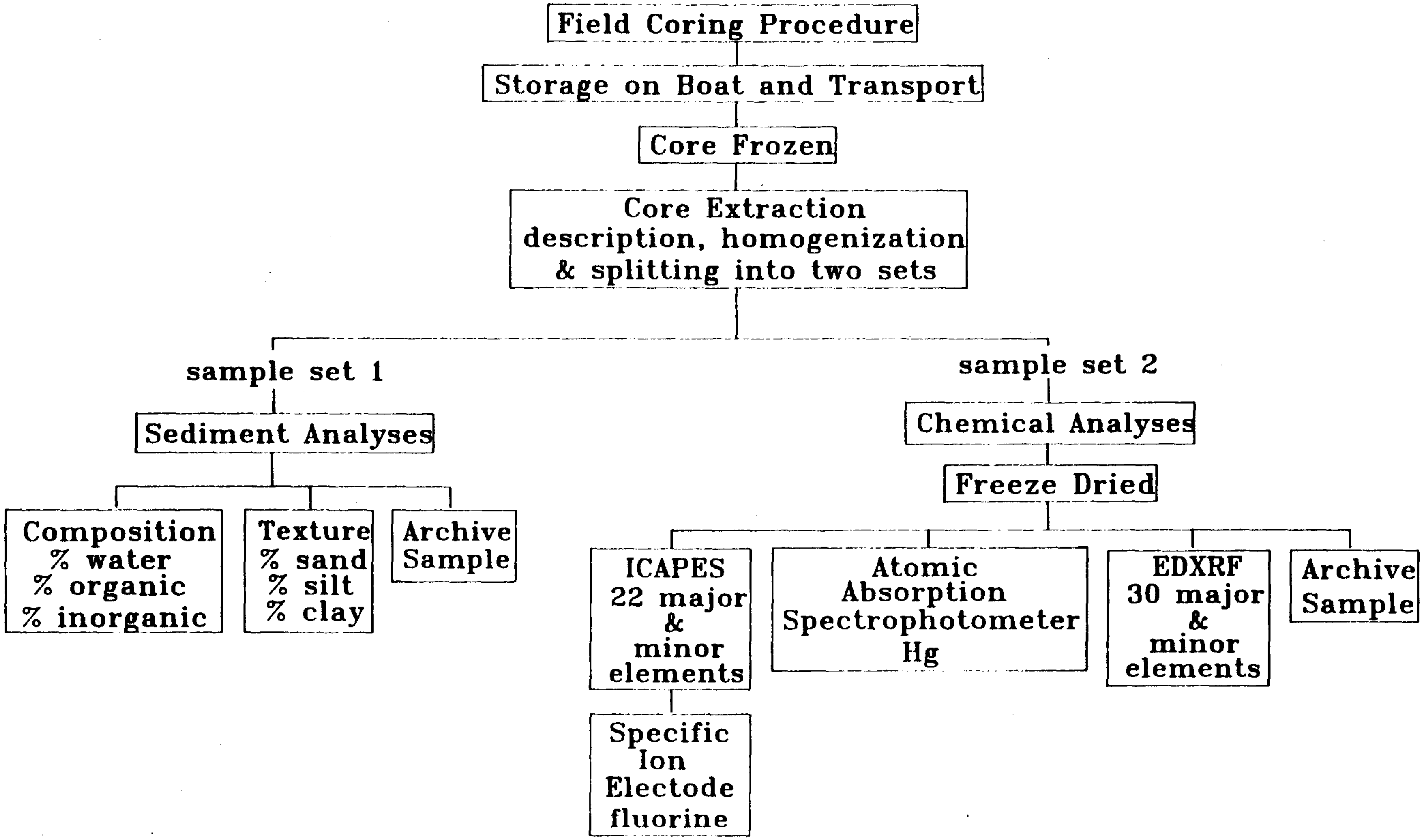


FIGURE 7. Flow sheet for sediment and chemical analysis of sediment cores

TABLE 7. Quantitative elemental analysis on mild leach extracts of sediment subsamples by ICAPES, AA spectrophotometry, and electrometric methods.

EPA PRIORITY POLLUTANT METALS	OTHER TRACE ELEMENTS	MAJOR ELEMENTS
Arsenic	Cobalt	Aluminum
Cadmium	Fluorine	Calcium
Chromium	Manganese	Iron
Copper	Molybdenum	Magnesium
Lead	Phosphorus	Potassium
Mercury	Selenium	Silica
Nickel	Silver	Sodium
Zinc	Titanium	
	Vanadium	

TABLE 8. Qualitative and semi-quantitative elemental analysis on total sediment by EDXRF.

EPA PRIORITY POLLUTANT METALS	OTHER TRACE ELEMENTS		MAJOR ELEMENTS
Arsenic	Barium	Bromine	Calcium
Cadmium	Cerium	Cesium	Chlorine
Chromium	Gallium	Iodine	Iron
Copper	Lanthanum	Manganese	Potassium
Lead	Molybdenum	Phosphorus	Silica
Nickel	Rubidium	Tin	Sulfur
Zinc	Titanium	Strontium	
	Vanadium	Yttrium	
	Zirconium		

Sediment Analysis Procedures

Water content of each subsample was determined by evaporation. Approximately 3 to 5 grams of thoroughly homogenized sediment was placed in a pre-weighed crucible and oven-dried at 95° to 105° C for at least 24 hours or until the final weight had stabilized. Water content was determined by subtracting the dry weight from the wet weight. Organic content was determined by placing the dried sediment in a muffle furnace at 385° C for at least 24 hours or until a constant final weight was achieved. The remaining ash was weighed and subtracted from the initial dry weight to yield the fraction of combustible organic matter in the sample.

Distribution of three major size fractions (sand, silt, and clay) in each subsample was determined using a modified pipet analysis procedure. Three to five grams of homogenized sediment were pre-weighed and transferred into a 120 ml plastic beaker with 20 ml of sodium oxalate and agitated to disperse the sediment. Following dispersion, the disaggregated sediment was rinsed with additional sodium oxalate solution through a 62.5 micron sieve into a 100 ml graduated cylinder separating sand-size material from the fines. Additional sodium oxalate was added until the volume in the graduated cylinder was brought to exactly 100 ml. The sieves were air dried for at least 48 hours and the sand content calculated by subtracting the empty sieve weight from the dry sieve weight containing the sand fraction. The remaining 100 ml mixture of sediment and sodium oxalate was carefully transferred into a 120 ml beaker and agitated until the sediment was suspended. Following a 15 second settling interval, 10 ml of suspension was withdrawn from the beaker with a pipet inserted 3/4 of the distance from the surface to the bottom of the cup. The suspension containing silt and clay-sized particles was transferred into a pre-weighed disposable polystyrene beaker and placed in a 95° to 105° C oven for 24 hours or until completely dry. The sediment was resuspended and allowed to settle for 22 minutes before a second 10 ml withdrawal was taken exactly 2 mm below the liquid surface. The suspension, now containing only clay sized particles, was transferred into a pre-weighed 10 ml disposable beaker and dried under the same conditions as the previous withdrawal. Four additional pre-weighed beakers were filled with 10 ml of sodium oxalate solution and allowed to evaporate in the 95° to 105° C oven. The dry weight of these beakers plus residue was used as correction for the weight contributed to the silt and clay samples by the oxalate residue. Silt and clay contents were calculated from the final dry weight of each beaker after being corrected for oxalate residues.

CHEMICAL ANALYTICAL PROCEDURES

Rationale for Analytical Procedures Utilized

Numerous attempts have been made to approximate "bioavailability" by identifying relationships between whole body or organ specific trace metal levels in biota to metal levels in the surrounding water and sediments (Pringle et al., 1968; Cross et al., 1970; Huggett et al., 1973; Valiela et al., 1974; Wharfe and Van Den Broek, 1977; Pesch et al., 1977). However, such studies usually develop an estimate of what is more accurately called "bioaccumulation" or "biomagnification" rather than "bioavailability".

Other investigators, concentrating exclusively on sediments, have applied various selective or sequential extraction schemes that are intended to identify the partitioning of elements among the various sedimentary phases previously identified (Chester and Hughes, 1966; Gupta and Chen, 1975; Engler et al., 1977; Agemian and Chau, 1977; Tessier et al., 1979; Salomons and Forstner, 1980; De Groot and Zschuppe, 1981; Mahan et al., 1987). Typically these extraction schemes are based on some variation of the following phase groupings:

1. Extraction with a salt solution to liberate metals at adsorption or ion exchange sites;
2. Mild acid treatment to free carbonate bound metals;
3. Reduction treatment to obtain oxide bound metals;
4. Nitric acid-peroxide treatment to release organic bound metals; and
5. Total digestion to soluablize all residual metals bound within the

Interpretations of the results of these various extraction procedures remains somewhat controversial (Kheboian and Bauer, 1987; Tessier and Campbell, 1988; Bauer and Kheboian, 1988).

A few investigators have attempted to look at both the composition of the organisms and associated sediments utilizing selective extraction procedures (Luoma and Jenne, 1976a, 1976b, 1977; Jenne and Luoma, 1977; Luoma and Bryan, 1979a, 1979b). The overall results from these studies are not unequivocal either. Still other investigators (Sinex et al., 1980; Cantillo et al., 1984) argue that the only true reference point for extractions that are to be used to make comparisons over time or between different systems is one that involves very vigorous attack of the sediment to result in a total or very nearly total digestion (such as hot nitric acid, hydrofluoric-boric acid mixtures, bomb digestions or fusion-dissolution techniques). It is argued that such a reference point is the only truly reproducible extraction that would allow for intercomparisons.

No matter what particular extraction procedure is followed, other than total or near total digestion, unless exacting specifications are described and followed, reproducibility or compatibility of the data suffers. Many small details that are seldom if ever published, are very important with respect to the results of an extraction. This includes such parameters as temperature; length of time of extraction; solid to solution ratios; and those things that affect the degree of agitation such as the particular agitation technique (e.g., magnetic stirrer, reciprocating shaker, wrist action shaker, etc.) speed or excursion rates for each of these, volume of the extraction compared with the vessel size, etc.

However, with appropriate control over all such laboratory aspects, the level of reproducibility needed for intercomparison purposes can be achieved. Of course, the less complex the procedure, the easier it is to exercise the necessary control. The results obtained with the procedure utilized in this study support this contention. The extraction procedure applied in this study was based on compromises among the following scientific as well as practical considerations: 1) cost effectiveness, 2) probability of future use, 3) reproducibility, 4) capability for determining a) the anthropogenic derived fraction and b) the bioavailable fraction.

This study is not the first to investigate heavy metals in the Albemarle-Pamlico Estuarine systems. However, the purpose and sheer scope of this research project guarantees that it will serve as an important base-line or reference study against which future data both from within this system as well as from other estuarine systems will be compared. Any analytical extraction procedure that is intended for potentially widespread, routine application by other investigators and by governmental research and regulatory agencies must, of necessity, be cost effective. It must also be sufficiently easy to perform that it can be readily applied in more than the rare "research" setting. No sequential extraction procedures are characterized by these two criteria; every added extraction step requires an added analysis step with its associated costs in manpower, instrument time, and reagents.

An absolute differentiation between naturally derived and anthropogenically derived trace metals in sediments is likely never to be possible. However it can be argued that, because of both time (on a geological reaction scale) and the nature of most imputs (as discharges of dissolved metals into the water column), the fraction of the total that is anthropogenically derived is likely to be present in those phases subject to attack by milder extraction techniques. Anthropogenic metals are not likely to be incorporated into the mineral or crystallographic lattices; likewise, metals that are biologically available are not likely to be incorporated into the mineral or crystallographic lattices. Consequently, a milder extraction that would liberate metals from pore water, easily exchangeable sites, carbonates (which are more readily formed and highly suseptible to pH conditions both in the environment and in digestive tracts of organisms), chelated in surface organic coatings, and coprecipitated with iron oxy-hydroxy precipitates, would more accurately model anthropogenic and bioavailable metals.

Like all such procedures, this is a defined procedure and is intended for use as a first approximation only. No claims are made as to the absolute meaning of the results, which are expressed as micrograms of element extractable from a gram of freeze dried sediment. No accounting is made for potential redistribution (i.e., solubilization from one phase with subsequent occlusion by some means into another) during the extraction process. The procedure is a slight modification of one described by W.S. Boothman (pers. comm., Jan. 1988) that has been applied by the U.S. EPA in Narragansett Bay and Booth Bay Harbor. It involves extracting 2.5 g dry sediments with 50 ml of 2N nitric acid for two days at room temperature with but very little agitation.

Although we have yet to find any other investigations which describe the action of a HNO_3 extraction exactly like this one, Pickering's (1986) comprehensive review article describes:

1. The extraction recovery of 0.1N HNO_3 on Zn, Cd, Pb, and Cu from various clay matrices for which the metals were loaded onto the clays from 10^{-4} M M^{+2}Chloride solutions and
2. The extraction recovery of 1N HNO_3 on the same metals loaded in the same fashion onto various humic, carbonate, and hydrous oxide phases.

With but one exception (Zn on montmorillonite extracted at pH 5 with 0.1N HNO_3), recoveries were all at least 50% of the loaded amount, and usually much greater. It was further pointed out by Pickering that 1N HNO_3 was effective in dissolving out most of these same metals present in soils augmented with sewage sludge. Based on the foregoing arguments, the 2N HNO_3 extraction procedure appears to meet all the criteria regarding cost, probability of use, reproducibility, as well as ability to approximate the anthropogenic and bioavailable fractions.

Sample Pre-Treatment

Though freeze drying may have some effect on the natural particle size characteristics of the sediments, the weighing of dry samples is much more accurate and reproducible than weighing them wet. In addition, these sediments were frozen for storage as cores, therefore any disruption that might have take place from the freezing process had already done so. Large particles such as shells, rocks, and twigs were removed from the core subsamples; the remainder of the sample was thoroughly homogenized and placed in plastic containers for freeze drying. Subsamples were frozen and placed in the lyophilizer till dry. The dried mass was broken up by mild stirring with a plastic spatula to thoroughly loosen all particles and to homogenize the dried material; no attempt was made to reduce the natural grain sizes. The intent was for extraction to proceed with as nearly the same particle size and surface area characteristics as occurs in the natural state.

Extraction Procedures

Samples for ICAPES analysis were processed utilizing a mild extraction technique as delineated by W.S. Boothman of the US EPA ERLN at Narragansett, R.I. (pers. comm., Jan. 1988). A 2N HNO_3 extraction procedure was utilized for chemical analysis of all Pamlico River estuarine samples.

A. Equipment

1. 120-mL urine specimen cups with lids (Fisher Brand, cat. no. 14-375-112A).
2. 50-mL graduated cylinder.
3. 50-mL syringes with Luer-Lok fitting (B-D).
4. 0.45-um disposable syringe filter assembly (Gelman Acrodisc-CR TFE filters #4219).
5. 50-mL plastic centrifuge tubes with caps.

B. Reagents

1. 2N HNO_3: 252-mL concentrated double distilled HNO_3 (GFS Chemicals, Columbus, OH) diluted to 2 L with high purity water.

C. Procedure

1. Weigh 2.500 g ± .005 g of freeze dried sediment into urine specimen cup.
2. At Hour 0 (Normally starting at 0830 in order to fit the schedule into regular working days) add 50-mL of 2 N HNO_3 to the sediment. CAUTION: Some sediments contain large amounts of shell material ($CaCO_3$) that react vigorously with the acid. First add a few mLs of acid to test for this situation. For those samples containing considerable $CaCO_3$, add the remaining acid slowly in 5 to 10-mL increments after the reaction has subsided.
3. After the acid has been added to all samples in a manageable batch (20 to 40 samples), swirl each sample five (5) times to thoroughly wet and suspend the sample in the acid.
4. Repeat the swirling step above at the following times
    a. Hour 4.5 (Same day 1300)
    b. Hour 8.0 (Same day 1630)
    c. Hour 24 (Next day 0830)
    d. Hour 28.5 (Next day 1300)
    e. Hour 32 (Next day 1630)

    CAUTION: It is important that the elapsed times at which these activities are begun be kept within ± 30 min. Repeatability of the extractions is an important requirement that can only be achieved with close adherence to the times and duration of these activities.
5. Promptly at Hour 48 (0830 of the third day) filter the samples.
    a. Using the 50-mL syringe, withdraw the plunger (in air) to about the 10 to 15-mL mark. This is to prevent contact

between the solution and black rubber tip of the plunger (an excellent source of metal contamination, especially Zn).

b. While keeping the barrel vertical, carefully insert the tip of the syringe into the solution and withdraw as much solution as possible.

CAUTION: i. Be careful to minimize the amount of sediment disturbed and drawn into the syringe: too much sediment in the barrel will clog up the filter. ii. Be careful to minimize contact between the solution and the black rubber tip of the plunger.

c. Remove the syringe from the cup, wipe off the excess material from the end of the syringe and clear the LuerLok tip by expelling a few drops of solution from the syringe.

d. Affix an Acrodisc filter to the Leur-Lok tip and expel the solution through the filter. Discard the first 2 to 3-mL and collect the rest into a 50-mL plastic, centrifuge tube appropriately labeled. In order to speed up the filtering process and minimize strain to the operator's hands, it is recommended that some type of syringe filtering aide be used at this step.

e. Cap the tube, mix by inversion 2 to 3 times, and save till analysis.

f. Rinse out and air dry the 50-mL syringes for future use but discard the filter.

6. Note: over the course of analyzing the eleven batches of samples in this study (a period spanning six months time) room temperature for the extraction varied from approximately 19° to 24° C.

Comparison of Extraction Procedures

The study of trace metals in the Pamlico River estuarine sediments was based on a partial dissolution/extraction procedure utilizing 2N HNO_3. It is essential to evaluate and compare the results obtained by this extraction procedure with results of similar studies.

The International Council for the Exploration of the Sea (ICES) recently sponsored an intercalibration exercise between more than 40 laboratories world-wide (Loring and Rantala, 1988). Participants analyzed replicate digests of three samples for concentrations of Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Ti and Zn. ICES utilized a total metal analysis (HF + aqua regia), a mercury analysis (HNO_3 + H_2SO_4), and three partial dissolution-extraction procedures including 1) aqua regia (HNO_3 + HCl), 2) 1N HCl, and 3) 25% (v/v) acetic acid (HOAc).

Figure 8 compares the means of results obtained by the various partial extraction procedures obtained by ICES and the Pamlico study; both sets of results are compared with analysis of the NBS Estuarine Sediment. These comparisons indicate that procedures used in the Pamlico study are most similar to extraction procedure two with 1N HCl; aqua regia dissolves significantly more metals and 25% acetic acid is slightly weaker. Loring (1981) suggested that the 25% acetic acid approach, was least likely to release metals bound in aluminosilicate mineral lattices; thus, this approach may represent material potentially available to biota. It is likely the 1N

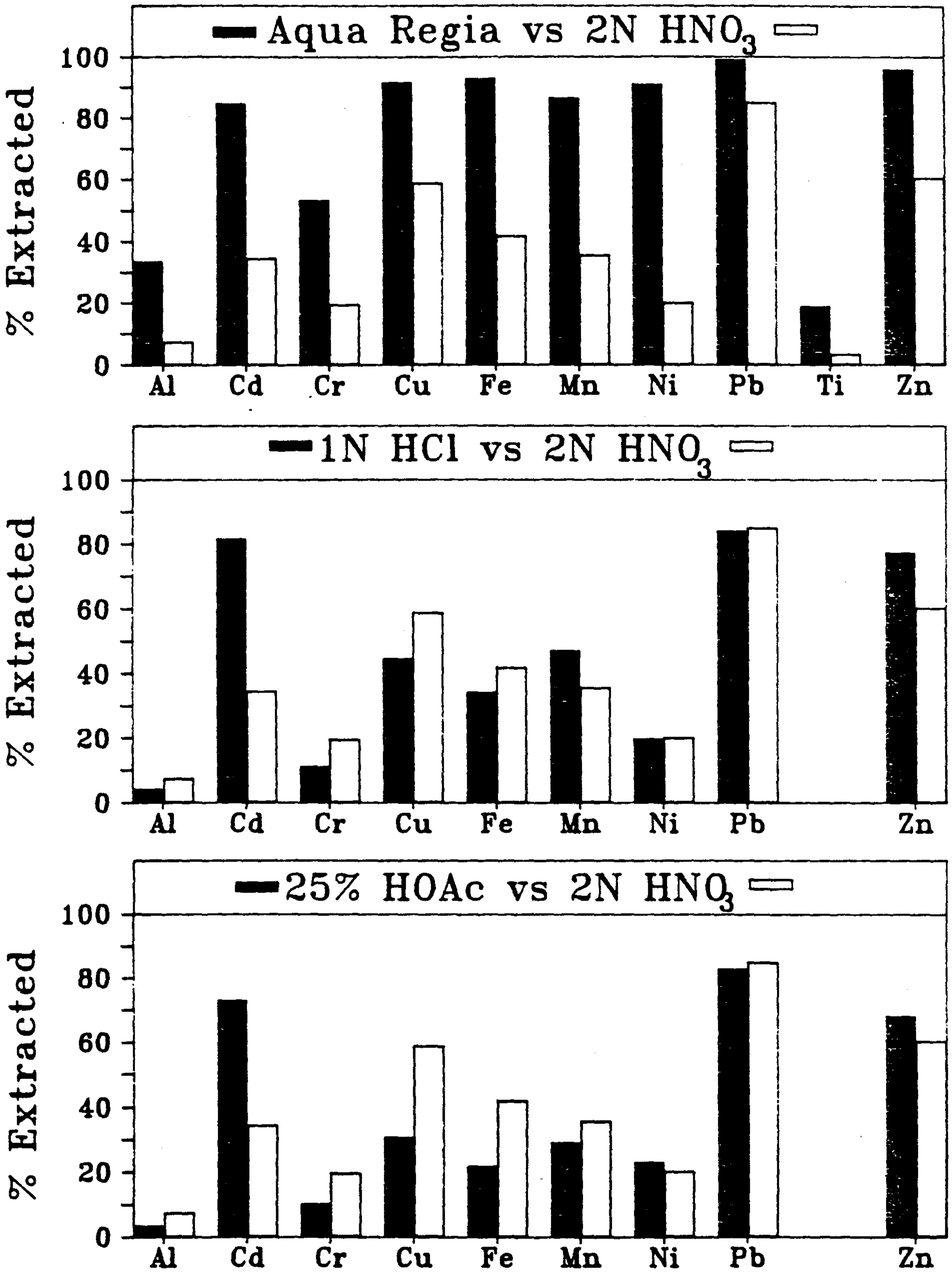


FIGURE 8. Comparison of means of results obtained by various partial extraction procedu by the International Council for Exploration of the Sea (Loring and Rantala, 1988) and this Pamlico River study

HCl and 2N HNO_3 extraction procedures release some metals from aluminosilicate minerals, especially considering the relatively high values of aluminum found in both the ICES and Pamlico samples. Consequently, the Pamlico results may overestimate, and almost certainly represents maximum amounts of metals potentially available to biota.

Figure 9 shows another comparison between the technique utilized in the Pamlico study and that used in a heavy metal pollution study in sediments one mile seaward of the Los Angeles wastewater-treatment outfall (LAWWTO) (Bruland et al., 1974). The latter study utilized a partial extraction procedure of 25% acetic acid in hydroxylamine hydrochloride (NH_2OH HCl) and 30% hydrogen peroxide (H_2O_2). Figure 9 also contains metal results for sediments from basins off Southern California (SC Basins) and the National Bureau of Standards estuarine sediment (NBSES). Sediments from the SC Basins were dated using radioisotopes indicating that they predated significant human influence.

Data in Figure 9 indicate a similarity in percent metals extracted between the LAWWTO (Bruland et al., 1974) and Pamlico studies, as indicated by the NBSES plot. Partial extraction procedures utilized in the Los Angeles study undoubtedly recovered heavy metals in the sediments derived from a known point source, the wastewater-treatment outfall. Similarities in percent extracted between the Los Angeles and Pamlico studies, indicates that the approach utilized in the Pamlico study should be able to determine anthropogenic inputs of heavy metals to the sediments.

ICAPES Analyses

The inductively coupled-argon plasma-emission spectrometer (ICAPES) used for the major analyses in this project is a Jarrell-Ash Plasma AtomComp (Mark II System), modified with the Ward Scientific, Ltd., WICS and MDA (Multiple Data Aquisition) hardware and software upgrades. Analyses are made with a simultaneous, five-point scan of all element profiles in order that sufficient information is obtained to provide on-peak and off-peak (baseline) readings for each element. The system is calibrated with appropriate matrix matched multi-element standards and corrections are made for inter-element interferences. Table 9 presents a list of the elements along with their analytical wavelengths (in nm) that were used in the ICAPES analyses.

ICAPES analyses for the Pamlico River estuarine system consisted of 11 batches that included 357 samples and 81 controls that were subjected to the HNO_3 extraction. The 81 controls represent blanks and internally prepared reference samples as well as several external, previously analyzed reference standards.

Control Samples

The first internal control sample, identified as APESA, was prepared by freeze drying a large sediment sample from the Pamlico River (at marker 16 near Whitchard's Beach). The dried sediment was dispersed in the fashion described above for samples and was mixed by tumbling for several minutes prior to taking subsamples. Two additional, but smaller, internal control samples, identified as APESB and APESC, were prepared from two additional sediment samples. Because the APESA control was being consumed more rapidly

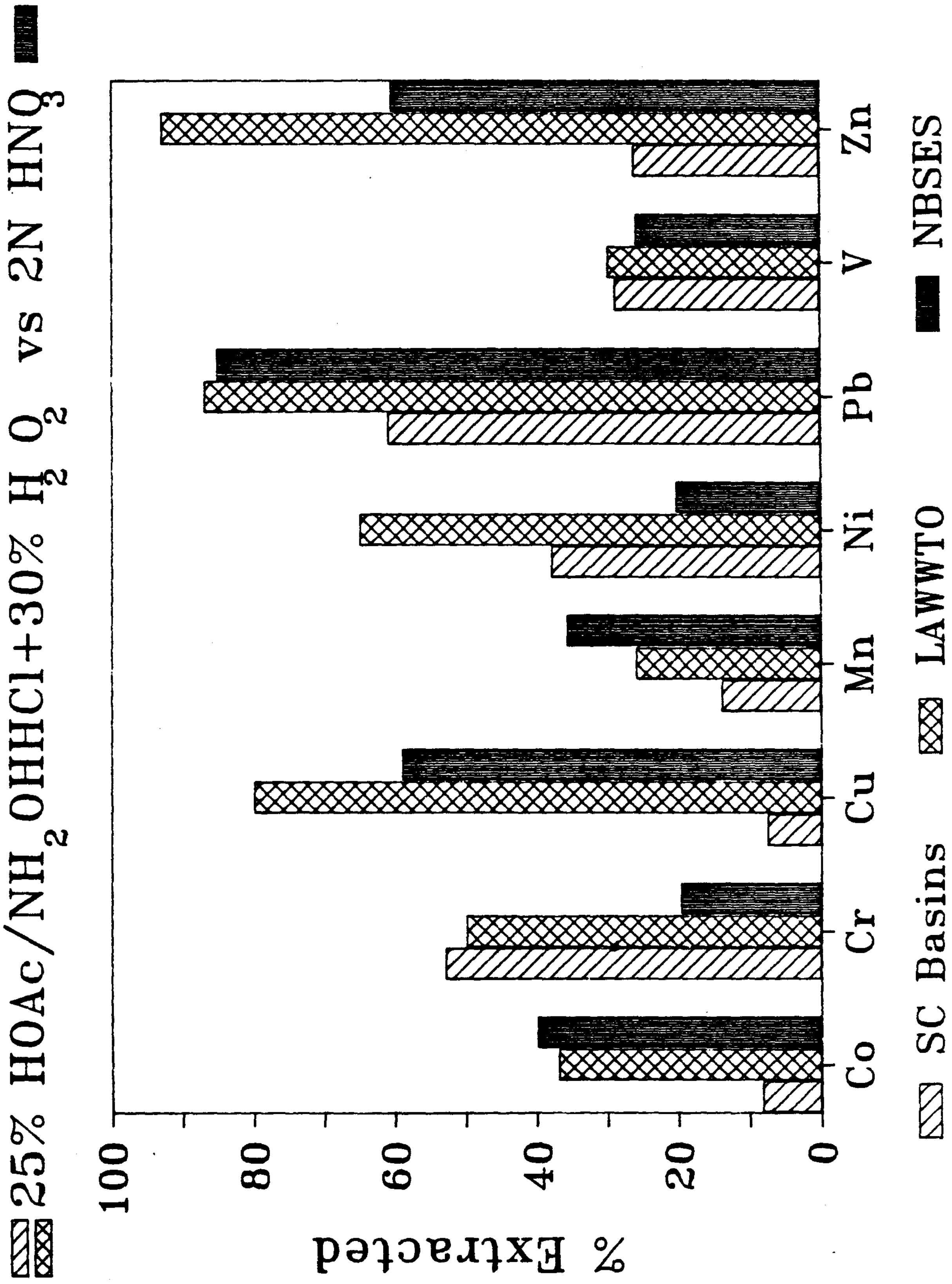


FIGURE 9. Comparison of means of results obtained by a partial extraction procedure for metal pollutant studies off the Los Angeles waste water treatment outfall (Bruland et al., 1974), southern California offshore basins, and the National Bureau of Standards estuarine sediment standard

TABLE 9. Analytical wavelengths (in nm) for 22 elements analyzed by ICAPES.

Ag	Silver	328.0	Mn	Manganese	257.6
Al	Aluminum	308.215	Mo	Molybdenum	202.0
As	Arsenic	193.6	Na	Sodium	588.99
Ca	Calcium	317.9	Ni	Nickel	231.6
Cd	Cadmium	228.8	P	Phosphorus	214.9
Co	Cobalt	228.6	Pb	Lead	220.3
Cr	Chromium	267.7	Se	Selenium	196.0
Cu	Copper	324.7	Si	Silicon	288.1
Fe	Iron	259.9	Ti	Titanium	334.9
K	Potassium	766.5	V	Vanadium	292.4
Mg	Magnesium	383.2	Zn	Zinc	213.8

than originally envisioned, it became necessary to prepare a larger internal control sample. APESD control was a Pamlico River composite sample that was freeze dried and passed through a 60 mesh polyester screen with gentle rubbing. Particles that did not pass through the screen were discarded. Sieving was used since there were several different types of sediments and an overall finer grain size lends itself to greater homogeneity. The resulting 1.5 kg sample was tumbled for nearly 20 hours on a Patterson-Kelly, twin shell, dry blender. It was then split into nine 250-mL plastic bottles. This control, identified as APESD, lasted through the completion of this project. In order to provide information on more accessible and universal standards, two National Bureau of Standards sediment standards (SRM 1645, Riverine Sediments and 1646 Estuarine Sediments) were also analyzed.

Reproducibility and Limit of Quantitation

The instrumental lower limit of quantitation, or lower limit of detection, is defined for purposes of this study as three times the standard deviation about the blanks, expressed in the same concentration terms as the samples (viz., µg/g extractable). Overall reproducibility for the entire analytical process, including actual precision of the instrumental measurement combined with precision of the extraction process was determined by running triplicates of either APESA or APESD with each analytical batch. Six replicate runs of APESB, APESC, NBS Estuarine Sediments and four replicate runs of NBS Riverine Sediments were made throughout the eleven batches. Table 10 presents the estimate for the lower limit of quantitation (LLQ = 3 X s.d. about blanks) as well as both the mean and two times the standard deviation about the means for both APESA and APESD. The larger of these two values (marked with an asterisk) is taken as the estimate of overall reproducibility. Overall, blanks were low for most elements except Cd, Hg, and Se (Table 10). Table 11 presents the means and two times the standard deviation of APESC, APESD and the two NBS standards.

TABLE 10 Lower limit of quantitation and reproducibility for ICAPES. The * indicates the overall reproducibility value utilized in this study (larger of the two values).

	LLQ	REPRODUCIBILITY			
	(3 X s.d. about blank)	APESA (n = 19)		APESD (n = 15)	
Element	(µg/g)	mean (µg/g)	2 X s.d. (µg/g)	mean (µg/g)	2 X s.d. (µg/g)
Ag	0.32	0.1	0.1	0.1	0.3*
Al	9.78	5944	437*	3808	243
As	2.32	9.4	4.0	8.8	5.2*
Ca	19.60	1894	162	5815	352*
Cd	0.50	0.2	0.1	0.4	0.3*
Co	0.24	5.4	0.4*	4.0	0.3
Cr	0.22	10.2	0.6*	6.7	0.4
Cu	0.26	12.2	0.5	9.2	0.7*
Fe	4.72	11780	701*	8927	456
K	45.05	735	43.1	463	178*
Mg	35.69	2121	106*	1312	91.3
Mn	0.88	85.6	4.7*	77.0	4.2
Mo	0.33	0.3	0.2	0.4	0.7*
Na	9.76	4924	270*	1985	126
Ni	1.14	0.7	0.3	0.9	0.7*
P	17.99	663	36.8	598	110*
Pb	1.62	45.5	2.0	28.1	4.0*
Se	1.08	-0.6	4.1	-1.5	4.2*
Si	26.16	1248	69.6*	1109	60.5
Ti	0.38	37.9	1.7	30.0	1.7*
V	0.23	24.5	0.9	15.3	1.0*
Zn	1.20	75.4	3.2	54.3	3.2*

TABLE 11 Means and 2 X s.d. (μg/g extractable) for accessory control samples.

	APESB (n = 6)		APESC (n = 6)		NBS Estuarine (n = 6)		NBS Riverine (n = 4)	
Element	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
Ag	0.0	0.1	0.1	0.1	0.0	0.0	0.9	0.1
Al	6467	492	5985	600	4825	500	3226	89.1
As	10.8	3.0	12.6	5.6	13.9	2.8	78.7	4.2
Ca	1553	83.8	2154	179	3150	166	27100	1409
Cd	0.1	0.1	0.2	0.2	0.1	0.1	7.5	0.4
Co	4.9	0.3	5.3	0.2	4.2	0.2	12.0	0.8
Cr	8.7	0.5	9.3	0.4	15.3	0.9	Off scale, high	
Cu	10.8	0.5	11.5	0.6	10.8	0.7	89.0	2.2
Fe	16160	1132	16160	1410	14190	800	34920	2000
K	731	47.5	1205	57.8	2003	152	178	10.5
Mg	2047	118	3308	155	5114	208	6274	126
Mn	88.0	5.1	149	6.5	136	7.0	373	12.0
Mo	0.4	0.2	0.7	0.2	0.8	0.1	11.8	1.3
Na	4764	322	10540	738	9679	599	958	32.4
Ni	0.6	0.3	2.2	0.5	6.8	0.9	22.2	0.7
P	603	18.8	967	32.3	353	22.3	314	11.2
Pb	36.4	1.9	42.3	2.9	24.3	1.2	538	13.7
Se	-0.2	4.4	-1.3	6.7	-0.5	3.1	1.5	5.8
Si	1305	55.1	1184	61.9	1324	28.8	2148	66.7
Ti	42.1	2.5	29.1	1.4	187	13.0	50.8	2.3
V	29.5	1.5	22.2	0.6	25.0	2.1	12.1	1.1
Zn	52.3	2.0	63.7	2.0	84.7	5.0	Off scale, high	

Accuracy

Instrumental accuracy was estimated during two separate runs. Unspiked levels of the elements were determined on the replicate APES controls, element spikes were made to additional replicate controls after the extractions were complete and the percent recoveries were calculated. Spikes were made at two different levels for all of the elements analyzed. Average percent recoveries from the second of the two runs (the more complete of the two) are presented in Table 12.

NBS References Standards

Table 12 lists the total elemental concentrations reported on the certificates of analysis for the two NBS standards, as well as the average percent of these values recovered by the extraction procedure utilized in this study. It should be pointed out that total recovery of the elements is not expected since the certificate values are based on total digestion techniques whereas extraction procedures utilized for this study represent a much milder treatment. These values are given to provide data on reference materials widely available to other workers.

Comments on Quality of Analytical Numbers

In general, overall quality of the values obtained in this study is quite good. Accuracy, as estimated from the recovery of spikes (Table 12), is within ± 10% of 100% recovery except for As and Ni. The slight error for As reflects the 1) inter-element effects of Fe and Al on the As emission line and 2) complexities of correcting for multiple interferences, especially since Fe and Al occur at very high and quite variable concentrations. The low recovery for Ni is still problematical. However, since the recovery results are quite consistent and the primary interest is in relative changes rather than absolute levels, the Ni concentrations were not corrected for the recovery error.

With only a few exceptions, reproducibilities are within ± 10% of measured values. Effects of Fe and Al are also observed in the values for As, Mo, and Se. The very low levels measured for Ni contribute to the proportionately higher variance. Similarly, values computed for the lower limits of quantitation appear reasonable. It should be pointed out that evidence from the various control runs, suggests that the LLQ reported for Cd may be erroneously high. This matter is under study.

Se and Ag are the only elements for which the results are uniformly poor. Many individual values are negative indicating a potential over-correction for interference. Standard deviation (hence uncertainty) about every group of replicates is significantly greater than any value reported.

Extractable levels for each element are quite repeatable for a given sample. However, results of extractions between the two NBS standards (Table 12) indicate high variability between different sediment types with respect to the percentage of a total element present that is solubilized and held in solution by the extraction procedure. For nearly every element, large differences in the percent extracted are observed between the two NBS standard samples. This is due to a very significant difference in sediment

TABLE 12 Accuracy estimates (as % recovery of spikes) and % of total element extracted from NBS standards. Note that certificate values (#) are based upon total digestion techniques, whereas % of total recovered (@) for this study is expected to be small and variable due to utilization of much milder extraction techniques. n.r. = not reported; N.R. = Not Reportable (either below zero or off scale high); and ( ) = non-certified or suggested value.

		NBS Estuarine (n = 6)		NBS Riverine (n = 4)	
Element	Average% Recovery on Spikes	Total # (µg/g)	% of Total @ Recovered	Total # (µg/g)	% of Total @ Recovered
Ag	90	n.r.	--	n.r.	--
Al	102	62,500	8	22,600	14
As	112	11.6	120	(66)	119
Ca	97	8,300	38	(29,000)	93
Cd	96	.36	28	10.2	73
Co	96	10.5	40	10.1	119
Cr	97	76	20	29,600	N.R.
Cu	100	18	59	109	82
Fe	102	33,500	42	113,000	31
K	100	(14,000)	14	12,600	1.4
Mg	100	10,900	47	7,400	85
Mn	93	375	36	785	47
Mo	95	(2.0)	40	n.r.	--
Na	100	(20,000)	48	5,400	18
Ni	79	32	21	45.8	48
P	97	540	65	n.r.	--
Pb	94	28.2	86	714	75
Se	107	(0.6)	N.R.	(1.5)	N.R.
Si	92	(310,000)	0.4	n.r.	--
Ti	97	(5,100)	3.7	n.r.	--
V	96	94	27	23.5	51
Zn	92	138	61	1,720	N.R.

type in the two standards which is reflected in the total quantity of major elements (Al, Ca, Fe, Na, and others) present.

An additional study involved spiking the extraction solutions before they were mixed with the control sediments then determining the recovery of these spikes. For some elements the recoveries were considerably different from those reported in column 2 (Average % Recovery on Spikes) of Table 12. Such results coupled with those described above for the NBS standards illustrate inherent problems in applying too simple an interpretation to results of this or any other extraction procedure. Not only are there differences in actual solubilization processes but there are undoubtedly differences between resulting solutions in what remains in solution. Reprecipitation or other equilibrium losses (to exchange sites or organic chelates, etc.) occur which causes a redistribution of elements among the insoluble phases. Such reactions may be very dependent on concentrations of the major elements. All of these matters are under active investigation at the present time.

AA Mercury Analysis

Atomic absorption spectrometry is being utilized for the mercury analyses. We adopted EPA's Method 245.5 (manual cold vapor technique for mercury in sediments) based upon "Methods for the Chemical Analysis of Water and Wastes" Procedural Manual (EPA, 1979) with slight modifications. The modifications involved the 1) use of a commercially available cold vapor generator (IL model AVA 440) rather than the arrangement originally described, 2) use of one gram of sample (because of the low concentrations expected), and 3) a slight alteration of the temperatures and times for heating. The first heating step as originally described was two minutes at 95°C. Unless a water bath of considerable dimensions is available, only two or three bottles can be inserted without significantly lowering the temperature for an extended period of time. This was not conducive to the analysis of many samples, at least not on a batch basis in which all of samples and controls in a particular batch are exposed to the same treatment. The same was true for the second heating step which called for 30 minutes at 95°C. The times were changed to 15 and 60 minutes, respectively and the temperature was changed to 50°C. This made it possible to use a larger water bath with better control.

Since we had reasoned that a "mild" extraction procedure would suffice for the characterization of the other elements, it was decided that a "mild" extraction procedure would suffice for Hg as well. All samples that were extracted and analyzed by ICAPES were also analyzed for Hg by this modified technique. Repetitive analyses on 30 APESA controls (two of which were rejected as outlyers) and 64 APESD controls indicate a lower limit of quantitation and an uncertainty about any one given analysis (defined as 2 X s.d. about the mean of these controls) of approximately 0.5 µg/g Hg extractable. This indicates that results for many samples fall below quantitative limits.

Due to the possible inability to detect methyl mercury at the lower temperature, EPA has recently suggested that we carry out intercomparison tests. These tests have been initiated to determine what differences in Hg levels, if any, might arise from the introduction of time/temperature modifications into Method 245.5. The results of any corrections or sample reanalyses that may come out of these tests will be made known as soon as possible.

Electrochemical Fluorine Analysis

An electrometric method was used for determination of extractable fluorine. This analysis was based on specific ion electrode measurements in a procedure adapted from standard F^- electrode techniques. Extractable F^- was analyzed in the acid extracts for each sample remaining after the ICAPES analyses. These acid extracts had to be diluted 1:200 in order to minimize the Fe and Al interference in the fluoride analysis; consequently, the lower limit of quantitation is at about 30 ug/g extractable. Nevertheless, a sufficient number of samples reported high enough concentrations that areas of relatively high extractable F-concentrations were delineated.

EDXRF Multi-Element Analysis

All 344 sub-samples have been analyzed as total sediment for elemental composition on the KEVEX 0600 Ultratrace EDXRF system. This energy dispersive x-ray fluorescence spectrometry analysis simultaneously provides qualitative and semi-quantitative estimates of 30 elements, ranging in atomic number from aluminum through uranium. These results are useful in identifying major changes and trends in the samples and are helpful in interpreting results from the ICAPES analyses. Analytical results are included in the computer data base but are not included in this report.

DATA ANALYSIS

Statistical Analysis

Data from sediment and chemical analyses were compiled and merged with data collected in the field and during laboratory subsampling and processing using a combination of Statistical Analysis System (SAS) programs and Symphony worksheets and data bases. Each sample number has a location with respect to latitude and longitude, LORAN-C coordinates, and name of water body (tributary name or segment of river). Additional information assigned to each sample number includes depth below sediment/water interface, hydrographic parameters (water depth, salinity, and temperature), concentrations of 24 elements (major, minor and trace elements), organic content, and concentrations of sediment size components (sand, silt, and clay). This data is stored in data bases on the ECU's IBM 4381 mainframe computer with backup copies stored on PC hard disks and floppy disks. These data can be transferred to other formats via 7-bit ASCII format files.

Simple statistics (mean, standard deviation, maximum and minimum values, etc.) were calculated for all samples (computer data base) and for groups of samples within individual tributaries or river segments (computer data base). These analyses provide for stratigraphic, sedimentologic, and regional comparisons in sedimentological and elemental concentrations. Results of these statistical analyses are presented and discussed in subsequent sections. Correlation coefficients were calculated for all combinations of sedimentological and chemical variables to evaluate simple linear relationships among the parameters. This procedure was applied to the data as a whole, by stratigraphic position, by major lithologic group, and regionally by tributary and river segment.

Contour Mapping of Data

Contour maps were assembled to provide a graphical illustration of the spatial distribution of metal concentrations in the sediment samples. Data for the maps was processed using the following procedure. Results of chemical analyses (reported in ug/g or ppm) were merged with the location data for each site. Samples representing the surface sediments at each site (from the surface to -10 cm) were sorted for the data set and a trimmed mean concentration for each element was calculated. The trimmed mean was obtained by eliminating all samples with concentrations greater than 2 standard deviations from the mean. This technique provides realistic background mean concentrations for each element that represents modern sedimentation concentrations within the Pamlico estuarine system; it specifically excludes extreme values resulting from anthropogenic inputs and the influence of relict sediments.

Elemental concentrations for each individual sample within the study area were then ratioed to the trimmed means to yield enrichment factor ratios that are either positive or negative with respect to the trimmed mean. Enrichment factor is often used differently in the geochemical literature. For example, Zoller et al. (1974) and Bruland et al. (1974) develop enrichment factors by ratioing the element to either Fe or Al within the analyzed air, water, or sediment and to some reference material such as crustal abundance. In this procedure, Fe or Al are used as normalizing factors because anthropogenic sources are generally considered to be negligible; therefore, the primary source would be from crustal weathering. The advantage of utilizing this definition is that it minimizes variations due to grain size of the sediments. Harding (1974), in a trace metal study of the middle Pamlico River area, normalized their elemental data to the concentration of clay plus organic matter. This resulted in an enrichment inversion whereby the highest anomalies occurred in the shallow waters dominated by quartz sand sediments. The small amount of mud that occurs within these quartz sand environments may be richer in metals; however, there is so little mud that it becomes insignificant with respect to the metal concentration in the total sediment.

An evaluation of the correlation coefficients in the present study demonstrated a generally strong correlation of metal concentration to the percent of fine-grained sediment fraction relative to sand within the Pamlico River system. However, generally most metals lacked a significant correlation between metal concentration and organic matter or clay content. Table 13 shows the wide variation of both organic matter and clay constituents within the most and least polluted portions of the system.

Application of general correction factors based upon metal/iron and metal/aluminum ratios, similar to Zoller et al. (1974) and Bruland et al. (1974), is not appropriate for this study. Such enrichment factors are utilized with results obtained by total digestion techniques; however, this study utilized a partial extraction procedure and it is not known how reproducable the percent extraction for each metal is for different sample

TABLE 13. Comparison of organic and clay concentrations within the surface sediments of the most and least polluted portions of the Pamlico River estuarine system.

	% ORGANIC MATTER			% CLAY-SIZE PARTICLES		
	Mean	Range	SD	Mean	Range	SD
MOST POLLUTED AREAS						
Kennedy Creek	22	16-29	4.7	20	5-37	7.5
Whichards Creek	11	10-12	1.8	34	26-42	11.5
Middle Pamlico River	10	1-44	6.6	46	4-70	17.0
Broad Creek	10	7-12	2.0	48	30-58	10.6
LEAST POLLUTED AREAS						
Chocowinity Bay	16	5-43	13.7	14	5-47	16.3
Mixon Creek	13			32		
Durham Creek	10	8-12	2.3	44	35-49	7.4
Outer Pamlico River	7	1- 9	2.4	52	30-89	19.5

types. In addition, the sedimentological data suggest that 1) different parts of the River and adjacent tributaries operate independently of each other, 2) metals are generally concentrated within the mud sediments, and 3) local enrichment is primarily related to anthropogenic sources rather than natural variations in concentration between organic matter and the clay component. Also, if a specific metal has relatively high concentrations within the natural system and is released by the partial digestion procedure used in this study, it is in theory equally "bioavailable" and represents as great a potential problem as anthropogenic metals.

The enrichment factors, along with latitude and longitude, are then entered as xyz coordinates into files processed by a computer mapping program entitled SURFER (Golden Software, Golden, Co.). SURFER produces three-dimensional representations of surfaces consisting of xyz coordinates. The x and y data are longitude and latitude, respectively and z value is the enrichment factor. An inverse distance square method, or in some cases inverse distance cube method, was used to interpolate z-grid values between points. Sparseness of data points in some portions of the study area necessitated use of a splinning procedure or artificial thickening of the grid matrix to obtain reasonable results. Adjacent land areas were given a z value of close to zero so that no contours would be plotted in these regions. Each surface was contoured at appropriate contour intervals and shaded to clearly show the distribution of each range of z values.

Portions of the Pamlico River estuarine system that contain one or more sample sites with critical elements that are at least 2X enriched over the trimmed mean, are defined as areas of concern. Maps were produced for most elements that had enrichment factors of 2X or greater within each of the nine areas of concern. Only 11 representative maps are included within this report as examples of specific critical elements within the major areas of concern.

RESULTS

Estuarine Morphology and Sediment Composition

Table 14 summarizes the sediment particle size and composition for 344 subsamples analyzed throughout the Pamlico estuarine system. Note the extremely high, but variable concentrations of both organic matter and clay components. The distribution, concentration, and composition of these two components appear to be the most important factors in determining a) which metals are concentrated in the sediment, b) specific levels of metal concentration, c) chemical state of the metals, and d) chemical availability to the biological system. However, these factors are poorly understood at present and are a major part of ongoing research efforts.

TABLE 14. Summary of sediment composition and particle size for subsamples of the Pamlico River estuarine system.

AREA	N	% SAND	% SILT	% CLAY	% ORGANIC	% INORGANIC
Tar River Mouth	45	52.6	21.9	25.5	13.9	86.1
Tranters Creek	6	79.9	9.6	10.4	7.3	92.7
Kennedy Creek	32	46.6	28.0	25.4	25.0	75.0
Pamlico Trunk	113	18.6	30.9	50.9	8.2	91.8
Chocowinity Bay	10	81.0	10.0	9.0	17.7	82.3
Whichards Creek	5	38.5	32.2	29.3	9.8	90.8
Broad Creek	14	34.4	25.2	40.3	14.8	85.2
Blounts Creek	2	47.2	26.0	26.8	6.3	93.7
Bath Creek	8	17.1	45.1	37.8	10.0	90.0
Mixon Creek	2	38.6	25.2	36.2	28.9	71.1
Durham Creek	7	22.2	30.5	47.3	10.7	89.3
South Creek	30	14.6	28.0	57.4	11.1	88.9
Inner Pungo River	44	32.2	29.4	38.4	13.5	86.5
Outer Pungo River	10	11.1	34.7	54.2	7.6	92.4
Pantego Creek	13	42.9	22.1	35.0	8.2	91.8
Pungo Creek	4	16.7	29.6	53.7	11.0	89.0

Organic-rich mud sediments (up to 57% total organic matter) generally occupy the entire bottom environment within tributary estuaries and about 75% to 80% of the bottom environments within the fluvial and transition zones of the lower Tar River and trunk of the Pamlico River estuary (Fig. 10) (Bellis et al., 1975; Hartness, 1977; Hardaway, 1980; Riggs, 1985). Concentration of organic material in individual samples ranges up to 57% of the total sediment. Sediments that generally contain greater than 25% organic matter are peats that represent either in situ growth in swamp forests and grass marshes or secondary accumulations of coarse organic detritus eroded out of swamp forests and grass marshes. Organic-rich sediments generally having less than 25% organic matter are fine-grained muds with minor sand contents.

Swamp forest peat sediments are dominant in the fluvial and transition zones of the Tar River and headwaters of associated lateral tributary estuaries. Within the fluvial portion, organic material occurs as swamp

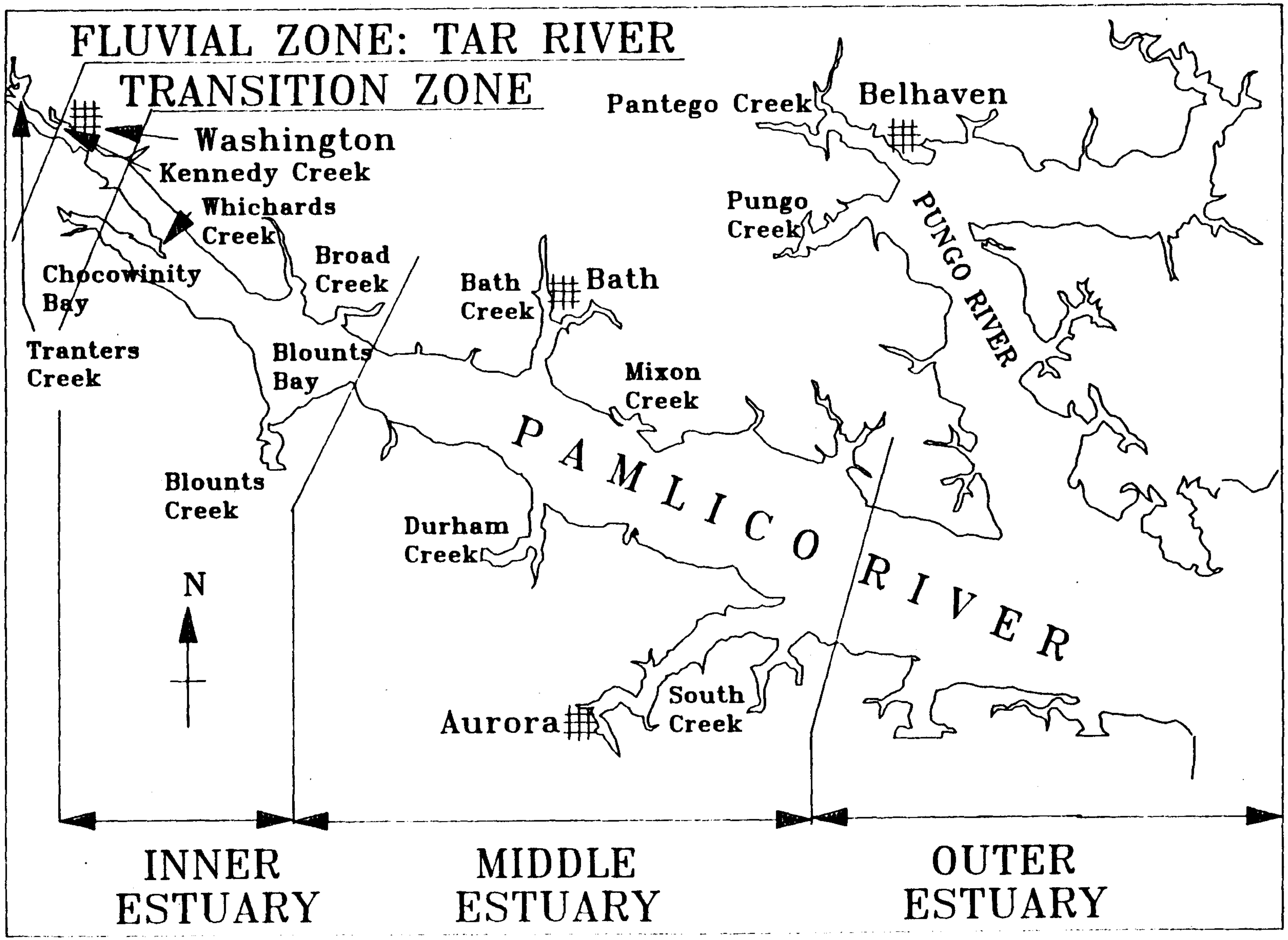


FIGURE 10. Designation of environmental components for the Pamlico River estuarine system

forest peats on the channel flanks and as coarse organic detritus mixed with coarse sand within the channel proper (Fig. 11). Within the narrow transition zone (Fig. 10) into a flooded estuary, the channel remains dominated by coarse sands and coarse organic matter; however, the swamp forest has been drowned and mud, containing high concentrations of very fine-grained organic detritus, begins to accumulate on top of swamp forest peats on the channel flanks. Swamp forest peats decrease in abundance into the main portions of the tributary and trunk estuaries; marsh peats occur around some of the perimeter areas while swamp forest peats occur preserved beneath increasingly thicker accumulations of the organic-rich muds. Immediately seaward of the transition zone, there is a sediment inversion (Riggs, 1985); the estuarine platforms are underlain by tight Pleistocene sediment units and covered by a thin and highly variable layer of well-sorted sand (Fig. 12) (Hartness, 1977; Hardaway, 1980). Within this main portion of the Pamlico River estuary, organic-rich mud sedimentation occurs within the broad, deeper portions of the estuaries. These mud-filled, depositional basins are incised into the shallow platforms that are underlain by older, more indurated Pleistocene sediment units.

The organic-rich mud increases in width, depth, and thickness in downstream directions within both the trunk and lateral tributary channels (Hartness, 1975). The content of organic matter is generally less than 25% in the organic-rich muds and is generally highest in the lateral tributaries and decreases into the trunk estuary and seaward down the trunk estuary (Fig. 13). Benthic environments associated with the organic-rich mud contain an oxidized zone of loose floc of variable thickness. The presence or absence and the degree of development of the loose floc at the sediment/water interface is a direct function of the productivity and storm energy levels, both of which vary greatly at scales ranging from daily to seasonal cycles. The surface sediments become reduced and increasingly compacted with depth. In addition to a large population of micro-organisms, this sediment/water interface zone contains a large community of filter-feeding macrobenthos, particularly polychaetes (Tenore, 1977), that appear to be important in concentrating, pelletizing, and depositing the mud sediment.

Rates of Sedimentation

Carbon 14 age-dates were obtained on four organic-rich samples in a 4 meter core (Fig. 14) from the inner portion of Blounts Bay (Fig. 10). The basal sample is from a swamp forest peat deposited in a lower fluvial environment, which was at or slightly above sea level at the time of formation. The upper three samples are organic-rich muds that represent deposition in an aquatic, inner estuarine environment seaward of the transition zone (Fig. 10). The resulting curve (Fig. 14) reflects the systematic rise in sea level, flooding up the lateral tributary stream to form a lateral estuary, and deposition of the organic-rich mud sediments.

General rates of deposition of the organic-rich mud can be calculated from Figure 14. The mean rate of deposition for the four numbers is 0.61 mm/yr (range from 0.45 mm/yr to 0.70 mm/yr). This suggests that sedimentation is very slow and that the anthropogenic effects of metal pollutants should not extend very deep within the sediments. Actual depth of impact within any specific portion of the estuarine system would be

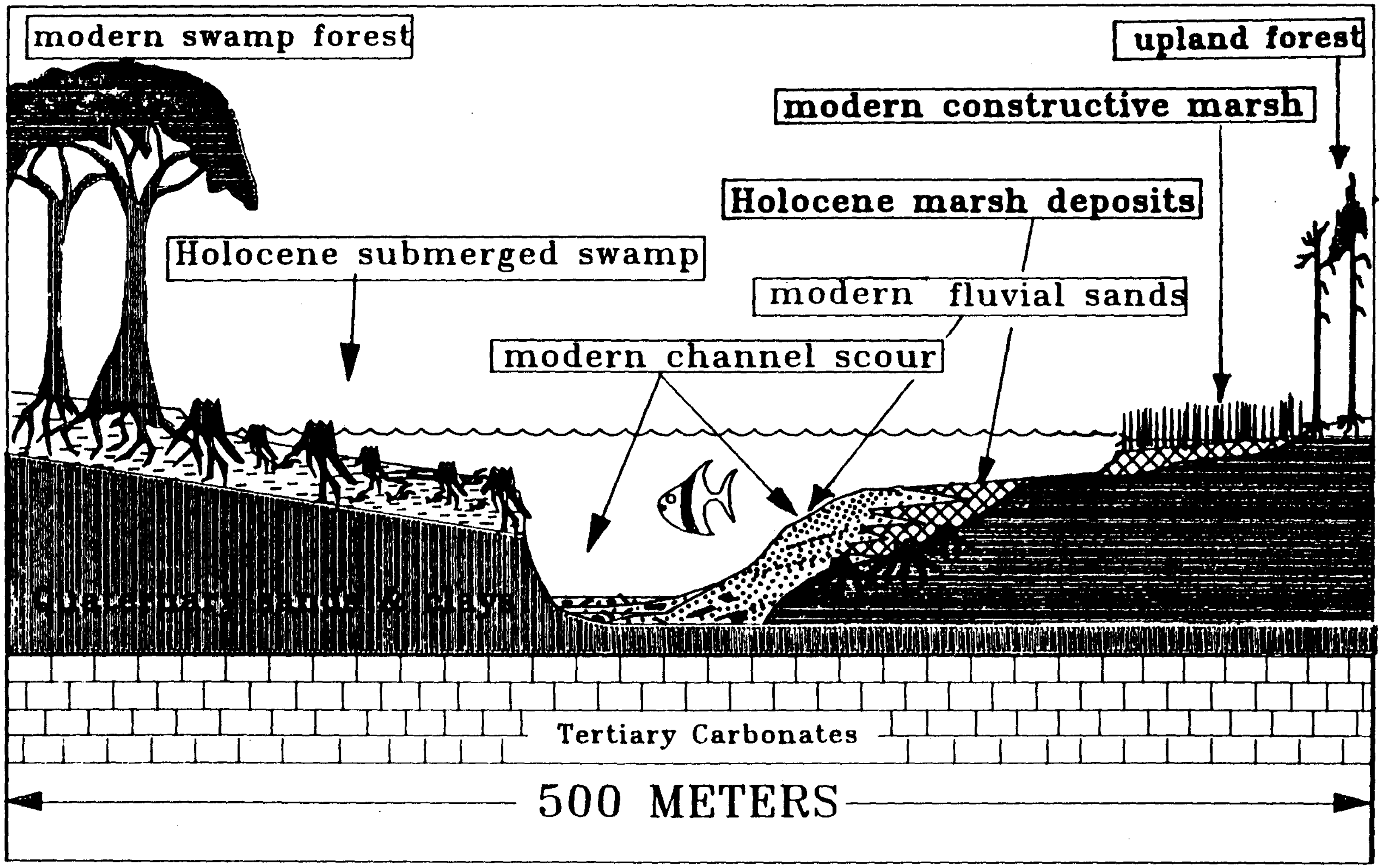


FIGURE 11. Schematic cross-section showing depositional environments within the fluvial zone of the Tar River

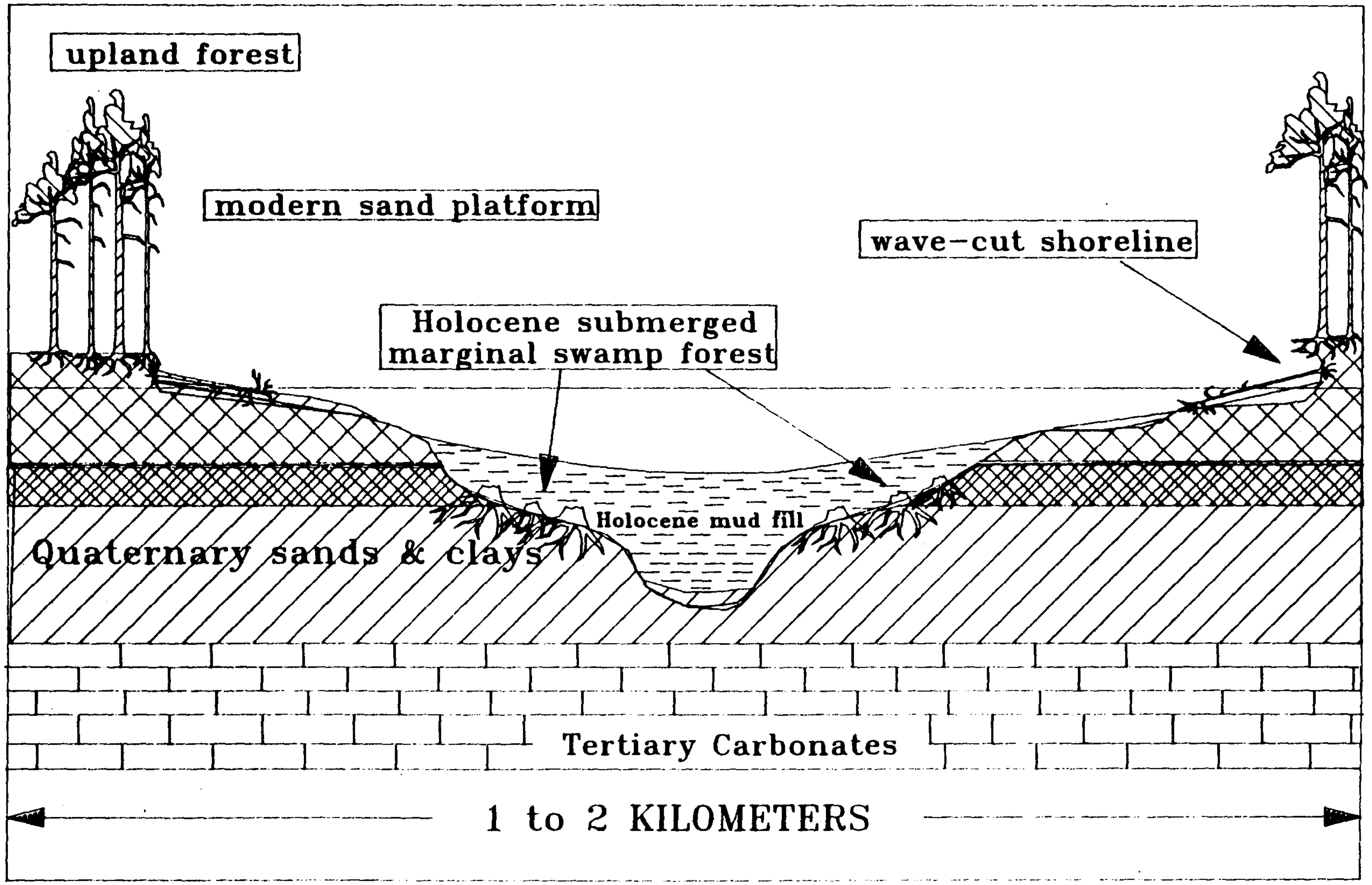


FIGURE 12. Schematic cross-section showing depositional environments within the trunk estuarine zone of the Pamlico River

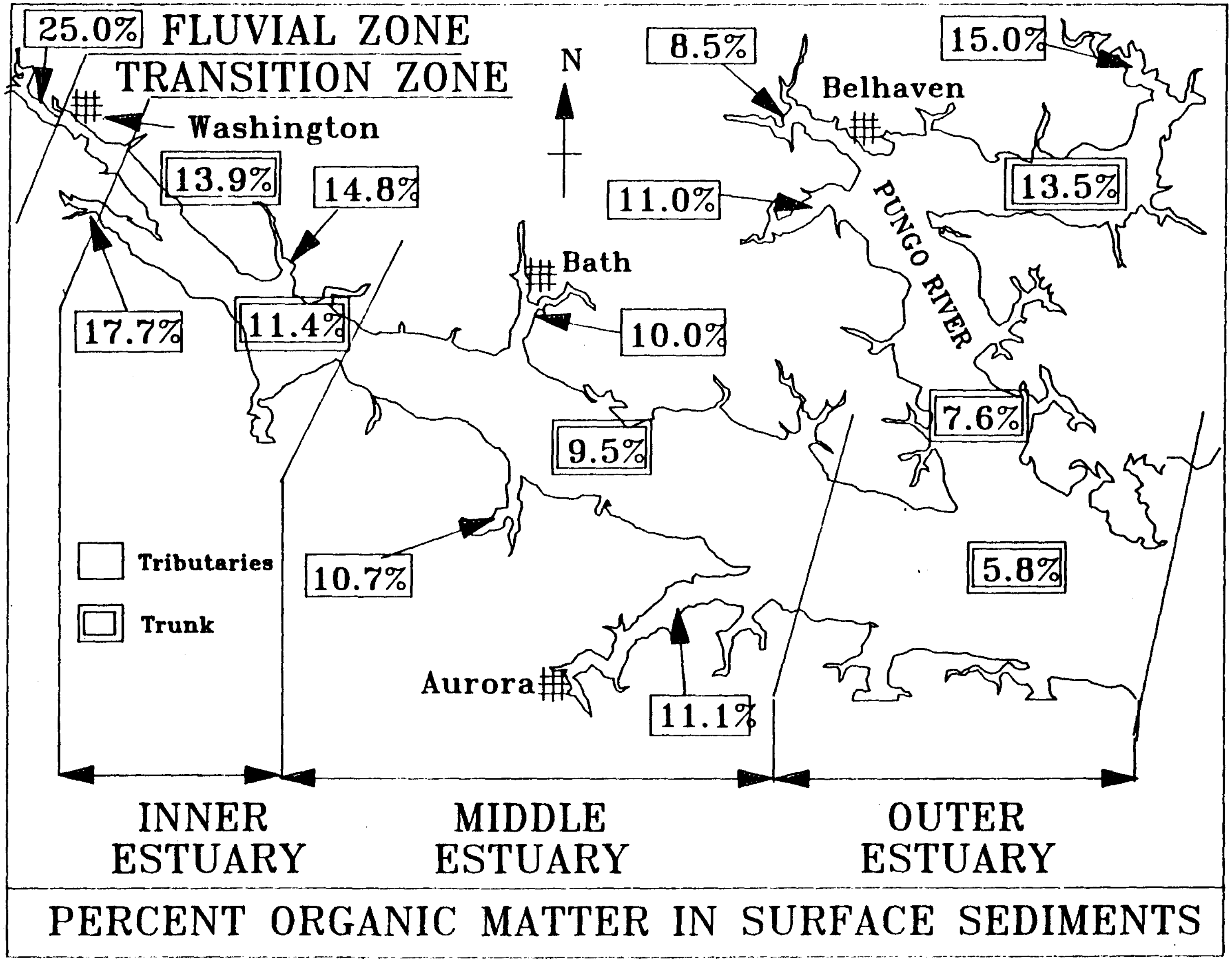


FIGURE 13. Distribution of organic matter within the surface sediments of the Pamlico River estuarine system

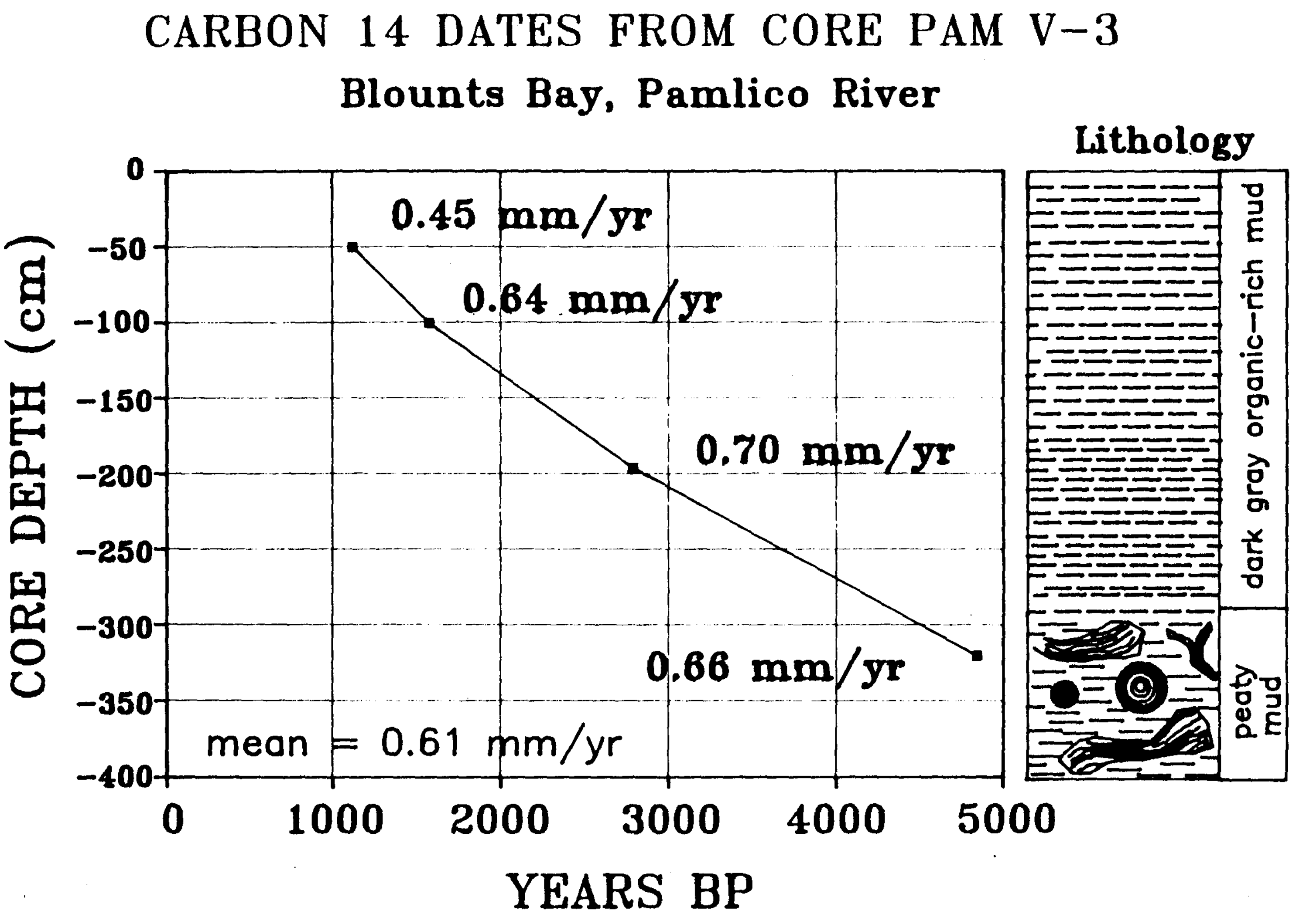


FIGURE 14. Times and rates of sediment deposition in Blounts Bay based upon downcore carbon 14 age dates

ultimately dependent upon secondary mixing processes such as bioturbation by the community of benthic organisms, wave and current processes resulting from major storm events, and mixing by man's activities such as fishing trawlers and dredging. The Blounts Bay depositional rate of 0.61 mm/yr is an order of magnitude lower than the 5 mm/yr rate estimated by Benninger and Martens (1983) for the main trunk of the Neuse River. Additional cores should be dated to establish whether this difference is characteristic of the whole Pamlico River estuarine system or whether there are significant variations throughout various parts of the system.

Vertical Distribution of Metals

Concentrations for many of the important heavy metals are significantly higher within the upper 10 cm of sediments than deeper within the sediments. Figures 15 and 16 display examples of these vertical differences with depth below the sediment-water interface for the 15 cores with the highest surface concentrations (elements Ag, Al, Cd, Cr, Cu, Ni, Pb, P, and Zn) within the Pamlico River system. Higher concentrations do occur at greater depths in several cores from Kennedy Creek; however, these metal-enriched subsurface samples were in peats with extremely high contents of organic matter (ranging between 30% to 57%). Presence of this organic-dominated sediment type probably accounts for the subsurface increase in heavy metal concentration. This metal enrichment within peats is unique to the Kennedy Creek area.

The amount of surface enrichment of heavy metals is directly related to the total elemental concentration; cores with low total concentrations (i.e., from the least polluted areas) have low upcore gradients whereas cores with high total concentrations (i.e., from the most polluted areas) have high upcore gradients. The elements P (Figure 16) and Al (Figure 15) also show distinct surface enrichments with down-core decreases similar to the heavy metals. The phosphorus data suggest that the organic-rich mud sediment represents an important source of nutrient input into the water column within the estuarine system. This corroborates the results of Matson et al. (1983) for both the Pamlico and Neuse River estuaries.

Figure 17 summarizes major element data down three cores from the sediment surface to -3.2 m for which there were many subsamples analyzed. The three cores were collected from different environmental settings with spatial separations of 15 to 20 km (Fig. 10) within the estuarine system. PV2 is from the main channel of the Pamlico River, SV1 is from South Creek which is a lateral tributary, and PV2 is from Blounts Bay which is an open lateral bay.

The excellent agreement in trends for cores separated spatially and representing different environmental settings within the estuarine system suggest that we can identify long term trends in the evolution of the Pamlico Estuary. The co-variation shown for these major elements is exceptional and suggests that our analytical approach and techniques allow comparison between samples.

These results also indicate that increases or decreases observed within the upper 1/2 to 1 meter of sediment in the short, diver-obtained cores, are not a clear indication of longer-term or deeper trends. This underscores the importance of determining radiometric ages of the sediments to define the time-frame involved in down-core chemical changes.

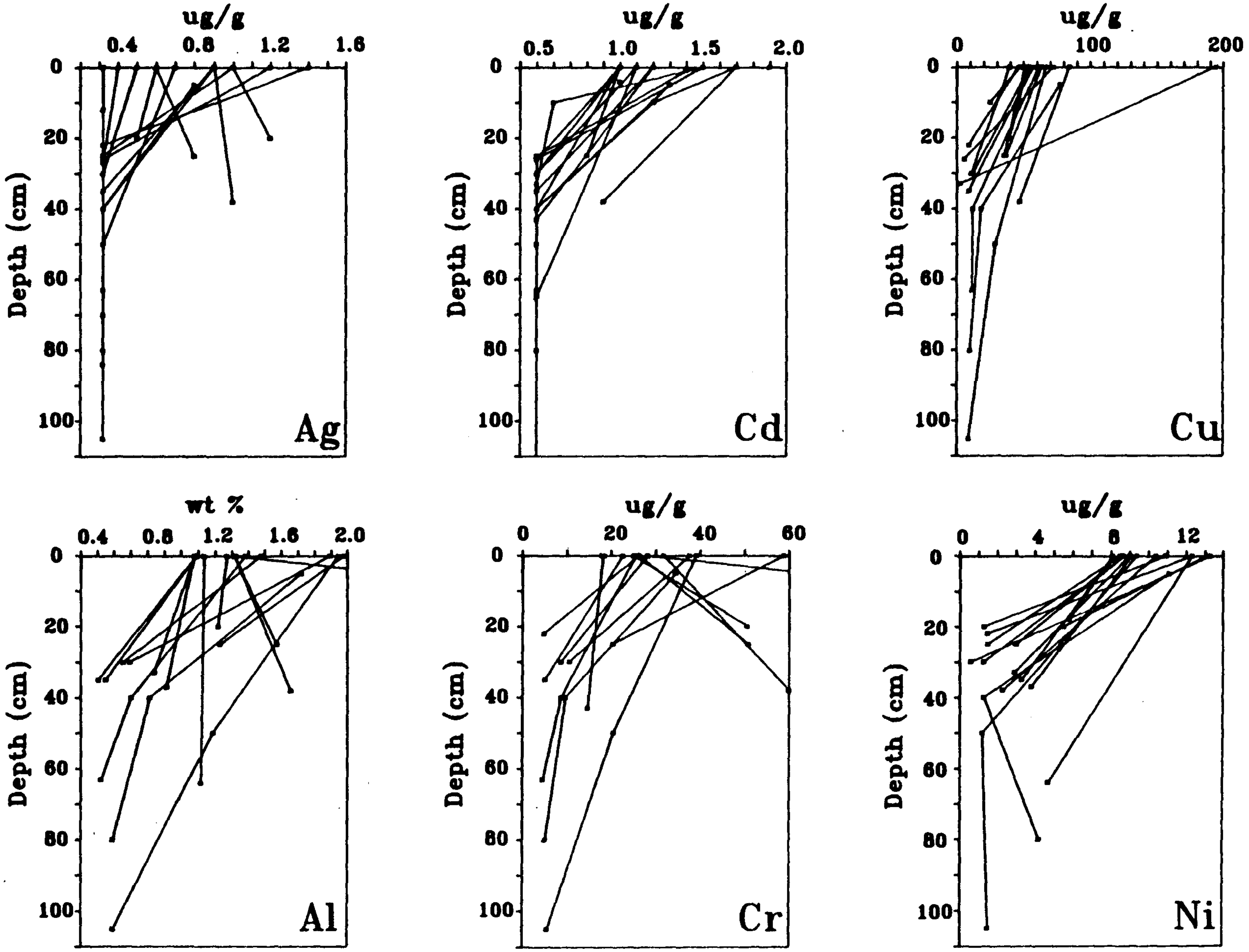


FIGURE 15. Selected downcore trace element concentrations for the 15 most polluted cores within the Pamlico River estuarine system

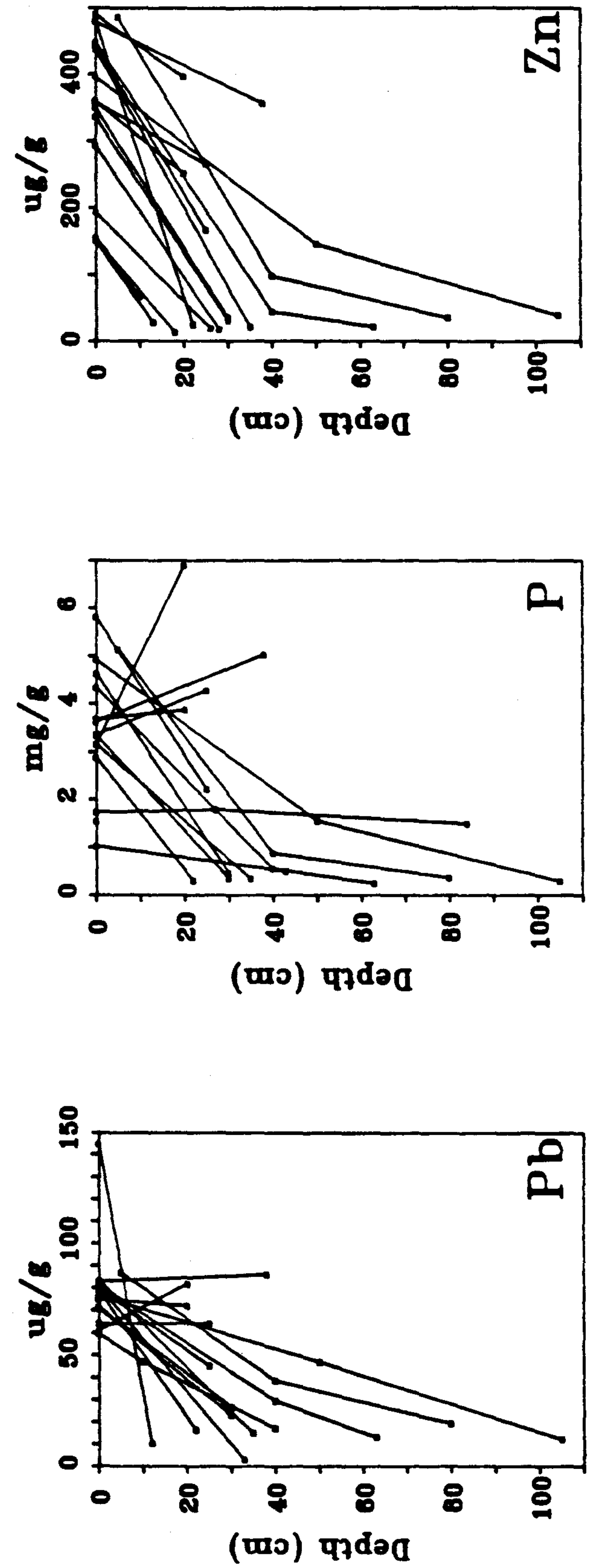


FIGURE 16. Selected downcore trace element concentrations for the 15 most polluted cores within the Pamlico River estuarine system

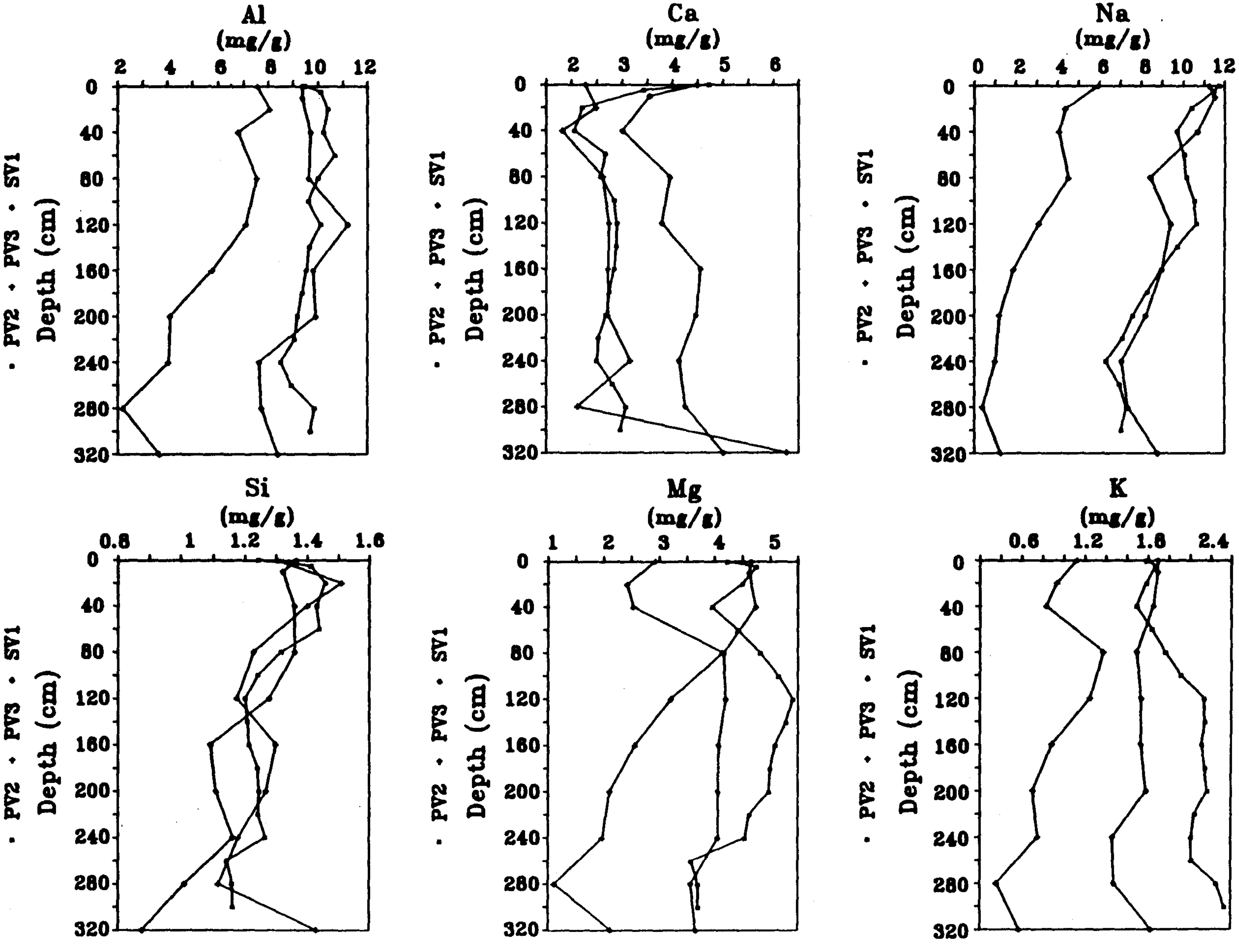


FIGURE 17. Selected downcore major element concentrations for the 3 deep vibracores within the Pamlico River estuarine system

Anthropogenic Flux of Metals

Results shown in Figures 15 and 16 were combined with data on water-content, grain density, and sedimentation rates to estimate potential anthropogenic fluxes of heavy metals into the sediments of the Pamlico River system. A sedimentation rate of 5 mm/year is assumed for the Pamlico flux estimates based upon estimated sedimentation rates in the Neuse River by Benninger and Martens (1983). Grain densities are estimated using bulk-density and textural data for Pamlico River sediments reported by Matson et al. (1983). A surface flux and a deep flux are calculated for each element, by averaging both the surface values and deep values below 25 cm for all cores displayed in Figures 15 and 16. The flux change is the surface flux divided by the deep flux. Results of the flux calculations are presented in Table 15.

TABLE 15. Estimated flux (flux change) of metals into the sediments of the Pamlico River estuarine system.

ELEMENT	SURFACE FLUX ($\text{mol cm}^{-2}\ \text{yr}^{-1}$)	DEEP FLUX ($\text{mol cm}^{-2}\ \text{yr}^{-1}$)	Flux Change
Cu	2.02×10^{-7}	4.59×10^{-8}	4.4 X
Ni	3.01×10^{-8}	7.04×10^{-9}	4.3 X
Pb	9.45×10^{-8}	2.65×10^{-8}	3.6 X
Zn	8.91×10^{-7}	2.58×10^{-7}	3.5 X
Cd	2.68×10^{-9}	8.40×10^{-10}	3.2 X
P	1.81×10^{-5}	8.58×10^{-6}	2.1 X
Ag	1.29×10^{-9}	6.46×10^{-9}	2.0 X
Cr	9.51×10^{-8}	6.08×10^{-8}	1.6 X
Al	8.63×10^{-5}	5.83×10^{-5}	1.5 X
As	7.46×10^{-8}	5.86×10^{-8}	1.3 X
Fe	9.22×10^{-5}	8.47×10^{-5}	1.1 X
Mn	1.47×10^{-6}	1.39×10^{-6}	1.0 X

Flux estimates (Table 15) can provide important evidence for the extent of anthropogenic influence on heavy metal concentration in sediments. Flux change values significantly greater than unity suggest an anthropogenic influence, assuming a negligible flux of metals caused by geochemical reactions within the sediments. Possibilities of upward migration of metals in response to diagenetic reactions in the sediments needs further investigation. However, the fact that iron and manganese fluxes show little change with depth suggests that metal-mobility due to changing redox conditions is minor compared to other influences.

The flux estimates indicate the greatest flux increase has occurred for copper. A comparison can be made between flux calculations for the core having the highest copper concentration, adjacent to a marine railway in Broad Creek (BRD-1), and estimates of copper leaching rates from antifoulant paint. The estimated flux of copper to the surface sediments at this site is 6.75×10^{-7} mol cm^{-2} yr^{-1}. In order for antifoulant paint to remain effective, copper must be leached out at a rate of 5.75 x 10^{-5} mol cm^{-2} yr^{-1} (Houghton, 1975). This represents a flux from a boat surface that is two orders of magnitude greater than the estimated surface sediment flux. These flux comparisons suggest antifoulant paint can readily account for the observed copper enrichment in the Broad Creek area. Obviously, the actual amount of copper accumulating near marinas will depend upon numerous variables: the character of the marina (it's age, number and size of boats, etc), character of the water body (it's size, shape, degree of restriction, water circulation patterns, etc.), and character of the bottom sediments (the type of sediment, mixing processes, rates of sediment accumulation, etc.).

Based upon the large flux change (3.2 X) and high surface cadmium values over a large areal extent of the middle Pamlico River around the active phosphate mining operation (Fig. 29), anthropogenic input of cadmium to the Pamlico is volumetrically the most significant of the metals studied. Cadmium values for many Pamlico deep samples were below reported detection limit (0.5 ug/g). Since the cadmium value for global shale is about 0.2 ug/g (Marowski and Wedepohl, 1971), the actual deep flux for the Pamlico could be two or more times smaller than the estimated flux. Consequently, the flux change would be higher than shown in Table 15.

Flux estimates for other elements suggest significant recent contributions of Ni, Pb, Zn and P. The data for phosphorus suggest an increase due to anthropogenic influence equal in magnitude to the background or "natural" flux. This apparent increase probably includes input from point sources such as the active phosphate mine, sewage treatment plants, etc. as well as non-point sources such as agricultural runoff, swamp forest discharge, and marsh shoreline erosion.

Samples from Kennedy Creek have the highest surface concentrations for many of the important heavy metals. Figure 18 shows an estimate of anthropogenic influence for all elements analyzed by ICAPES. The estimates are based on comparisons between the surface flux and deep flux, using averages for samples from Kennedy Creek (NAT-1 through NAT-12) and assumes all increases in surface fluxes result from anthropogenic input. The percent anthropogenic influence represents the portion of the surface flux attribitued to human input. More than half of the input of Cu, Ni, P, Pb and Zn and a significant portion of the Ag, As, Cd, and Mn into this tributary may result from human sources. High Mn values suggest that mobilization within sediments in response to changing redox chemistry may be important. Further work is needed to evaluate this possibility more fully.

Overall, flux estimates presented in Figure 18 and Table 15 are comparable to results using dated cores in a Norwegian fjord (Skei and Paus, 1979) and in coastal basins off southern California (Bruland et al., 1974). The greatest uncertainty in the Pamlico River flux estimates involves sediment accumulation rates. The value of 5 mm/yr used for these estimates, based on work from the Neuse River near New Bern (Benninger and Martens, 1983), falls about mid-way between a range of values for similar environments including the Savannah River (13 mm/yr by Goldberg et al., 1979), Chesapeake Bay (2.5 to 5 mm/yr by Helz, 1976), and preliminary results from our own radiocarbon data from Blounts Bay (0.61 mm/yr). Pending results from ongoing ^{210}Pb anaylses and additional radiocarbon dates will provide additional sediment accumulation estimates for the Pamlico River estuary and enable further refinement of our flux estimates.

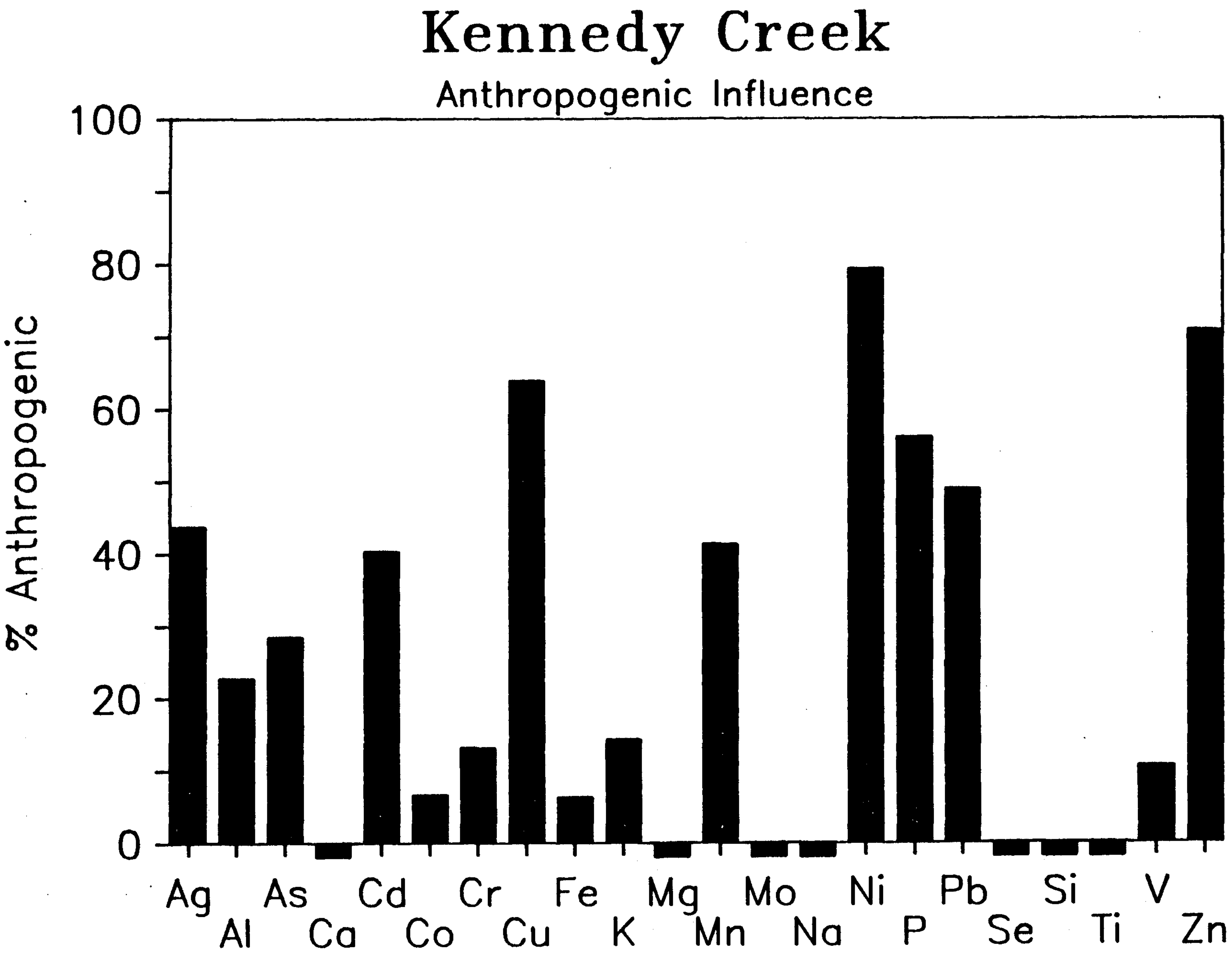


FIGURE 18. Estimate of anthropogenic influence of all elements analyzed by ICAPES for Kennedy Creek

AREAS OF CONCERN

Ten areas of concern have been delineated in the Pamlico River estuarine system (Fig. 1). These areas have surface sediments that are enriched in one or more of the "critical elements" that include the eight EPA priority pollutant metals (As, Cr, Cd, Cu, Ni, Pb, Zn, and Hg) and other important trace elements (Co, Mn, Mo, Ti, V, F, and the nutrient element P). Enrichment is determined by comparing the concentration for each critical element to the trimmed mean for surface samples in the estuarine system. Areas containing one or more sample sites with critical elements that are at least 2 X enriched over the trimmed mean are defined as areas of concern.

Table 16 contains the trimmed mean concentrations for 21 elements within the surface sediments of Pamlico River estuarine system. Trimmed means were calculated by averaging all surface samples that fall within two standard deviations of the mean for all surface samples analyzed. This produces a background level of concentrations that can be used to compare enriched samples that are assumed to result from anthropogenic inputs.

TABLE 16. Trimmed mean concentrations for 21 elements (in ug/g) in surface sediments of the Pamlico River estuarine system.

ELEMENT	TRIMMED MEANS (N=138)	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
EPA PRIORITY METALS:				
As	12.78	5.89	2.9	26.8
Cr	10.49	5.08	2.5	26.3
Cd	0.36	0.32	0	1.2
Cu	13.6	10.47	2.1	57.4
Ni	2.66	2.29	0.2	9.4
Pb	35.92	14.7	7.2	78.9
Zn	77.01	66.53	11.3	396.8
Hg	0.09	0.07	0.01	0.43
OTHER TRACE ELEMENTS:				
Co	5.55	1.79	1.6	10.1
Mn	153.83	78.5	43.2	371.2
Mo	0.5	0.25	0.1	1.1
P	804.72	569.56	218.3	3367.0
Ti	38.56	15.46	10.6	72.4
V	21.42	8.78	4.6	38.2
MAJOR ELEMENTS:				
Al	6664.26	2829.1	1402.3	13168.9
Ca	3678.91	1730.48	1249.1	9583.4
Fe	14692.3	5785.8	3156.9	25677.7
Mg	2707.12	1262.59	582.4	5075.9
K	931.83	579.47	157.4	2011.6
Si	1174.05	155.0	747.0	1434.7
Na	4519.14	3187.82	364.5	11256.0

The following discussion considers both polluted and nonpolluted portions of the Pamlico River estuarine system. The purpose is to contrast areas with elevated levels of heavy metal loading associated with known point and nonpoint sources of anthropogenic pollutants to the large portions of the system that have low metal concentrations.

Washington Area

Washington (Figs. 1, 10, and 19) is a small city that is characterized by the highest levels of development within the Pamlico River estuarine system. The city has an extensive paved area with curbs, gutters, and storm sewers; numerous small industries and one large industrial facility; a moderate-sized municipal waste treatment plant; and numerous historic industrial facilities and waste disposal sites in and adjacent to wetlands including a coal-fired power plant and fertilizer plants along the railroad. The Washington area presently has 6 industrial and 1 municipal NPDES waste water discharge permits that discharge over 4,012,000 gallons per day into adjacent waters (see permits in App. I).

Consequently, the estuarine area around Washington reflects a high level of anthropogenic influence. Significant elemental enrichment was encountered in samples from two portions of the Washington area and represent important "areas of concern": Kennedy Creek and the Tar-Pamlico Rivers along the Washington waterfront. Kennedy Creek is an area of extensive historic waste disposal sites and landfills, both historic and modern industries, and a major municipal sewage outfall. Several known historic landfills occur in the upstream area and in the areas of present discharge sites. At least portions of the textile and sewage treatment plants are known to have been sited on top of old municipal waste disposal sites in and adjacent to the Kennedy Creek swamp forest. The Washington waterfront receives extensive urban runoff and is the highly modified site of both an historic harbor and historic and modern industrial complexes.

Kennedy Creek

Highly elevated levels of 11 critical trace elements and 2 major elements occur in the surface sediments from Kennedy Creek (Fig. 19 and Table 17). Enrichment factors are highest for mercury at 14.44 X (Fig. 20) with enrichment factors of at least 2 X or more in 14 of 15 samples taken in the Creek. Enrichment factors of greater than 2.4 X occur for Zn (Fig. 21), Cu, Cr, Ni, Cd, and Pb (Fig. 22) in samples immediately adjacent to known outfalls for the waste water treatment plant and a large textile plant. Other elements including As (Fig. 23) and V increase upstream. It is interesting to note that an agricultural chemical, toxic waste dump existed in the upper reaches and immediately adjacent to the floodplain of Kennedy Creek; this site was cleaned up as an EPA "superfund" site in January of 1989. Phosphorus (Fig. 24) has an enrichment factor of 7.23 X which occurs throughout a broad portion of the entire Creek; this may be related to the combined effects of the sewage treatment plant, the historic waste dump facilities, and adjacent dump sites associated with old fertilizer plants.

Sediments in Kennedy creek have relatively high concentration of clay-sized particles with the highest concentration of organic matter within the

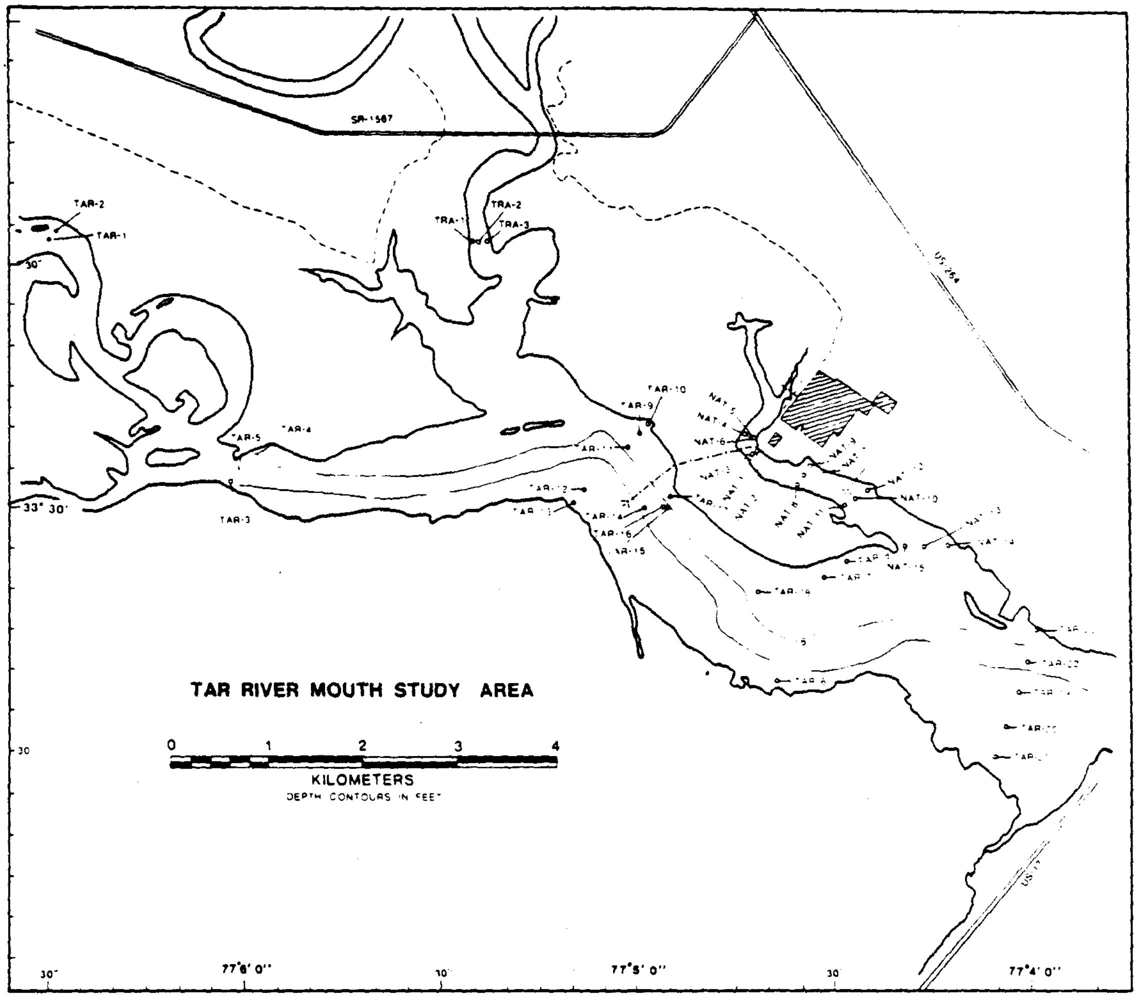


FIGURE 19. Sample location map for the Tar River (TAR), Tranters Creek (TRA), and Kennedy Creek (NAT) areas

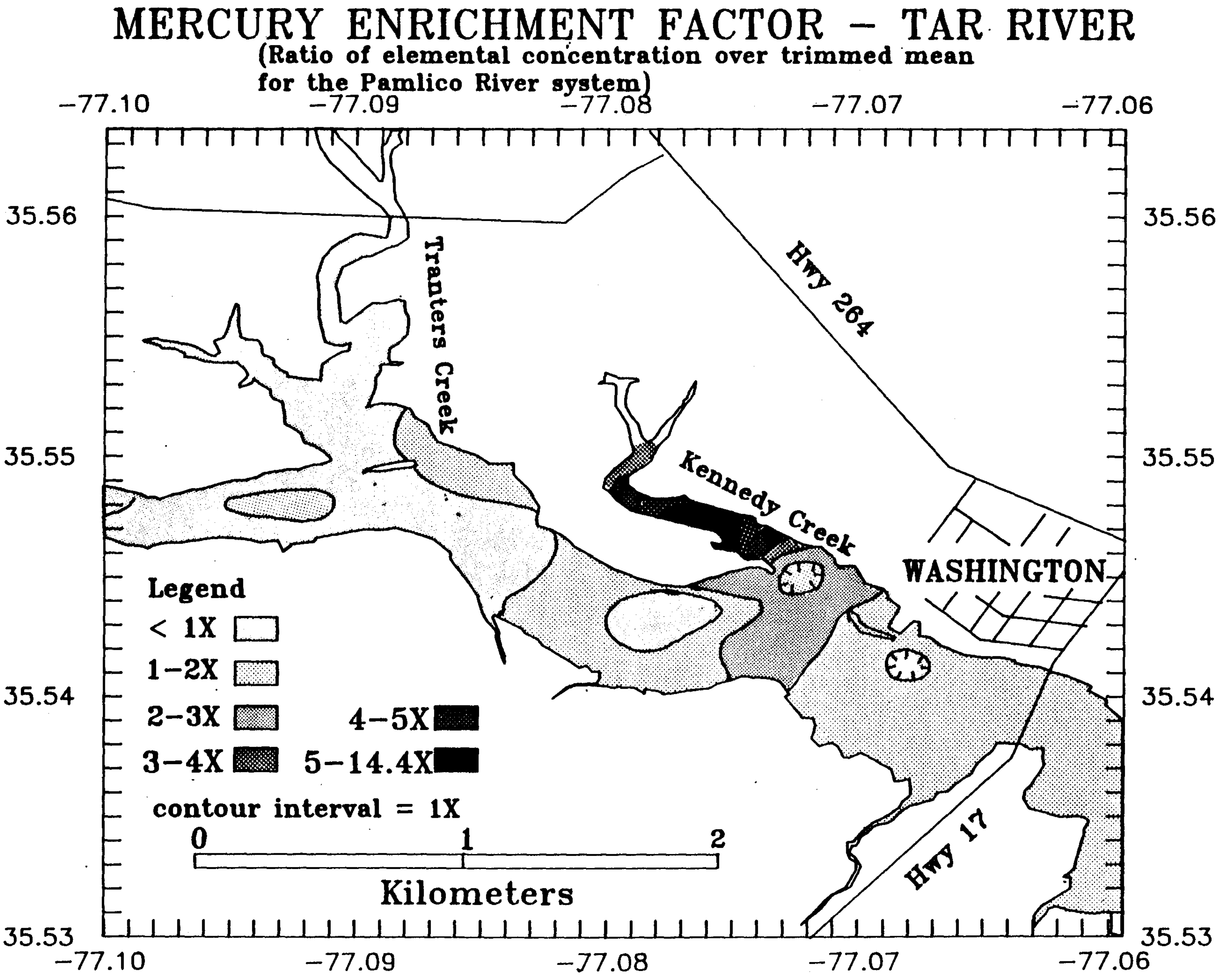


FIGURE 20. Enrichment factor map of mercury concentrations in surface sediments in the lower Tar River, Tranters Creek, and Kennedy Creek areas

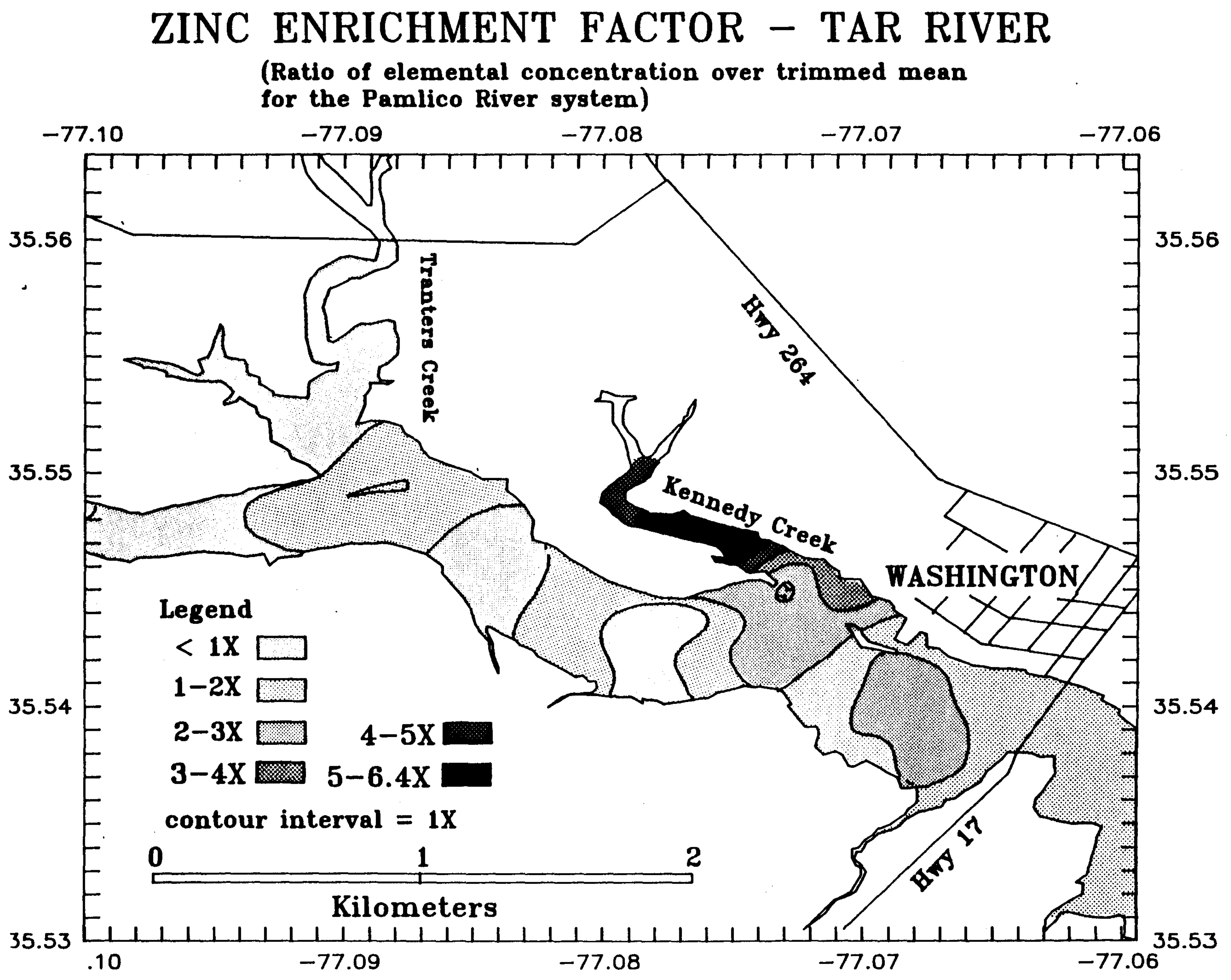


FIGURE 21. Enrichment factor map of zinc concentrations in surface sediments in the lower Tar River, Tranters Creek, and Kennedy Creek areas

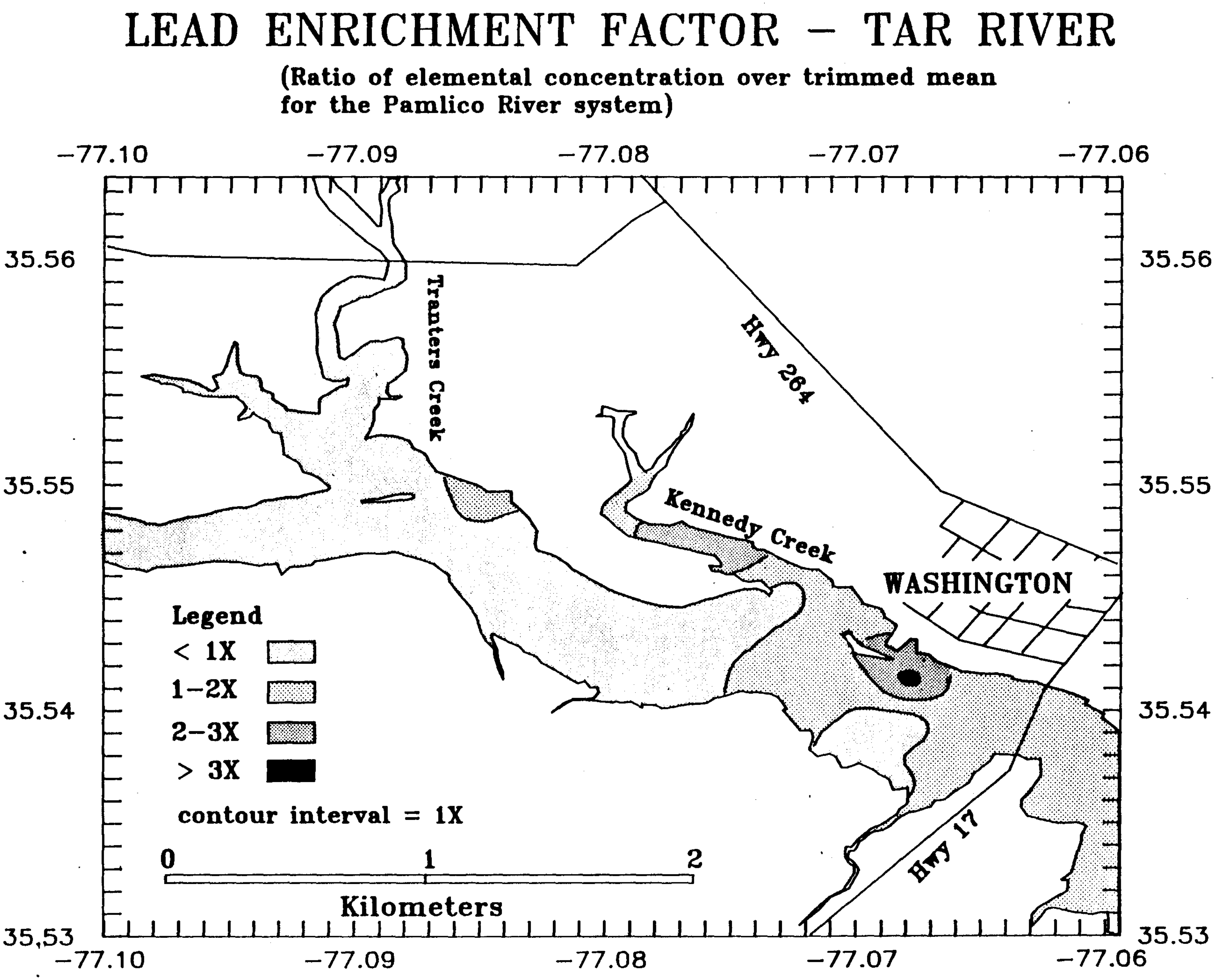


FIGURE 22. Enrichment factor map of lead concentrations in surface sediments in the lower Tar River, Tranters Creek, and Kennedy Creek areas

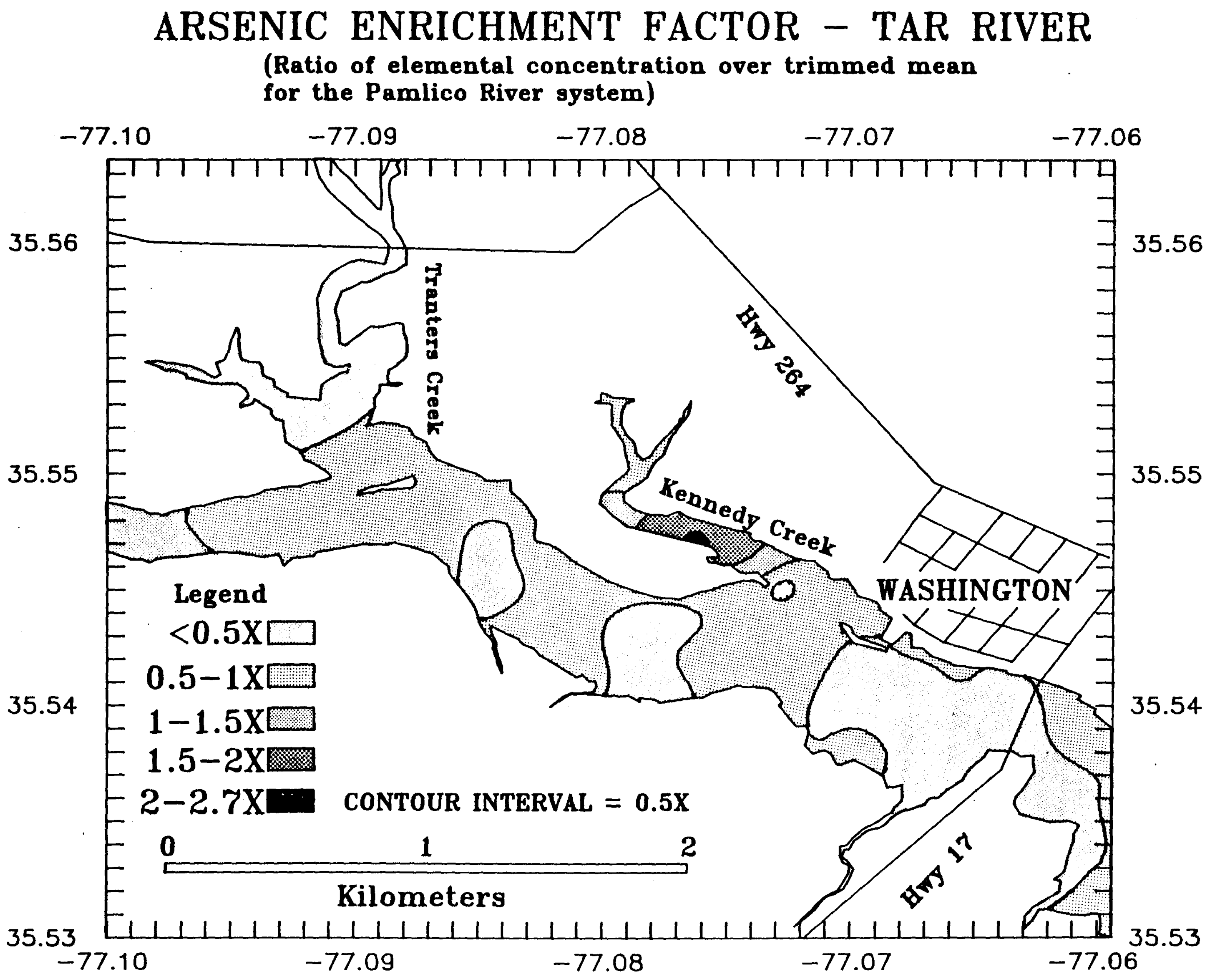


FIGURE 23. Enrichment factor map of arsenic concentrations in surface sediments in the low Tar River, Tranters Creek, and Kennedy Creek areas

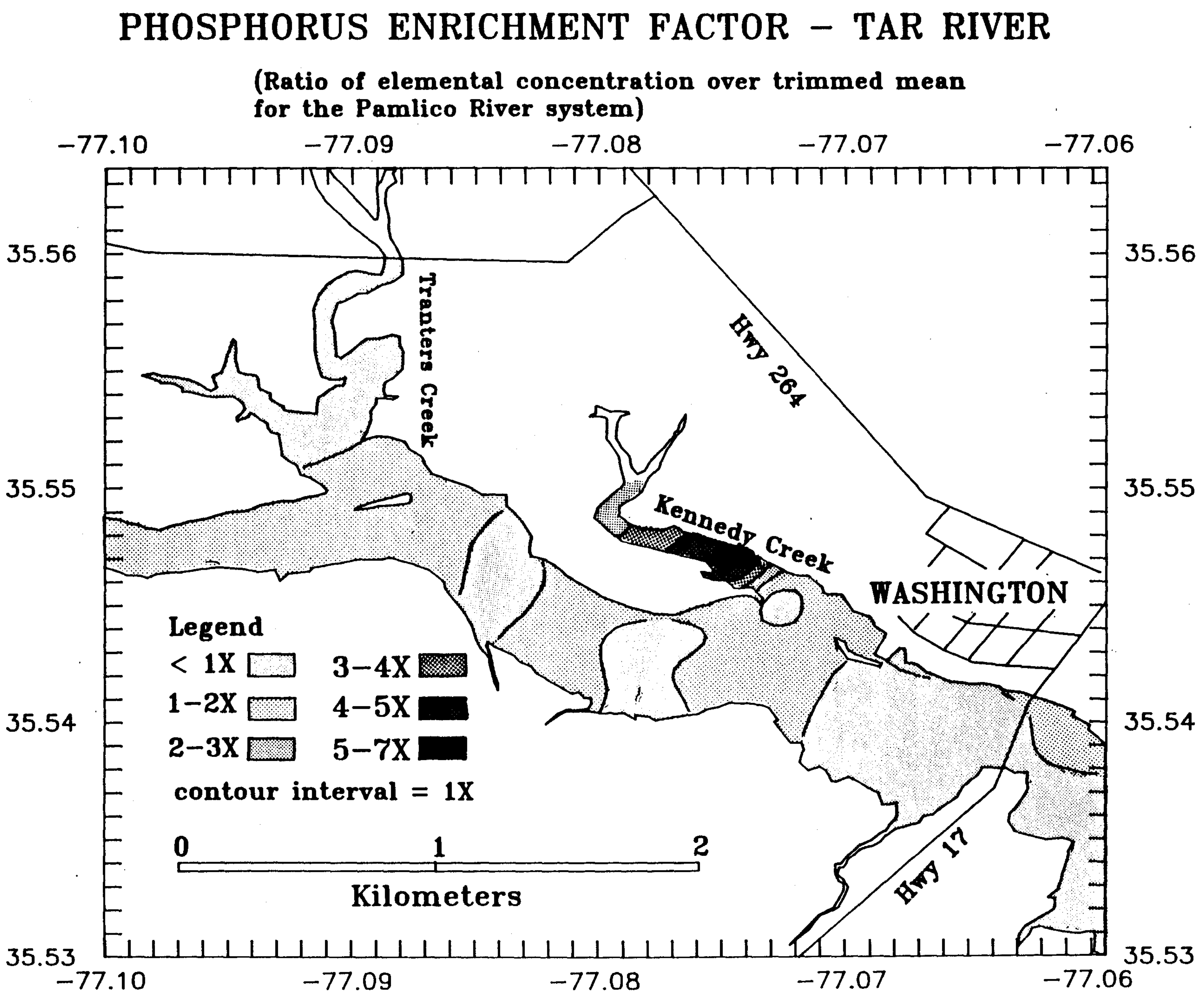


FIGURE 24. Enrichment factor map of phosphorus concentrations in surface sediments in the lower Tar River, Tranters Creek, and Kennedy Creek areas

Pamlico River estuarine system. This compositional characteristic may contribute to the assimilation of available metals into the sediment from available point and non-point sources, both natural and anthropogenic.

TABLE 17. Average concentrations (in ug/g) of enriched elements (enrichment factor = or > 2 X the trimmed mean) in samples from Kennedy Creek, N.C.

ELEMENT	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:						
Hg	14	0.46	0.27	0.17	1.3	14.44
P	12	4011.37	939.36	2888.6	5821.4	7.23
Zn	14	394.13	94.33	154.5	490.3	6.37
Cu	13	56.53	14.98	27.4	84.4	6.21
Cr	12	32.03	9.9	22.7	58.8	5.61
Ni	12	9.98	2.28	5.8	13.3	5.00
Cd	8	1.14	0.27	0.9	1.7	4.72
Co	1	16.5	*****	16.5	16.5	2.97
As	3	34.07	1.4	32.6	35.4	2.77
V	1	56.5	*****	56.5	56.5	2.64
Pb	8	80.65	3.85	75.2	86.9	2.42
MAJOR ELEMENTS:						
Al	6	17326.88	2517.73	13833.4	19778.7	2.97
Ca	1	8198.1	*****	8198.1	8198.1	2.23

All enriched elements within Kennedy Creek, except lead (Fig. 22), mercury (Fig. 20), and zinc (Fig. 21), decrease to average or below average concentrations immediately outside the mouth of the Creek. Thus, concentrations of phosphorus (Fig. 24) and arsenic (Fig. 23), as well as most other elements occur in concentrations within the Tar River and Tranters Creek sediments in concentrations that are at or below the trimmed mean for the Pamlico River estuarine system. This suggests that metals comming either from higher within the Tar River drainage system or the large NPDES waste water discharge site (permit number 3 in App. I) located on the north side of the Tar River and just west of the mouth of Kennedy Creek, are not having a significantly adverse impact upon the Tar River sediments. This could be a result of the specific water chemistry, higher current flows, or the dominance of inorganic sediments within the Tar River. However, it is possible that some of the metal loading occurring within the abundant organic-rich muds of Kennedy Creek could be a direct result of discharge waters into the Tar River being periodically trapped within lower Kennedy Creek.

Also, it is not known which of the potential modern or historic sources of pollutants have contributed in the past or are presently contributing nor which elements they are contributing to the Kennedy Creek sediments. It is realistic that each of the sources have had some contribution to the system over a fairly long period of industrial development. Additional work needs to be done within this entire area in order to fully understand the sources, fluxes, and concentrations of enriched elements within this complex and highly polluted area. This work should involve more detailed sampling of the sediments within the lower Tar River and adjacent tributaries, as well as monitoring shallow drill holes around waste disposal sites adjacent to the creeks. This is essential before the problems within Kennedy Creek can be resolved.

Washington Waterfront

Enriched levels of six elements (Table 18) occur in up to three sites in the Tar River along the Washington waterfront and east of the mouth of Kennedy Creek (Figs. 1, 10, and 19). Lead, zinc and mercury (Figs. 22, 21, and 20, respectively) are most enriched in the sample closest to the north shore of the River and decrease southward away from the shore. Based upon preliminary analyses of additional samples collected eastward along the Washington waterfront, metal enrichment appears to continue at least to Runyan Creek.

TABLE 18. Concentrations (in ug/g) of enriched elements from the Tar River along the Washington waterfront, east of the mouth of Kennedy Creek, N.C.

ELEMENT	N	CONCENTRATION	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:			
Pb	1	144.7	4.03
Mn	3	468.83	3.81
Mo	1	1.3	2.60
Co	1	13.6	2.45
Hg	1	0.19	2.11
Zn	1	154.7	2.01

Metal enrichment along the Washington waterfront is thought to result from a combination of at least four factors. First is urban runoff; storm water from roads, parking lots, and industrial sites are all discharged directly into the north shore of the River through abundant storm sewers. Second are contributions from historic waste disposal sites and landfill areas; low-lying wetland areas around Runyan, Jacks, and Kennedy Creeks, as well as the waterfront itself, have been extensively filled for subsequent development. Third are the warehouses and small industries that have been historically located along the waterfront; these industries could have discharged almost anything into the water during their operation. Fourth is the potential pollutant leakage and subsequent downstream loading from the Kennedy Creek industrial area.

Phosphate Mining Area

The largest industrial complex within the entire Tar-Pamlico River drainage basin is located on the south bank of the middle Pamlico River and along South Creek (Figs. 1, 10, and 25). This large phosphate mining and chemical processing facility has 5 NPDES permitted waste water discharge sites with design flows of 60,840,000 gallons of waste water per day (permits numbers 1, 11, 12, 112, and 113 in App. I). Three of the five discharges, including the largest permitted discharge site (60 mgpd), are located along the south shoreline of the Pamlico River and about midway between Durham Creek to the west and South Creek to the east (Fig. 25). Two discharges with design flows of 84,000 gallons of waste water per day are permitted into South Creek (Fig. 25). Both the middle Pamlico River and South Creek represent significant areas of concern (Fig. 1).

Middle Pamlico River

A large area of elemental enrichment occurs in the middle portion of the Pamlico River surrounding the major discharge sites from the southern shore (Fig. 25). Within this area, six metals (Cd, Mo, As, Mn, V, and Ti), three major elements (Ca, Na, and K), plus fluorine and phosphorus are significantly enriched (Table 19). All of these elements occur as either major components or important trace elements within the phosphate grains (Table 3). These elements are released during the chemical production of fertilizer; however, the subsequent partitioning of the various components with respect to their ultimate fate is poorly understood. Obviously, significant concentrations are discharged with the waste water.

TABLE 19. Average concentrations (in ug/g) of enriched elements in sediments from the middle Pamlico River associated with the active phosphate mining area.

ELEMENT	N	MEAN	STANDARD DEVIATION	MINIMUM VALUES	MAXIMUM VALUES	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:						
Cd	32	0.9	0.4	0.4	1.9	5.23
Mo	39	0.88	0.4	0.5	2.5	5.04
As	32	18.8	5.22	13.4	34.0	2.66
Mn	28	244.2	74.4	154.9	398.2	2.59
V	32	32.27	7.22	22.1	53.7	2.51
Ti	24	58.04	10.14	40.2	77.4	2.01
MAJOR ELEMENTS:						
Ca	30	14179.58	24637.63	3733.4	124960.1	33.97
P	13	1132.42	442.01	846.1	2553.2	3.17
Na	46	7717.21	3113.88	485.4	13565.0	3.00
K	39	1624.18	301.41	973.3	2114.0	2.27
F	12	98.2	124.1	detec limit	478.0	not calc

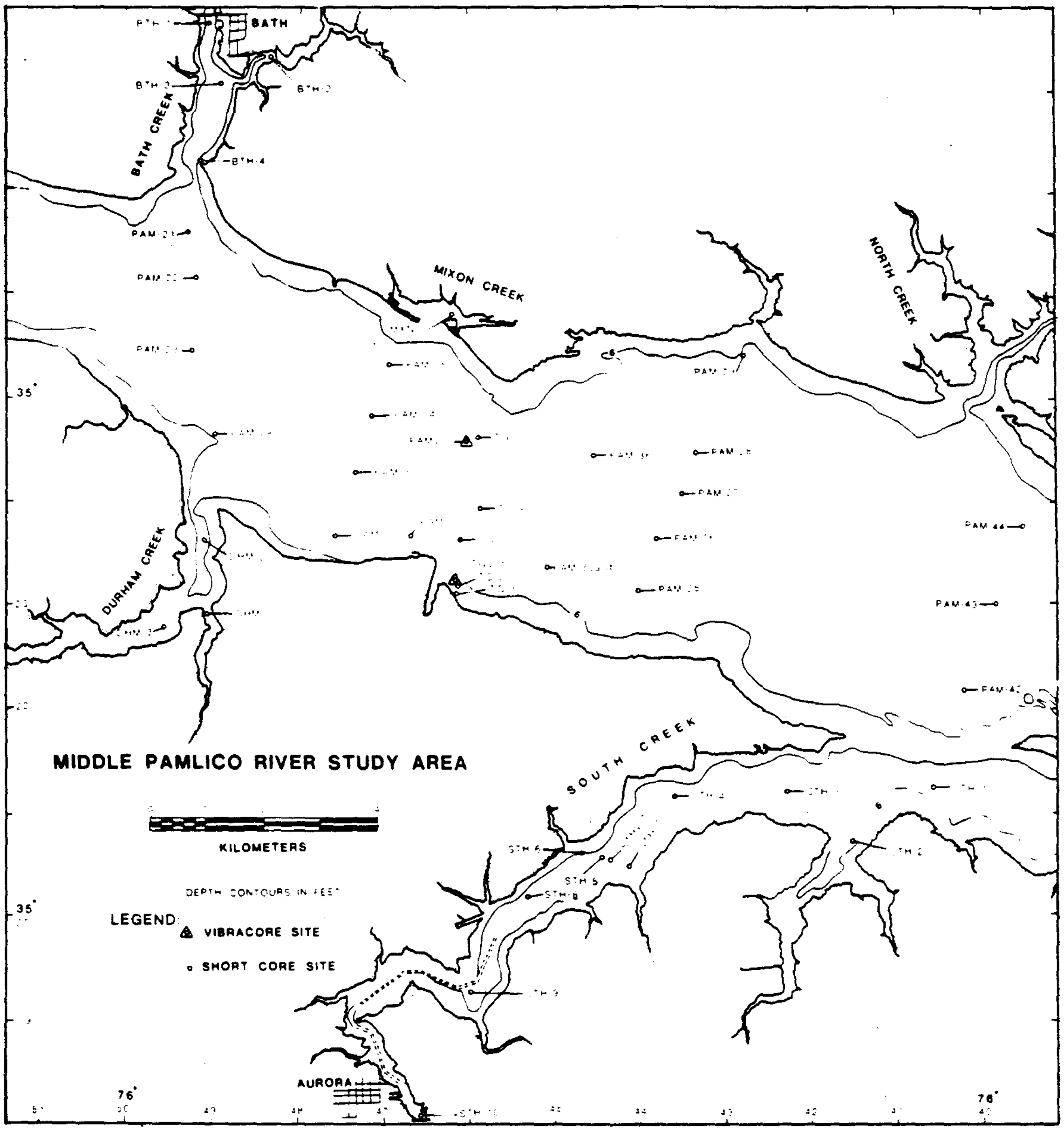


FIGURE 25. Sample location map for the middle Pamlico River and South Creek areas which include the phosphate mining district

The distribution of enrichment factors for fluorine (Fig. 26) and phosphorus (Fig. 27) form an assymetric hotspot around the main waste water discharge site immediately east of the rectangular barge slip. Concentrations generally decrease fairly rapidly to the west and north but form elongate plumes that extend eastward downstream. All enriched elements basically follow this pattern with slight variations in the distance of decreasing concentrations. For example, calcium enrichment factors (Fig. 28) drop off very rapidly compared to fluorine enrichment (Fig. 26) where significant enrichment extends to the north shore, east into the outer Pamlico River area, and into South Creek. Calcium concentrations adjacent to the outfall canal are 34 X enriched. Calcium has historically been added to the acid waste water as a buffering agent just prior to discharge from the mining facility. This has resulted in a major plume of white carbonate sediments on the estuarine floor around the discharge site.

Cadmium is enriched (up to 5.23 X) in the surface sediments of the middle Pamlico (Table 19). The general pattern of cadmium enrichment (Fig. 29) around the discharge canal is similar to the other elements with two major differences. First, samples near the mouth of the discharge have cadmium levels that are at or near the trimmed mean. Enrichment occurs away from the outfall and appears to be the inverse of the calcium enrichment (Fig. 28). This probably reflects changes in bottom sediment composition due to carbonate deposition and the specific chemistry of cadmium. Second, there are two distinct centers of concentration of cadmium that occur both on the upstream and downstream side of the outfall canal. This same pattern is only slightly apparent in each of the other elemental maps (F, P, and Ca in Figs. 26, 27, and 28, respectively). The largest of these two hotspots occurs eastward of the outfall and in the direction of dominant water flow. It is possible that the western hotspot reflects a changing water flow pattern; however, it is more likely that this reflects either an historic discharge site or major leaking from the waste water holding ponds located adjacent to the shore and directly landward of this area. Molybdenum, arsenic, manganese, vanadium, and titanium are also significantly enriched in the same area and have distributions similar to the F, P, and Cd.

In the middle Pamlico area there are fewer elements that are significantly enriched in the surface sediments than in the Kennedy Creek area. However, the areal extent of enrichment of the critical elements (P, F, Cd, Mo, As, V, Ti, and Mn) represents a very large portion of the middle Pamlico River area. This area of impact is orders of magnitude more extensive than any of the other areas of concern.

South Creek

Elevated levels of cadmium (4.72 X), molybdenum (2.40 X), and arsenic (2.01 X) occur in surface sediments near the middle of South Creek (Figs. 1, 10, and 25; Table 20). Highest concentrations (Fig. 29) occur adjacent to a mining waste disposal pond located on the peninsula on the southeast side of South Creek. The area of enrichment is relatively small and proximal to a pipeline used to carry mining waste across South Creek to the disposal pond. This area was the site of at least one major waste spill from a rupture in the pipe in 1985. Also, six outfalls related to the mining waste disposal ponds empty into South Creek near the area of metal enrichment.

FLUORINE CONCENTRATION – MIDDLE PAMLICO R.

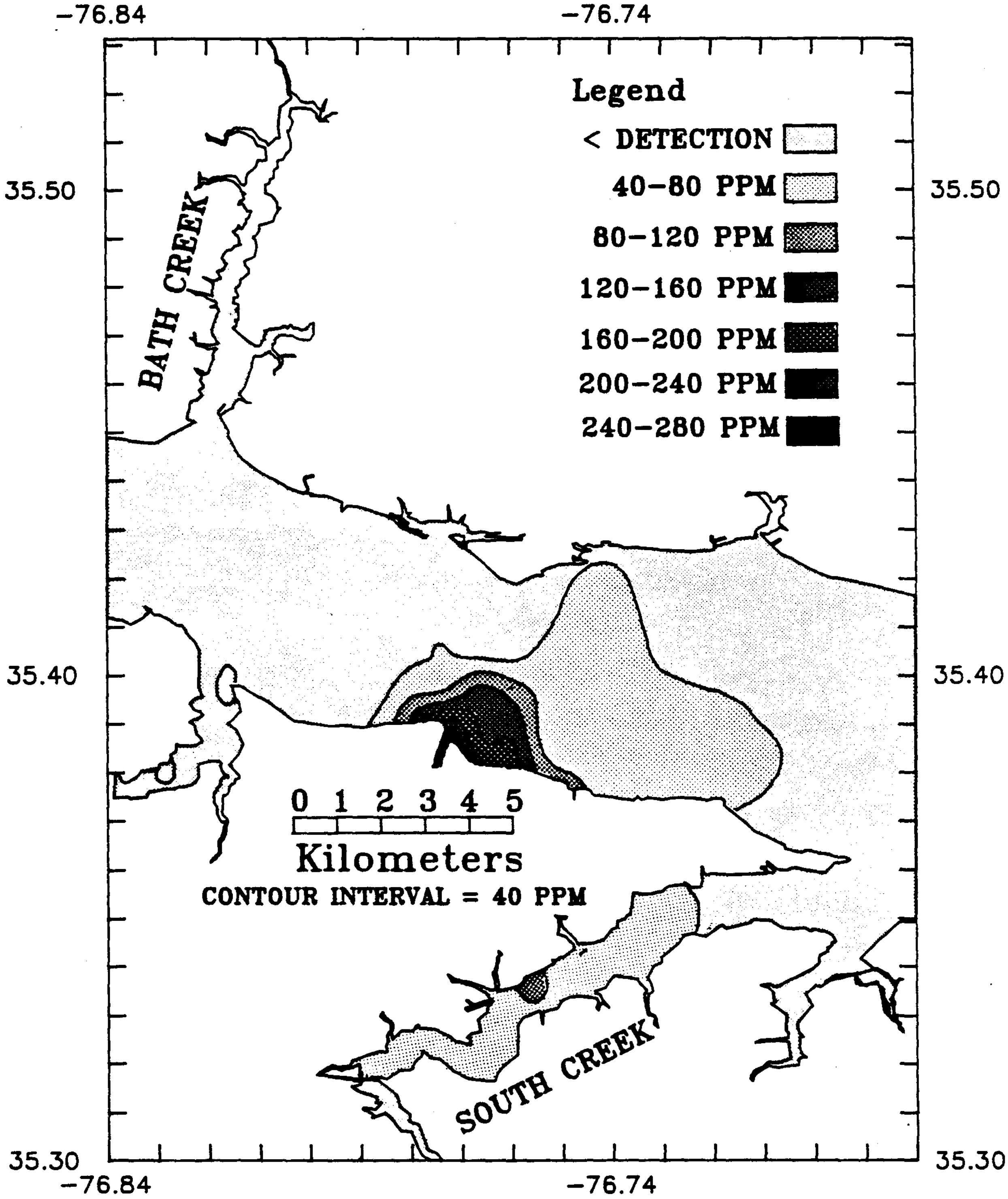


FIGURE 26. Map showing fluorine concentrations occurring in surface sediments in the middle Pamlico River area (contours are in µg/g of concentrationd above and below the trimmed mean for the Pamlico River)

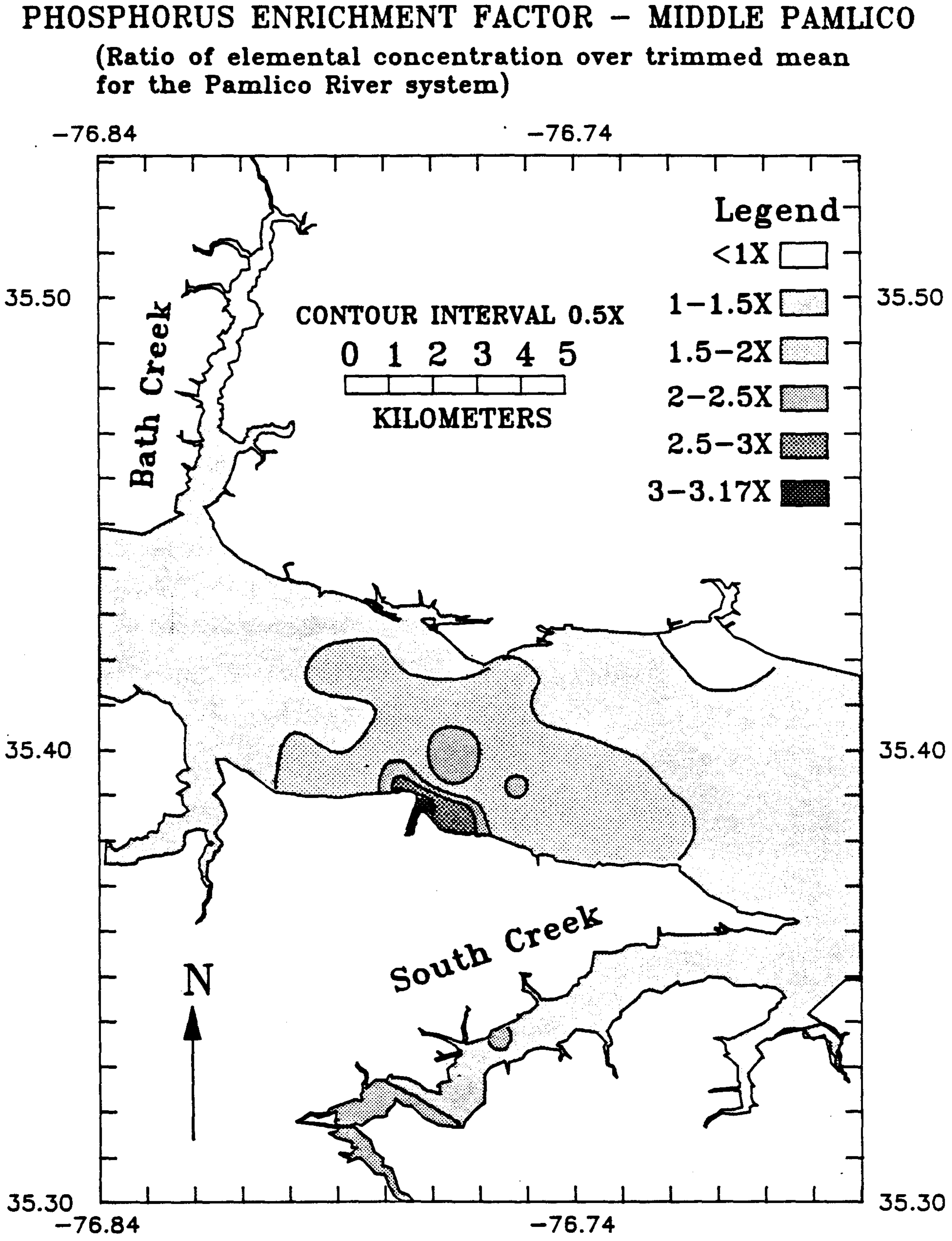


FIGURE 27. Enrichment factor map of phosphorus concentrations in surface sediments of the middle Pamlico River and South Creek areas

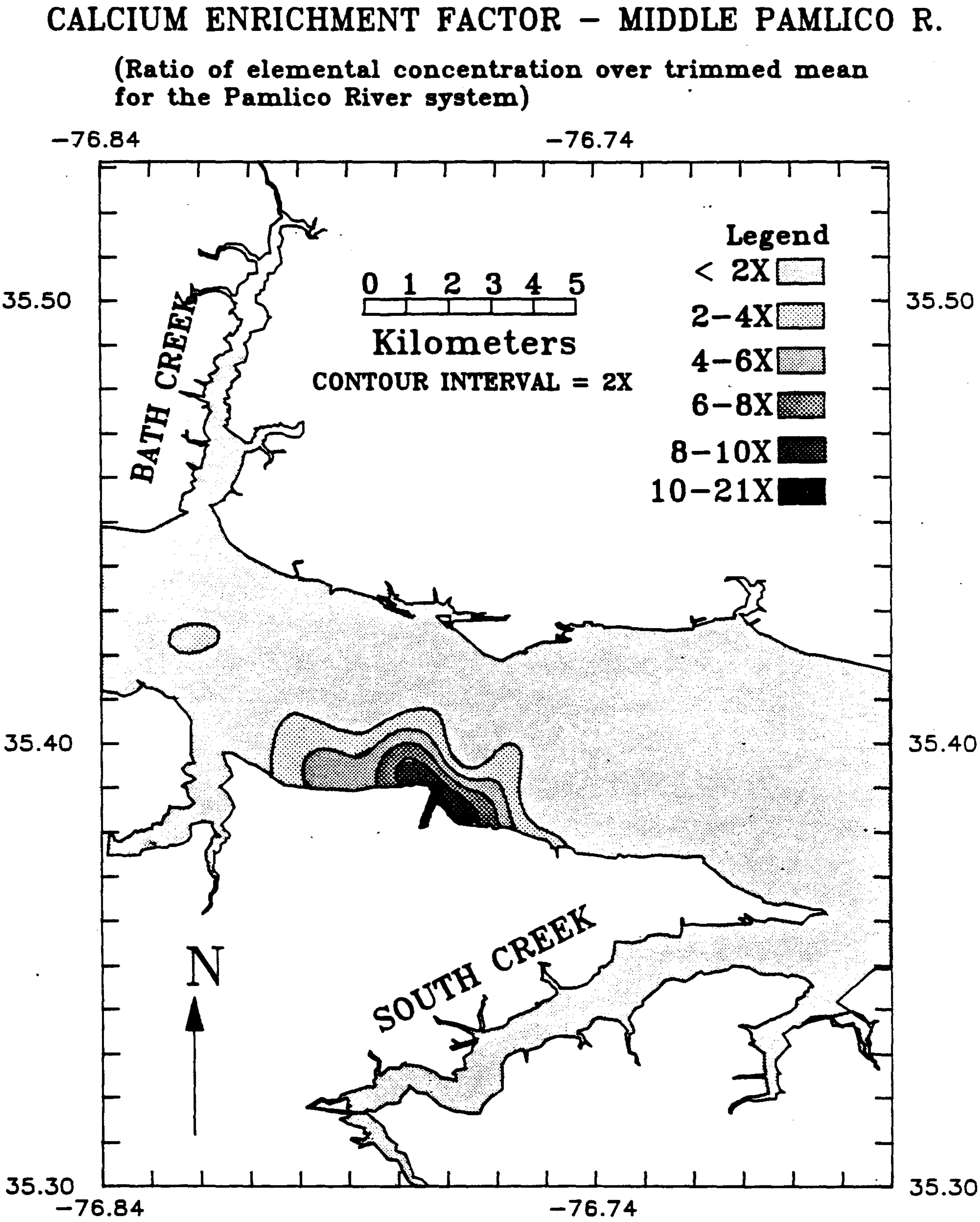
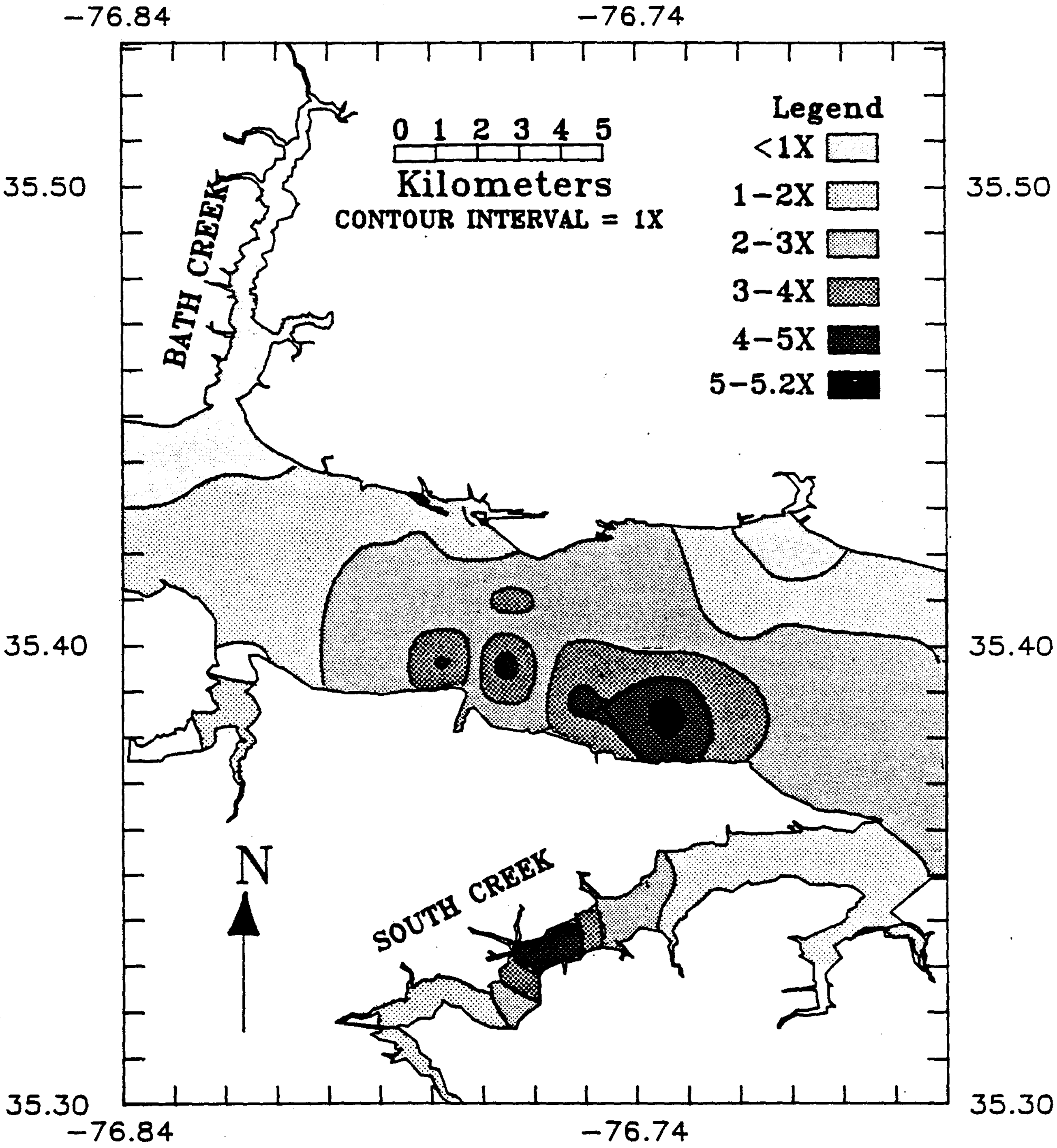


FIGURE 28. Enrichment factor map of calcium concentrations in surface sediments of the middle Pamlico River and South Creek areas


CADMIUM ENRICHMENT FACTOR – MIDDLE PAMLICO R.

(Ratio of elemental concentration over trimmed mean for the Pamlico River system)

FIGURE 29. Enrichment factor map of cadmium concentrations in surface sediments of the middle Pamlico River and South Creek areas

TABLE 20. Average concentrations (in ug/g) of enriched elements occurring in sediments from South Creek, N.C,

ELEMENT	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:						
Cd	3	1.23	0.42	0.9	1.7	4.72
Mo	3	1.07	0.12	1.0	1.2	2.40
As	1	25.7			25.7	2.01
MAJOR ELEMENTS:						
K	1	1894.5			1894.5	2.03
Na	11	7536.05	2035.23	3507.7	11256.0	2.49

A positive correlation between arsenic concentration and percentage of clay plus organics (0.78) in samples from South Creek suggests that the distribution of arsenic is at least partly controlled by sediment type. However, no significant correlation between these same parameters was observed for cadmium. However, the distribution of enriched cadmium seems to be concentrated in the pipe crossing area.

Belhaven Area

Belhaven is a small town (Figs. 1, 10, and 30) that is characterized by intermediate levels of development including paved areas, small industries, and a waste-water treatment plant. Consequently, the estuarine area around Belhaven reflects an intermediate effect by anthropogenic influences. Significant elemental enrichment occurs in samples from two portions of the Belhaven area (Fig. 31) and represents two areas of concern. Battalina Creek on the east side of Belhaven receives the municipal sewage outfall and Pantego Creek forms the Belhaven waterfront.

Battalina Creek

Battalina Creek is a very small lateral tributary that is characterized by very organic-rich mud sediments. This creek receives the discharge from the Belhaven waste-water treatment plant with a design flow of 500,000 gallons per day (municipal permit number 15 in App. I). Elevated levels (Table 21) of copper (5.32 X), nickel (2.89 X), cadmium (2.78 X), molybdenum (2.60 X), and zinc (2.51 X) occur in a single core taken several hundred meters downstream from the waste water treatment discharge point (Fig. 31). A second core taken just outside the mouth of Battalina Creek shows that there are major declines in concentrations of these metals over a very short distance from the point source. A slight enrichment still exists in cadmium (1.7 X) at the mouth of the creek but all other metals are at or below average.

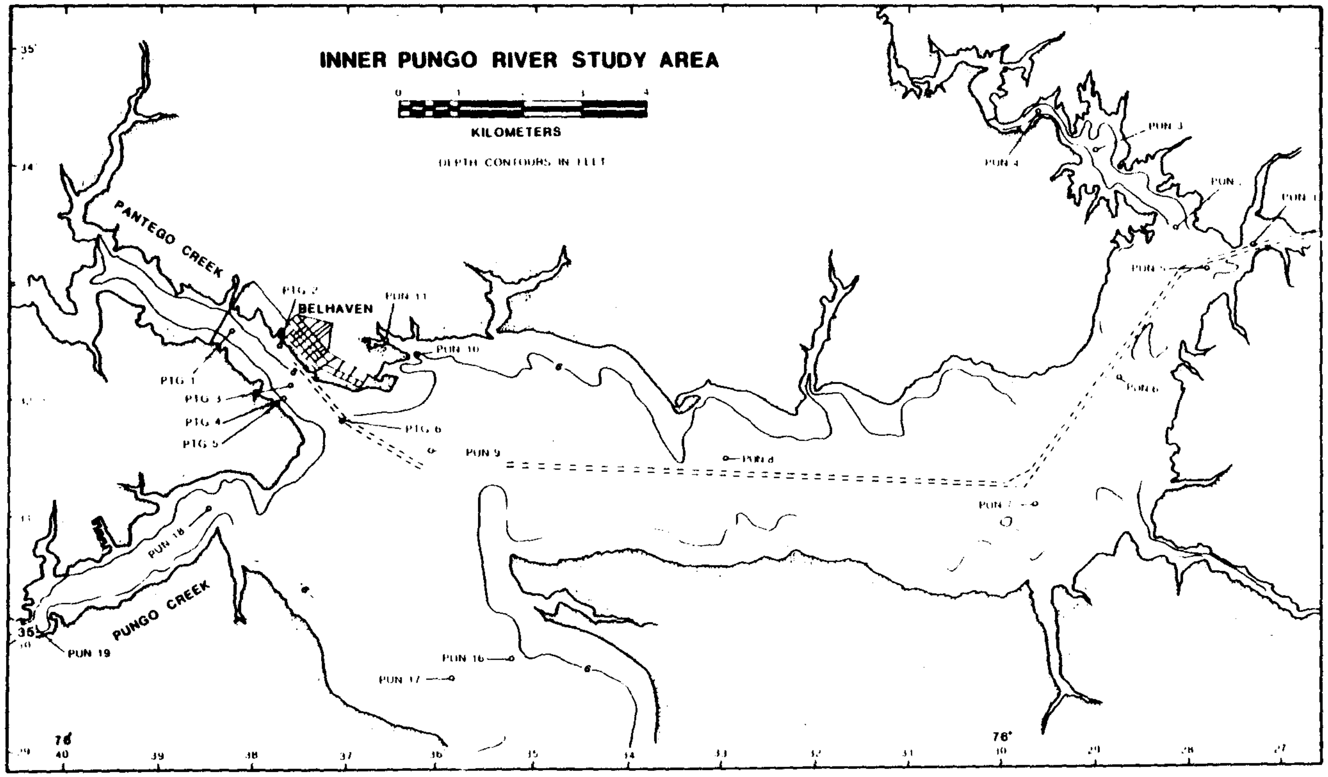


FIGURE 30. Sample location map for the inner Pungo River area

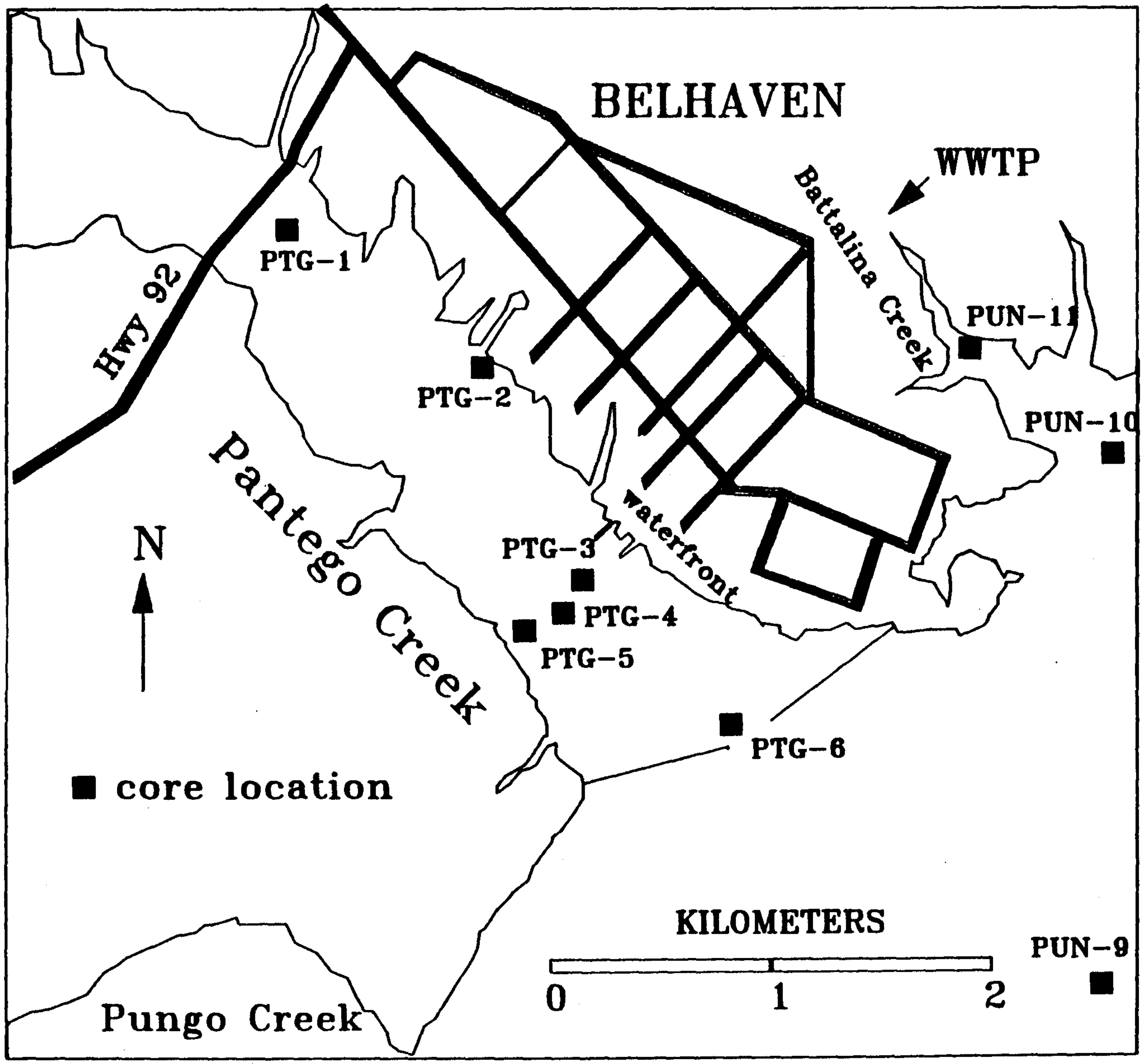


FIGURE 31. Sample location map for the Belhaven area

TABLE 21. Concentrations (in ug/g) of enriched elements in Battalina Creek, Belhaven, N.C.

ELEMENT	N	CONCENTRATION	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:			
Cu	1	72.4	5.32
Ni	1	7.7	2.89
Cd	1	1.0	2.78
Mo	1	1.3	2.60
Zn	1	193.0	2.51
MAJOR ELEMENTS:			
Na	1	6076.75	2.14

Lower Pantego Creek

The Belhaven waterfront (Fig. 31) has 8 industrial NPDES permitted discharges into Pantego Creek with a total design flow of 125,200 gallons per day, mostly from seafood processing plants (permit numbers 7,8, 40, 69, 72, 116, 117and 120 in App. I). Elevated levels of nickel (4.62 X) and cobalt (2.41 X) occur in Pantego Creek in four and two surface samples, respectively (Table 22). The highest nickel enrichment occurs about 100 feet south of the Highway 92 bridge crossing Pantego Creek (Fig. 31). Nickel enrichment factors decrease (Fig. 32) in samples extending downstream from the bridge to the jettied harbor entrance with a nickel enrichment factor of 2.7 X. Cobalt enrichment follows a similar trend but is only enriched in two of the samples. Cores not enriched in nickel and cobalt are located in areas characterized by quartz (SiO_2) sand bottoms; these are chemically inert and not conducive to metal accumulation. A moderately strong positive correlation (0.86) exists between the percentage of clay and concentration of nickel and cobalt in this area, suggesting that distribution of these metals is partly controlled by sediment type.

TABLE 22. Average concentrations (ug/g) of enriched elements occurring in Pantego Creek, Belhaven, N.C.

ELEMENT	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:						
Ni	4	9.62	1.84	8.1	12.3	4.62
Co	2	12.4	1.41	11.4	13.4	2.41

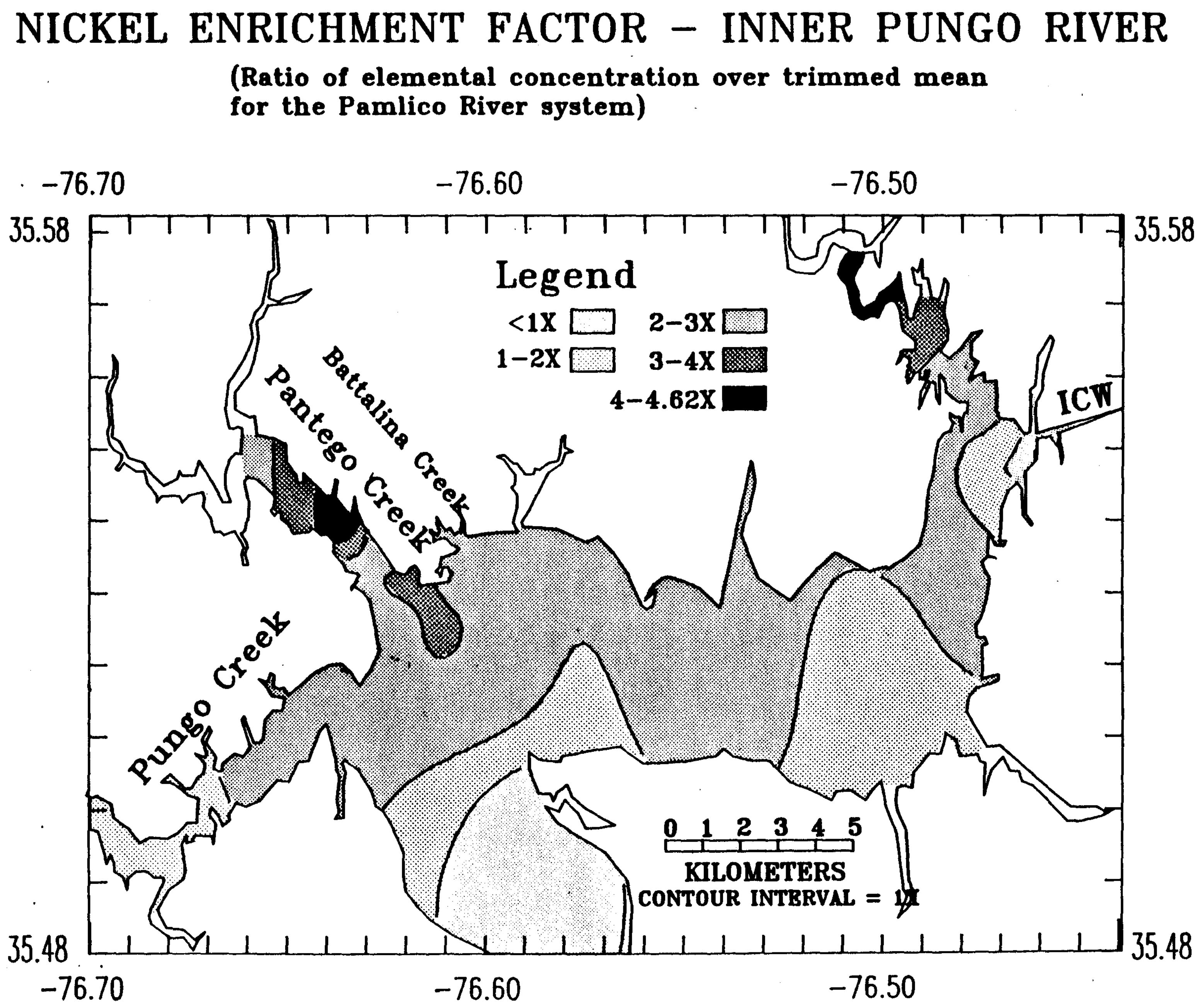


FIGURE 32. Enrichment factor map of nickel concentrations in surface sediments of the Pungo River and outer Pamlico River areas

The area affected by metal enrichment in Pantego Creek is relatively large and extends well beyond the confines of the present harbor. The original source of the nickel and cobalt to the estuarine system in this area is not clear.

Inner Pungo River Area

The inner Pungo River area (Figs. 1, 10, and 30) is enriched in three critical trace elements and four major elements (Table 23). In general, the level of nickel enrichment is fairly constant over a large portion of the inner Pungo River study area (Fig. 32). A transect of cores extending from the Highway 92 bridge over Pantego Creek west of Belhaven, eastward through the inner Pungo River to the Highway 264 bridge, north of the Alligator River canal, all have nickel enrichment factors in excess of 2 X with the highest factors occurring in the upper reaches of the two tributaries nearest the bridges.

A positive correlation was obtained between the concentration of nickel with aluminum (0.81) and with percent clay plus organic matter (0.70). This suggests that the distribution of nickel is at least partly controlled by sediment type. A negative correlation (-0.72) between the concentration of nickel with percent sand in these sediments also supports this conclusion.

TABLE 23. Average concentration (in ug/g) of enriched elements occurring in sediments from the Inner Pungo River.

ELEMENT	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:						
Ni	7	6.74	0.77	5.7	8.1	3.05
Mn	2	389.15	35.85	363.8	414.5	2.69
Ti	2	82.95	1.48	81.9	84.0	2.18
MAJOR ELEMENTS:						
Mg	5	6447.7	645.68	5792.0	7350.6	2.72
Ca	2	8933.75	918.74	8284.1	9583.4	2.60
K	2	2009.45	44.34	1978.1	2040.8	2.19
Na	16	6688.97	1994.27	1540.6	9076.2	2.01

Other trace metals such as Ti and Mn and major elements Mg, Ca, K, and Na were slightly enriched in sediments in the inner Pungo River area. Unlike nickel and cobalt, no correlation was observed between the distribution of these elements with percentages of sand or clay. However, a moderately strong correlation exists between the concentrations of calcium and organic matter in the sediments and magnesium correlates with the percentage of clay plus organic matter. Increased concentrations of magnesium, calcium, and potassium may be derived from soil ammendments and fertilization associated with large scale agriculture that occurs in the regions adjacent to the inner Pungo River.

Pungo Creek

No permitted discharges are located in Pungo Creek (Figs. 1, 10, and 30), but large agricultural areas and a small marina facility may represent potential sources of nickel enrichment (Table 24). Nickel enrichment in excess of 2 X occurs at two sites in Pungo Creek (Fig. 32) similar to that in other areas of the inner Pungo River.

TABLE 24. Concentration (in ug/g) of enriched elements occurring in sediments from Pungo Creek, N.C.

ELEMENT	N	CONCENTRATION	ENRICHMENT FACTOR
CRITICAL TRACE ELEMENT:			
Ni	1	5.6	2.11

Marina Complexes

Broad Creek

Broad Creek (Figs. 1, 10, and 33) contains the highest concentration of boat slips in the Pamlico River estuarine system, as well as a marina railway system. A large portion of this marina complex is relatively new, particularly those on the eastern shore; however, much of the western shore complex has been in existence for many decades. Elevated levels of copper (14.26 X), lead (2.26 X), and mercury (2.22 X) were encountered at two sites immediately adjacent to the marina railway facility (Table 25). Although the enrichment factor for copper is high (14.26 X) the areal extent of contamination appears to be confined to a small radius surrounding the railway system. Samples both upstream and downstream of the railway have copper concentrations at or below the average for the Pamlico River (Fig. 34). Lack of correlation between enriched metals with sediment characteristics suggests that metal enrichment distribution in Broad Creek is directly related to proximity of point sources.

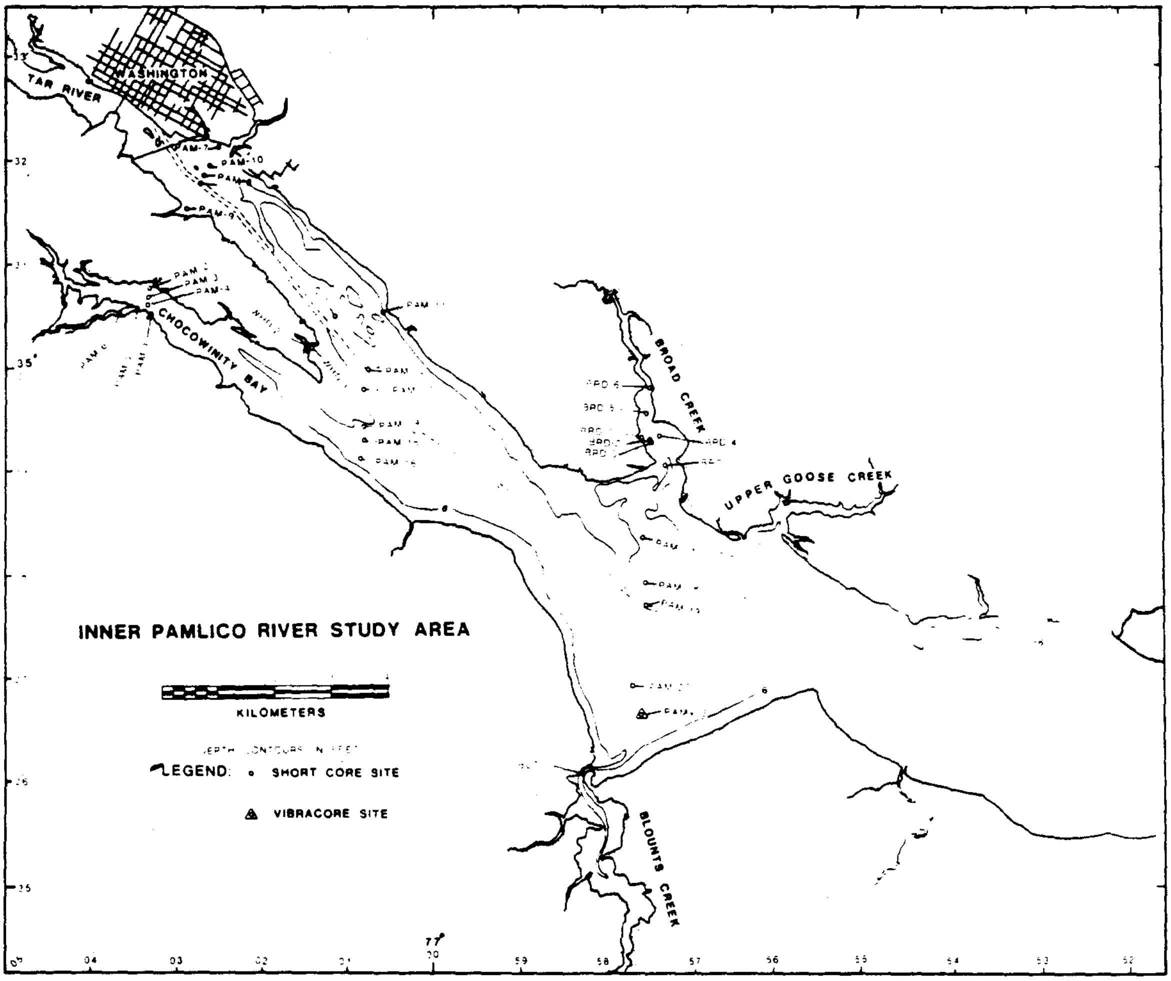


FIGURE 33. Sample location map for the inner Pamlico River area including Broad Creek, Chocowinity Bay, and Whichards areas

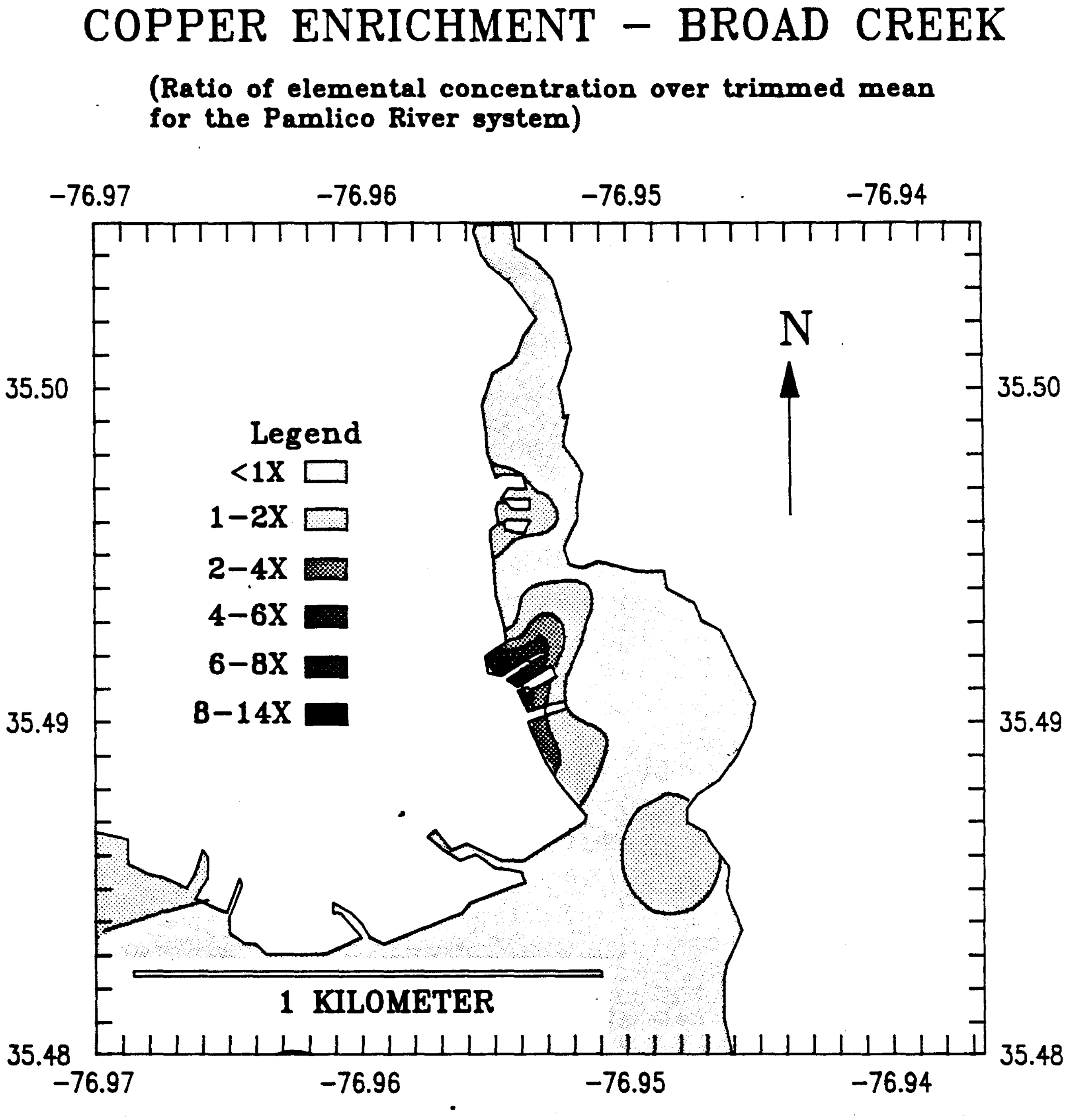


FIGURE 34. Enrichment factor map of copper concentrations in surface sediments of Broad Creek and the inner Pamlico River areas

TABLE 25. Average concentrations (in ug/g) of enriched elements occurring in Broad Creek, N.C.

ELEMENT	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	MAXIMUM ENRICHMENT FACTOR
CRITICAL TRACE ELEMENTS:						
Cu	2	111.0	117.38	28.0	194.0	14.26
Pb	1	81.0	*****	81.0	81.0	2.26
Hg	1	0.2	*****	0.2	0.2	2.22

Whichards Beach

Whichards Beach area (Figs. 1, 10, and 33) contains a small, older marina and boat maintenance facility, as well as a small residential area; however, there are no permitted NPDES discharges located in this area. Sample sites located adjacent to the marina facility at Whichards Beach are enriched 3.15 X in copper; it decreases to 1.5 X and 1.2 X into the deep portions of the adjacent canal and east into the open river, respectively. Also, slightly elevated levels of phosphorus occur in the area surrounding the marina (1.4 X) and increase into the channel east of the marina (2.2 X). Phosphorus enrichment is believed to be related to septic tanks from the adjacent housing development.

Nonpolluted Regions

Outer Pamlico River and Outer Pungo River

This is a large area underlain by an extensive deposit of organic-rich mud with no major municipalities or known major wastewater discharges. A large number of fishing trawlers work in this region and continously disrupt the mud bottom and suspends fine-grained sediments. Fortunately, no significant metal enrichment was found in the nine cores taken on a wide-spaced grid through this estuarine area (Fig. 35). As can be seen on Figures 26 (fluorine), 27 (phosphorus), and 28 (calcium), most of the elemental enrichment associated with active phosphate mining to the west has decreased. Consequently, sediments in this area are either below detection limit (fluorine) or are equal to or below the trimmed mean (most other elements) for the estuarine system. Nickel enrichment (Fig. 32) in the inner Pungo River has also decreased southward to values below the trimmed mean in this area. However, the vast area of cadmium enrichment associated with phosphate mining, does extend eastward into this area (Fig. 29).

Chocowinity Bay

Chocowinity Bay (Figs. 10 and 33) has no NPDES discharge sites, industrial sites, urban areas, major residential developments, or

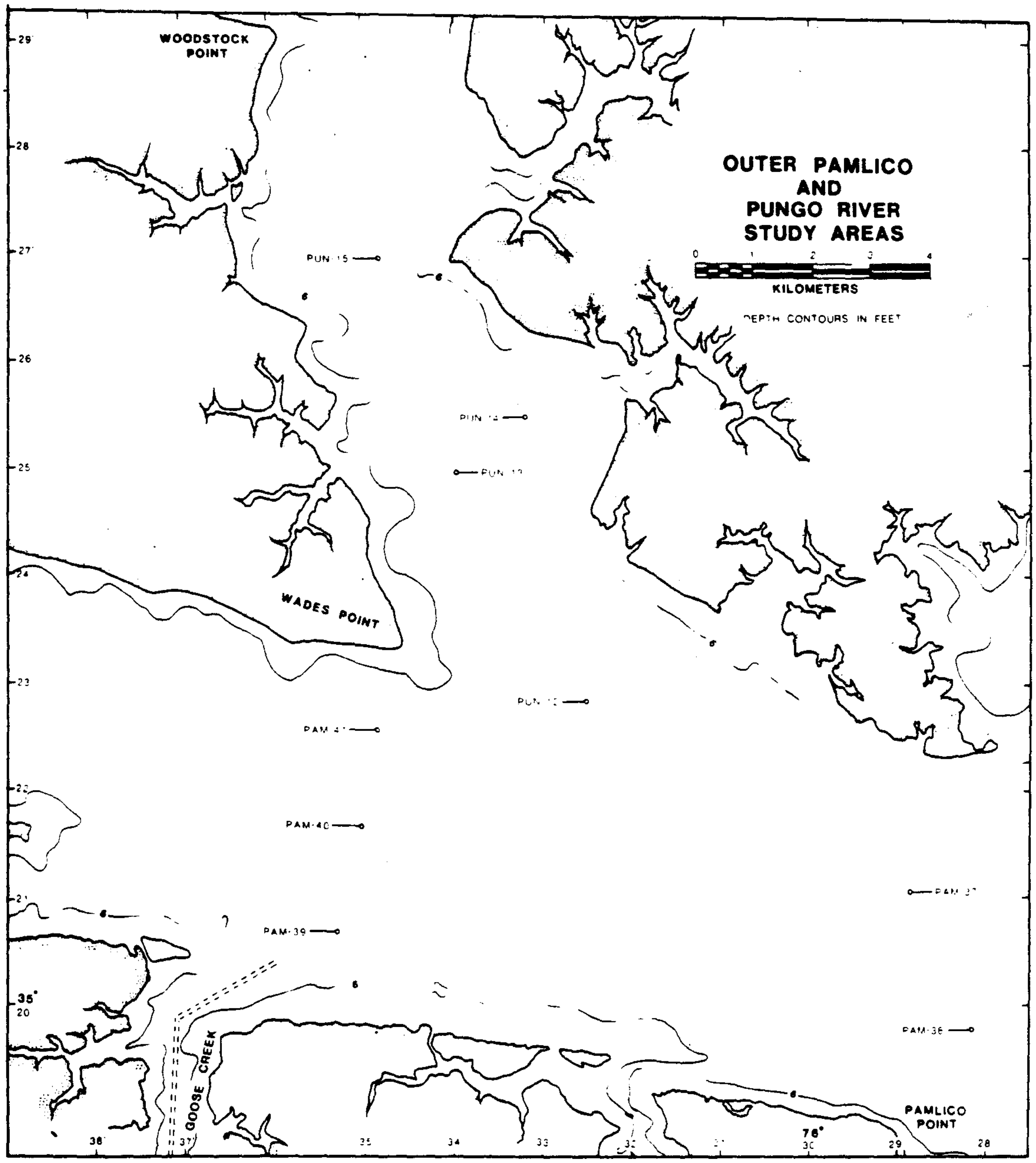


FIGURE 35. Sample location map for the outer Pamlico and outer Pungo River areas

agricultural activity in close proximity to the shoreline. Consequently, the concentration of priority pollutant metals in Chocowinity Bay are among the lowest in the Pamlico River estuarine system (Table 26). Elevated levels of manganese and molybdenum do occur in one of six cores in this area. However, this may reflect higher natural background levels which may be due to the very high organic content (43%) in the sediment.

TABLE 26. Mean concentration of 21 elements (in ug/g) in surface sediments of Chocowinity Bay

ELEMENT	MEAN (N=6)	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
EPA Priority Metal Pollutants:				
As	7.77	3.26	3.6	12.6
Cr	4.55	2.32	2.5	8.3
Cd	0.18	0.17	0.0	0.4
Cu	6.4	2.51	3.5	9.8
Ni	0.98	0.74	0.1	2.1
Pb	21.68	11.25	11.9	40.9
Zn	35.57	16.53	17.1	56.6
Hg	0.06	0.02	0.03	0.08
Other Trace Elements:				
Co	5.32	1.36	3.4	7.0
Mn	175.92	103.91	100.0	371.2
Mo	0.5	0.3	0.2	1.0
P	464.6	212.16	217.3	707.3
Ti	20.95	4.95	14.4	27.6
V	11.07	5.0	5.9	19.9
Major Elements:				
Al	3986.97	1857.47	1910.0	6922.5
Ca	2880.57	1579.71	1188.4	5888.5
Fe	12622.67	4113.19	5910.1	16878.7
Mg	2270.5	1470.85	962.9	4869.5
K	492.97	232.75	245.0	852.0
Si	938.05	211.63	665.0	1241.0
Na	3301.93	2144.94	1336.5	6898.5

Blounts Creek

No significant metal enrichment occurred in one core taken just inside the mouth of Blounts Creek (Figs. 10 and 33). Concentrations of the priority pollutant metals in this location are among the lowest in the entire estuarine system.

Bath Creek

In colonial times, Bath Creek (Figs. 10 and 25) was used as a coastal seaport supporting a considerably larger population than the small, rural town of today. Today, Bath Creek is surrounded by scattered residences with small scale agriculture and local marinas. The area lacks extensive paved areas, storm sewers, small industries, and waste treatment plants do not exist. Consequently, Bath Creek is an area which appears to be only slightly affected by anthropogenic influences. No significant elemental enrichment was encountered in samples from four stations in Bath Creek; concentrations are generally close to the trimmed mean for the Pamlico River estuarine system (Table 27).

TABLE 27. Mean concentrations of 21 elements (in ug/g) in surface sediments of Bath Creek

ELEMENT	MEAN (N=4)	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
EPA PRIORITY METAL POLLUTANTS				
As	15.92	0.45	15.7	16.6
Cr	11.5	0.85	10.5	12.5
Cd	0.2	0	0.2	0.2
Cu	14.4	1.07	12.9	15.3
Ni	1.55	0.21	1.3	1.8
Pb	44.37	1.75	42.0	45.7
Zn	60.02	4.57	54.0	65.1
Hg	0.07	0.02	0.03	0.08
OTHER TRACE ELEMENTS				
Co	4.17	0.46	3.7	4.8
Mn	155.72	14.98	143.8	176.7
Mo	0.7	0.22	0.4	0.9
P	587.42	61.30	507.6	651.6
Ti	35.72	3.49	32.8	40.2
V	25.37	2.45	22.5	28.5
MAJOR ELEMENTS				
Al	8168.35	339.39	7748.6	8575.6
Ca	3362.5	929.35	2271.1	4247.1
Fe	20734.77	1669.82	18566.9	22316.9
Mg	2779.32	238.3	2636.4	3133.9
K	1272.22	78.83	1215.0	1388.5
Si	1220.32	71.42	1141.8	1300.3
Na	4757.35	1566.29	3815.7	7093.5

Durham Creek

Samples from Durham Creek (Figs. 10 and 25) have metal concentrations which are at or below average in all of the priority pollutant metals. Elevated levels of calcium in this area may reflect the influence of calcium compounds added to discharge waters from the adjacent mining facility.

Tranters Creek

No metal enrichment was observed in any of three cores located one half mile upstream from the mouth of Tranters Creek (Figs. 10 and 19). Levels of metal concentrations in these samples were among the lowest encountered in the entire estuarine system.

Mixon Creek

No metal enrichment was encountered in sediment from one core taken just inside the mouth of Mixon Creek (Figs. 10 and 25).

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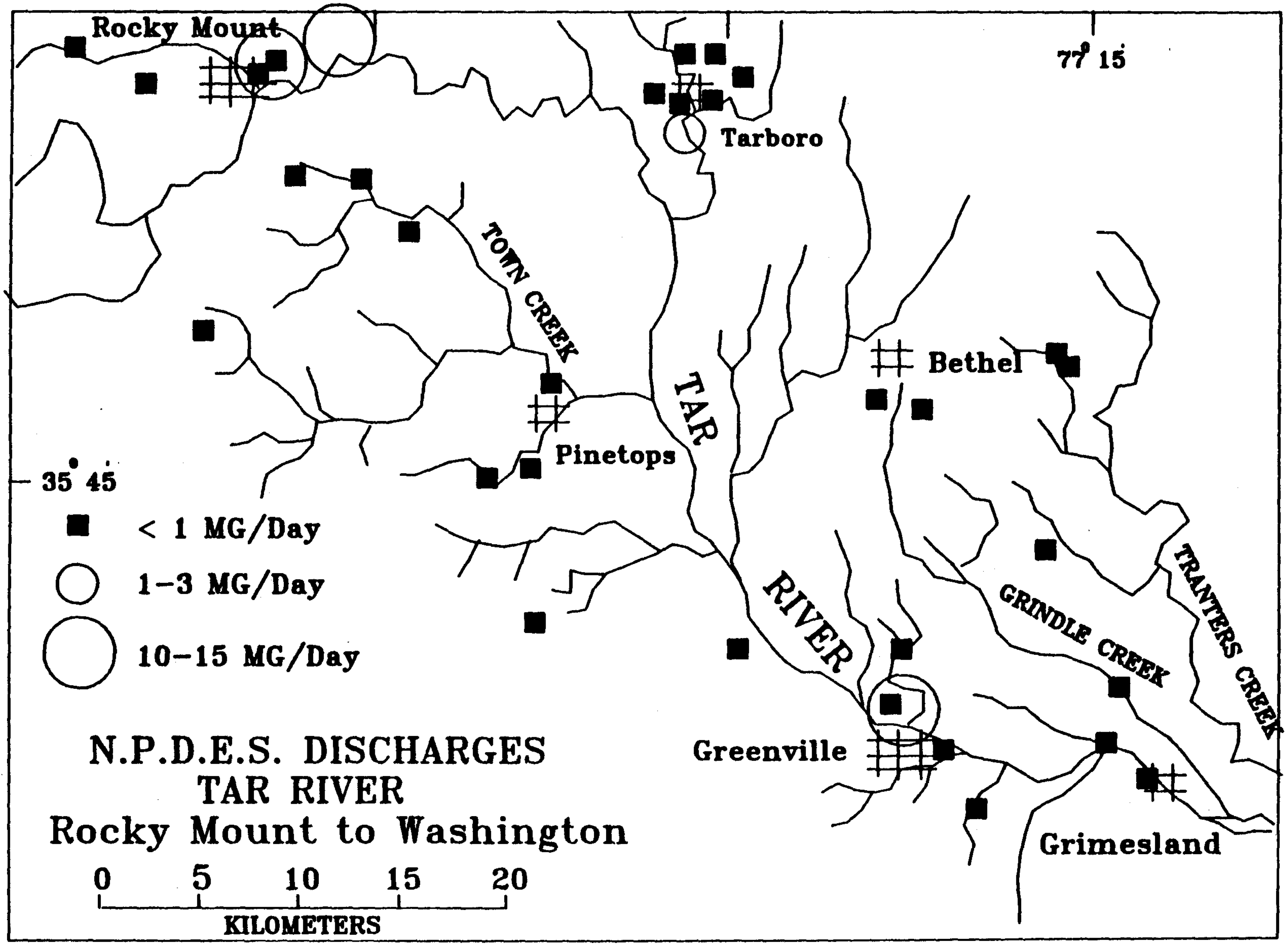
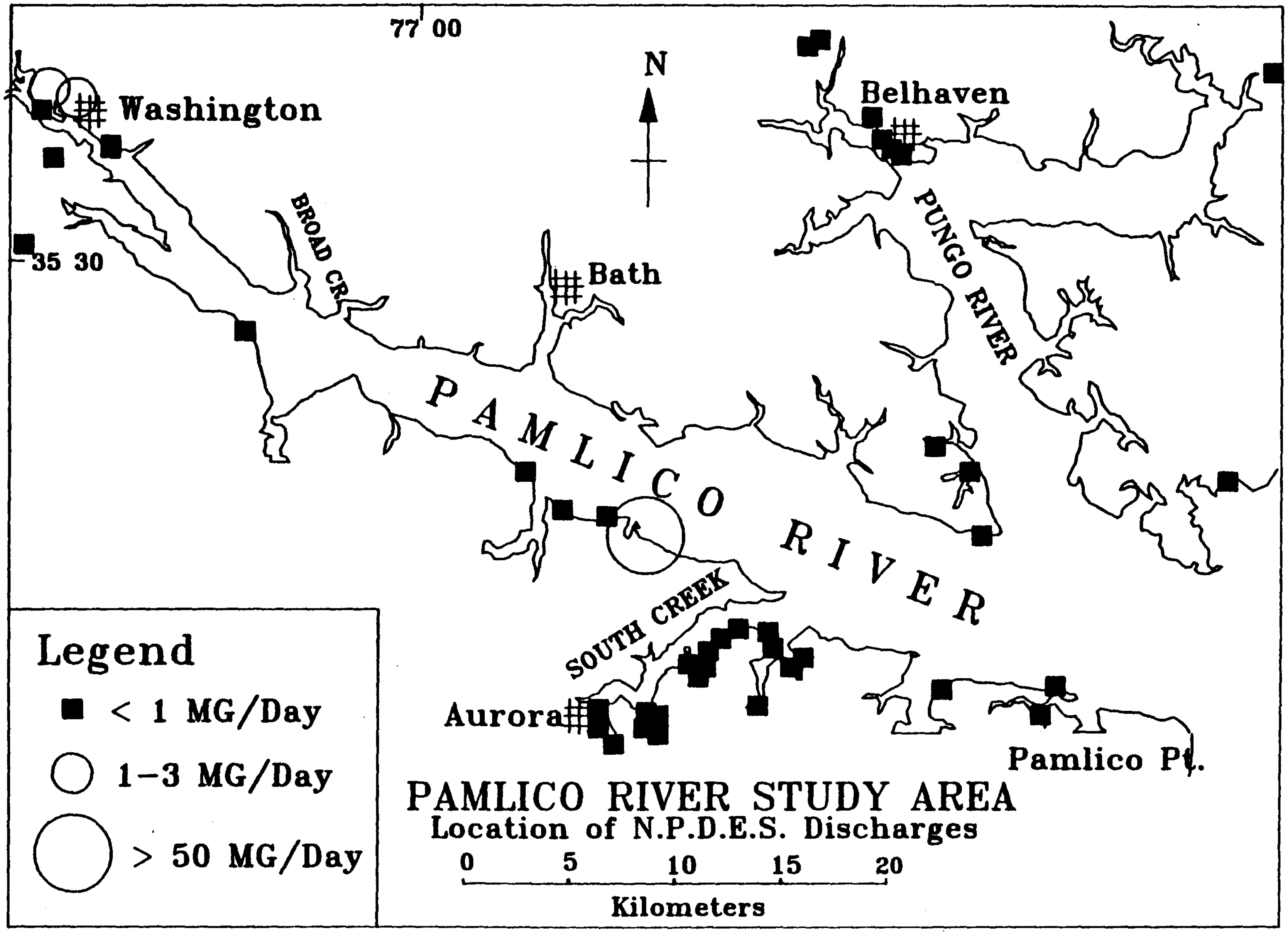
APPENDIX I

NPDES WASTE WATER DISCHARGE PERMITS FOR THE TAR/PAMLICO DRAINAGE BASIN AS OF 2/15/89

1. Location map of NPDES waste water discharge permits for the Tar River between Rocky Mount and Washington
2. Location map of NPDES waste water discharge permits for the Pamlico River
3. Table delineating the permittee, location, and design flow for industrial and municipal NPDES waste water discharge permits for the Tar/Pamlico drainage basin


Rocky Mount
Tarboro
77° 15'
TOWN CREEK
Bethel
TAR
Pinetops
35° 45'
■ < 1 MG/Day
○ 1-3 MG/Day
◯ 10-15 MG/Day
RIVER
GRINDLE CREEK
TRANTERS CREEK
Greenville
Grimesland
N.P.D.E.S. DISCHARGES
TAR RIVER
Rocky Mount to Washington
0
5
10
15
20
KILOMETERS


77 00
N
Washington
Belhaven
BROAD CR.
Bath
35 30
PUNGO RIVER
PAMLICO RIVER
SOUTH CREEK
Aurora
Pamlico Pt.
Legend
■ < 1 MG/Day
○ 1-3 MG/Day
○ > 50 MG/Day
PAMLICO RIVER STUDY AREA
Location of N.P.D.E.S. Discharges
0
5
10
15
20
Kilometers

N	Facility Name	Township	Latitude Decimal	Longitude Decimal	Design Flow (MG/D	Monitoring Parameters
Non-municipal:						
1	Texasgulf Chemicals	Aurora, NC	35.35944	76.77722	60.0000	Fluoride
2	Greenville Utilities	Greenville, NC	35.59056	77.30139	10.5000	
3	National Spinning Co. Washington	Washington, NC	35.54778	77.07694	1.7500	Cr, Phenol
4	Blount Property (Judson H., Jr.)	Greenville, NC	35.60778	77.24278	1.0000	
5	Seaboard RR-Rocky Mount	Jacksonville, Fl.	35.92417	77.81222	0.1000	MBAS
6	Riviera Util./Lake Royalle	Bunn, NC	35.95028	78.18944	0.0800	
7	Harbour Point Associates	Belhaven, NC	35.52750	76.54306	0.0600	
8	Harris Crab-Orleans Food Co.	Belhaven, NC	35.53500	76.62333	0.0550	
9	Georgia Pacific - Enfield	Enfield, NC	36.15583	77.69611	0.0500	Phenols, M
10	Lake Vance Mobile Home Estates	Henderson, NC	36.34111	78.46667	0.0480	
11	Texasgulf Chemicals Co.-(NCPC)	Aurora, NC	35.40972	76.82639	0.0420	
12	Texasgulf Chemicals Co.-NCPC	Aurora, NC	35.40972	76.82639	0.0420	
13	DOT-Granville Co. Rest Area	Oxford, NC	36.23389	78.64194	0.0400	
14	Kittrell Job Corp. Center	Kittrell, NC	36.22944	78.44944	0.0300	
15	Family Park Trailer Court	*******	36.24028	78.61111	0.0250	
16	Ban Inn, Inc. DBA Scottish Inn	Battleboro, NC	36.06833	77.81806	0.0250	
17	DOC-Nash Advancement Center	Nashville, NC	35.96528	78.02389	0.0241	
18	Azalea Gardens MHP	Greenville, NC	35.58194	77.32417	0.0240	
19	Vance-Granville Comm College	Henderson, NC	36.32306	78.48389	0.0200	
20	N.C. State Indian Housing Auth.	Gaston, NC	36.26167	77.94861	0.0200	
21	Nash Co Sch-Northern Nash HS	Rocky Mount, NC	35.99500	77.89694	0.0200	
22	Nash Co. Sch-Benvenue Elem.	Rocky Mount, NC	35.97750	77.81111	0.0200	
23	Edgecombe Co. Sch-N. Edgecombe	Tarboro, NC	35.98056	77.59444	0.0200	
24	Singer Furniture	Chocowinity, NC	35.52056	77.10222	0.0200	Chromium,
25	Halifax Co. Sch-Northwest HS	Halifax, NC	36.38694	77.79306	0.0170	
26	DOC-Vance Subsidiary	Raleigh, NC	36.27028	78.36278	0.0150	
27	Nash Co Sch-S. Nash Jr. HS	Spring Hope, NC	35.88194	78.08750	0.0150	
28	Pitt Co. Sch N-Pitt Co. High Sch.	Greenville, NC	35.74722	77.36444	0.0150	
29	Mid-East Regional Housing Auth	Washington, NC	35.42583	76.33333	0.0120	
30	Lemon Tree Inn	Chocowinity NC	36.60278	77.10028	0.0110	
31	Pines Mobile Home Park	Louisburg, NC	36.14250	78.45306	0.0100	
32	DOC-Franklin Co. Subsidiary	Raleigh, NC	35.94056	78.24583	0.0100	
33	Nash Co Sch-Coopers Elem	Elm City, NC	35.88222	77.94556	0.0100	
34	Halifax Co. Sch-Arelian Spring	Halifax, NC	36.36250	77.80861	0.0100	
35	Edgecombe Co. Sch-W. Edgecombe	Tarboro, NC	35.90389	77.73500	0.0100	
36	Edgecombe Co. School, W. Bullock	Tarboro, NC	35.88444	77.71917	0.0100	
37	Edgecombe Co. Sch-Phillips	Tarboro, NC	36.00472	77.68639	0.0100	
38	Halifax Co. Sch-Eastman High	Halifax, NC	36.23972	77.85083	0.0096	
39	Halifax Co. Sch-Pittman Elem.	Halifax, NC	36.26361	77.74417	0.0096	

N	Facility Name	Township	Latitude Decimal	Longitude Decimal	Design Flow (MG/D	Monitoring Parameters
40	Sea Safari LTD	Belhaven, NC	35.53500	76.62167	0.0080	
41	USFWS-Mattamuskeet Wild. Refug.	Swanquarter, NC	35.45000	76.17639	0.0080	
42	USFWS - Mattamuskeet Wildlife Ref	Swanquarter, NC	35.45000	76.17639	0.0080	
43	Halifax Co. Sch-Thomas Shields	Halifax, NC	36.03417	77.39250	0.0077	
44	Halifax Co. Sch-Dawson Elem.	Halifax, NC	36.16917	77.52306	0.0073	
45	Vance Co. Sch-Yancey	Henderson, NC	36.30583	78.40083	0.0070	
46	Nash Co Sch-Cedar Grove Elem	Nashville, NC	36.07833	77.96556	0.0070	
47	Vance Co. Carver High Sch.	Henderson, NC	36.37278	78.32861	0.0065	
48	Corryhiebert, Inc.	Louisburg, NC	36.08028	78.32722	0.0060	
49	Franklin Co Sch-Best Middle	Franklin, NC	36.09306	78.16778	0.0060	
50	Halifax Co. Sch-Hollister Elem.	Halifax, NC	36.25861	77.94278	0.0060	
51	Nash Co Sch-Whitakers Elem	Whitakers, NC	36.11472	77.77083	0.0060	
52	Pitt Co. Sch. G. R. Whitfield	Greenville, NC	35.56556	77.18250	0.0060	
53	Beaufort Co. Sch-Beaufort Elem.	Washington, NC	35.58667	76.66778	0.0060	
54	Granville Co. School-Wilton Sch.	Franklinton, NC	36.14639	78.58278	0.0053	
55	Nash Co Sch-Swift Creek Elem	Whitakers, NC	36.10778	77.89417	0.0052	
56	Exxon Co.-Murphy & Wollet	Enfield, NC	36.27528	77.72028	0.0050	
57	Martin Co. Sch-Bear Grass Elem	Bear Grass, NC	35.76861	77.12889	0.0050	
58	Hyde Co. Sch-Mattamuskeet	Swanquarter, NC	35.43778	76.21694	0.0050	
59	Pitt Co. Stokes Elem.	Stokes, NC	35.71667	77.28333	0.0040	
60	Spencer's Rest Home	Panteo, NC	35.58556	76.67222	0.0040	
61	Wilson Co. Sch.-Gardners	Gardners, NC	35.74306	77.78194	0.0038	
62	Pitt Co. Falkland Elem. Sch.	Falkland, NC	35.67111	77.48583	0.0035	
63	Warren Co. Sch-Vaughan Elem.	Vaughn, NC	36.42083	78.00167	0.0034	
64	Warren Co. Sch-South	Warrenton, NC	36.32139	78.20083	0.0030	
65	Martin Co Sch-N Everetts Elem	Williamston, NC	35.84167	77.17417	0.0020	
66	Little Huff,INC/Elliot's P&S	Oxford, NC	36.30972	78.59389	0.0015	
67	Robbies Inc. Texaco	Enfield, NC	36.27389	77.72361	0.0015	
68	Henderson Head Start Center	Henderson, NC	36.35639	78.47611	0.0012	
69	Belhaven TW-Beau.	Belhaven, NC	35.54722	76.62889	0.0012	
70	Lee Oil Co.	Rocky Mount, NC	36.16861	77.77222	0.0010	
71	Daniels Seafood	Aurora, NC	35.33667	76.69028	0.0010	
72	Hopkins Seafood And Grocery	Belhaven, NC	35.41111	76.60500	0.0010	
73	Kittrell Coll. Faculty Housing	Kittrell, NC	36.22167	78.45417	0.0007	
74	Heritage Meadows Long Term Care	Oxford, NC	36.38139	78.66250	0.0001	
75	Bandag Inc.	Oxford,NC	36.29389	78.61278	0.0000	
76	Becton Dickinson & Co./ Edmont	Tarboro, NC	35.91333	78.58500	0.0000	
77	Martin Marietta-Franklin Quarr	Franklin, NC	36.07111	78.49722	0.0000	
78	Novo Biochemical Ind. Inc.	Franklinton, NC	36.10306	78.41389	0.0000	
79	Brentwood Rest Home	Louisburg, NC	36.07500	78.30306	0.0000	

N	Facility Name	Township	Latitude Decimal	Longitude Decimal	Design Flow (MG/D	Monitoring Parameters
80	Peck Manufacturing Co.	Warrenton, NC	36.40722	78.16083	0.0000	
81	Warren Plaza Rest Home	Warrenton, NC	36.40167	78.13250	0.0000	
82	Perdue Farms-Nashville	Nashville, NC	35.96611	78.00194	0.0000	
83	Rocky Mount, City of (Tar River)	Rocky Mount, NC	35.90028	77.88361	0.0000	
84	Rocky Mount, City of (Sunset)	Rocky Mount, NC	35.95250	77.81889	0.0000	
85	Mohasco Uphols. Furn.-Rocky Mt.	Rocky Mount, NC	35.97083	77.78333	0.0000	
86	USAR Center- Rocky Mount	Rocky Mount, NC	35.94222	77.77611	0.0000	
87	Phillips Fibers Corp.	Rocky Mount, NC	35.96139	77.77472	0.0000	
88	Schlage Lock Co.	Rocky Mount, NC	36.02528	77.76611	0.0000	
89	Abbott Labs-Hospital Prod	Rocky Mount, NC	36.03083	77.76083	0.0000	Chloride,
90	Garland Langley Inc.	Rocky Mount, NC	36.04389	77.75639	0.0000	
91	Poly-Tech, Inc.	Battleboro, NC	36.05972	77.74250	0.0000	
92	Robbies Inc.-Gulf	Enfield, NC	36.27500	77.72167	0.0000	
93	Martin Marietta-Fountain	Fountain, NC	35.67361	77.62694	0.0000	
94	Masonite Corp Melamine Div.	Tarboro, NC	35.90833	77.58611	0.0000	
95	Long MFG CO-Tarboro	Tarboro, NC	35.92500	77.55333	0.0000	MBAS
96	Farmer Oil Co.	Tarboro, NC	35.91306	77.54750	0.0000	
97	TI-CARO Inc.-Tarboro Plant	Tarboro, NC	35.89778	77.53972	0.0000	
98	American Peat Company Inc	Pantego, NC	35.68139	77.53250	0.0000	As, Cd, Cr
99	Empire of Carolina Inc.	Tarboro, NC	35.91417	77.53222	0.0000	
100	Abbott Laboratories	Battleboro, NC	35.76528	77.50000	0.0000	Chloride,
101	TRW	Greenville, NC	35.64611	77.36611	0.0000	
102	Empire Brushes	Greenville, NC	35.65222	77.36333	0.0000	
103	Eagle Snacks Inc.	Robersonville, NC	35.79417	77.25333	0.0000	
104	Robersonville Ice & Coal Co.	Robersonville, NC	35.82528	77.24639	0.0000	
105	Edinburg Hardwood Lumber	Washington, NC	35.62583	77.20222	0.0000	
106	National Spinning Co. Washington	Washington, NC	35.55472	77.07667	0.0000	Cr, Zn.
107	Maola Ice Co.	Washington, NC	35.54083	77.05500	0.0000	
108	Coastal Water Systems, Inc.	Washington, NC	35.55333	77.05139	0.0000	
109	Camp Hardee Girl Scouts	Blounts Creek, NC	35.49167	76.99167	0.0000	
110	Pamlico Plantation TOA	Washington, NC	35.49222	76.96667	0.0000	
111	Potter Oil Co. Inc.	Aurora, NC	35.30139	76.80917	0.0000	
112	Texasgulf Chemicals	Aurora, NC	35.35944	76.77722	0.0000	
113	Texasgulf Chemicals	Aurora, NC	35.35944	76.77722	0.0000	Fluoride
114	Carolina Seafood	Aurora, NC	35.33667	76.69083	0.0000	
115	Carolina Fisheries	Aurora, NC	35.33056	76.66944	0.0000	
116	Selby Dirt Hauling	Belhaven, NC	35.51528	76.66528	0.0000	
117	Belhaven Fish & Oyster Co.	Belhaven, NC	35.53667	76.62389	0.0000	
118	Sadler and Son Seafood, Inc.	Lowland, NC	35.32583	76.60917	0.0000	
119	USCG Station - Hobucken	Portsmouth, VA	35.24722	76.59250	0.0000	

N	Facility Name	Township	Latitude Decimal	Longitude Decimal	Design Flow (MG/D	Parameters Monitoring
120	Jordan Seafood	Belhaven, NC	35.41389	76.59167	0.0000	
121	Lowland Seafood	Lowland, NC	35.29500	76.58667	0.0000	
122	Harbor Packing Co.	Lowland, NC	35.32056	76.56111	0.0000	
123	Caroon Bros. Seafood	Lowland, NC	35.31944	76.55944	0.0000	
124	Capt'n Carls Seafood	Scranton, NC	35.42611	76.45722	0.0000	
125	Whitetail Farms	Fairfield, NC	35.55694	76.42500	0.0000	
126	Rose Bay Oyster Co.	Swanquarter, NC	35.54444	76.40361	0.0000	
127	Newman Seafood	Swanquarter, NC	35.40278	76.34000	0.0000	
128	Clarks Marina & Seafood	Swanquarter, NC	35.40444	76.33472	0.0000	
129	Swanquarter Crab Co.	Swanquarter, NC	35.40556	76.33444	0.0000	
130	Far Creek Seafood-Engelhard	Engelhard, NC	35.50861	75.99611	0.0000	
131	Johnson & Johnson Seafood	Engelhard, NC	35.50806	75.99583	0.0000	
132	Standard Products Co.	Rocky Mount, NC	********	********	0.0000	
133	Burroughs-Wellcome Co.	Greenville, NC	35.65667	77.35667	0.0000	
Municipal:						
1	Rocky Mount, Tar River WWTP	Rocky Mount, NC	35.64361	77.72417	14.0000	
2	Rocky Mount WWTP, Leggett Road	Rocky Mount, NC	35.97694	77.72472	12.0000	
3	Tarboro WWTP, Town of	Tarboro, NC	35.88306	77.53833	3.0000	Copper, Zi
4	Littleton WWTP, Town of	Littleton, NC	36.41500	77.90611	2.8000	
5	Washington WWTP, Town of	Washington, NC	35.55139	77.07611	2.2500	
6	Warren Co. WWTP	Warrenton, NC	36.37972	78.16861	2.0000	
7	Oxford (Renovated WWTP)	Oxford, NC	36.29556	78.58472	1.2500	
8	Robersonville, WWTP, Town of	Robersonville, NC	35.81111	77.25833	1.2000	TTO
9	Louisburg WWTP, Town of	Louisburg, NC	36.08333	78.29028	0.8000	
10	Oxford (Southside WWTP)	Oxford, NC	36.30194	78.59528	0.7500	
11	Oxford (Northside WWTP)	Oxford, NC	36.32139	78.58361	0.6300	
12	Scotland Neck WWTP, Town of	Scotland Neck, NC	36.11778	77.43361	0.6750	
13	Franklin Water & Sewer Authority	Franklinton, NC	36.06806	78.42639	0.5000	
14	Enfield WWTP, Town of	Enfield, NC	36.19000	77.65444	0.5000	
15	Belhaven WWTP, Town of	Belhaven, NC	35.54083	76.60944	0.5000	
16	Spring Hope WWTP, Town of	Spring Hope, NC	35.90528	78.11222	0.4000	
17	Franklinton WWTP, Town of	Franklinton, NC	36.08889	78.45000	0.3000	
18	Pinetops WWTP, Town of	Pinetops, NC	35.80667	77.61778	0.3000	
19	Nashville, Town of WWTP	Nashville, NC	35.97889	77.94861	0.2500	
20	Bethel, Town of WWTP	Bethel, NC	35.79333	77.37833	0.2250	
21	Macclesfield WWTP, Town of	Macclesfield, NC	35.74500	77.66667	0.1750	
22	Whitakers, WWTP, Town of	Whitakers, NC	36.10417	77.70139	0.1500	
23	Aurora WWTP, Town of	Aurora, NC	35.29583	76.77611	0.1200	
24	Franklinton WTP, Town of	Franklinton, NC	36.10583	78.47306	0.0600	Cr

N	Facility Name	Township	Latitude Decimal	Longitude Decimal	Design Flow (MG/D	Monitoring Parameters
25	Bunn WWTP, Town of	Bunn, NC	36.94389	78.26028	0.0600	
26	Macclesfield WWTP, Town of	Macclesfield, NC	35.74500	77.66611	0.0500	
27	Aulander WWTP, Town of	Aulander, NC	36.23722	77.11000	0.0080	
28	Elm City WWTP, Town of	Elm City, NC	35.81417	77.85333	0.0000	
29	Hyde County Water System	Swanquarter, NC	32.55000	76.30000	0.0000	
30	Englehard Shrimp, Fish & Oyster	Engelhard, NC	35.50861	75.99611	0.0000	

APPENDIX II

CORE SAMPLE LOCATION DATA FOR THE PAMLICO RIVER ESTUARINE SYSTEM

Column 1: Core hole number as used for all analytical work, on maps, and within the text.
Column 2: Loran coordinate S1; no entry where shoreline interference was too great to obtain a meaningful number.
Column 3: Loran coordinate S2; no entry where shoreline interference was too great to obtain a meaningful number.
Columns 4, 5, and 6: Latitude in degrees, minutes, and seconds.
Columns 7, 8, and 9: Latitude in degrees, minutes, and seconds.
Column 10: Location description.

See Figures 110 (Mouth of the Tar River), 116 (Middle Pamlico River), 121 (Inner Pungo River), 122 (Belhaven), 124 (Inner Pamlico River), and 126 (Outer Pamlico and Pungo Rivers) for general core sample locations on the regional maps.

CORE HOLE ABBREVIATIONS

BLT = Blounts Creek
BRD = Broad Creek
BTH = Bath Creek
DHM = Durham Creek
MXN = Mixon Creek
NAT = Kennedy Creek
PAMV = Pamlico River vibracore
PAM = Pamlico River
PTG = Pantego Creek
PUN = Pungo River
STHV = South Creek vibracore
STH = South Creek
TAR = Tar River
TG = Texasgulf
TRA = Tranters Creek
WHD = Whichards Creek

CORE I.D.	LORAN S1	LORAN S2	LAT DEG	LAT MIN	LAT SEC	LONG DEG	LONG MIN	LONG SEC	LOCATION DESCRIPTION
BLT-1	*******	*******	35	26	7	76	58	16	JUST INSDE MTH BLNT'S CRK - EST SDE OF SHARP BEND
BRD-1	27237.2	40143.2	35	29	22	76	57	34	END OF HAUL-OUT SLIP @ MCCOTTER'S MARINA
BRD-2	27237.3	40143.5	35	29	20	76	57	30	BETWEEN COVERED DOCKS @ MCCOTTER'S
BRD-3	27237.2	40144.2	35	29	17	76	57	6	MID CHAN BRD CRK NR 2ND-3RD CVRD DCK @ MCOT NR SGN
BRD-4	27236.4	40144.5	35	29	23	76	57	23	OFF EASTERN MOST DOCK @ PAMLICO PLANTATION MARINA
BRD-5	*******	*******	35	29	36	76	57	31	END OF 1ST 2 CVRD DOCK HOUSES @ WASH COUNTRY CLUB
BRD-6	*******	*******	35	29	51	76	57	30	BRD CRK UPSTREAM FROM YACHT CLUB @ 90 DEG BEND
BRD-7	27236.3	40141.7	35	29	6	76	57	18	MOUTH OF BROAD CRK 150' NORTH OF "3" MID CHAN
BTH-1	27208.4	40157.9	35	28	41	76	49	2	BATH CREEK 150' SOUTH OF HIGHWAY BRIDGE
BTH-2	27205.6	40156.3	35	28	18	76	48	18	BACK CREEK 100' SW OF MIDDLE OF BRIDGE
BTH-3	27207.0	40151.7	35	28	7	76	48	53	OFF POINT BETWEEN BATH CR AND BACK CREEK
BTH-4	27207.0	40143.0	35	27	19	76	49	9	100 YDS NORTH OF "2" IN CHANNEL
DHM-1	27199.9	40093.4	35	22	55	76	49	8	JUST INSIDE ENTRANCE TO PORTER CREEK
DHM-2	27201.4	40091.1	35	22	48	76	49	37	JUST INSIDE MOUTH OF LOWER DURHAM CREEK
DHM-3	27201.3	40101.9	35	23	39	76	49	3	INSDE MTH DURHAM CRK 1000 YDS SW OF GARRISON POINT
MXN-1	27194.9	40134.3	35	25	48	76	46	14	JUST INSIDE MIXON CREEK
NAT-1	*******	*******	35	33	5	77	4	41	50 FT. SE OF PIPE CROSSING KENNEDY CREEK TRANS-1
NAT-2	*******	*******	35	33	6	77	4	40	50' SE OF PIPE CROSSING IN KENNEDY CREEK
NAT-3	*******	*******	35	33	4	77	4	42	ON TRANS-1 50 FT. SE OF PIPE CROSSING, KENNEDY CR.
NAT-4	*******	*******	35	33	8	77	4	42	TRANS-2 100 FT. NW OF PIPE CROSSING, KENNEDY CR.
NAT-5	*******	*******	35	33	7	77	4	41	TRANS-2 100 FT. NW OF PIPE CROSSING, KENNEDY CREEK
NAT-6	*******	*******	35	33	7	77	4	40	TRANSECT-2 100' NW OF PIPE CROSSING, KENNEDY CR.
NAT-7	*******	*******	35	33	3	77	4	33	TRNSCT-3, MID-CHAN STH OF BIG BLK TANK (MID OF 3)
NAT-8	*******	*******	35	33	2	77	4	34	TRNSCT-3, STH OF BIG BLK TANK (SOUTHERN OF 3)
NAT-9	*******	*******	35	33	4	77	4	32	TRNSCT-3, 50' FROM NTH SHR OF K. CRK. (NTHRN OF 3)
NAT-10	*******	*******	35	33	0	77	4	25	TRNSCT-4, MID-CHAN 100' NW OF PWR LINES (MID OF 3)
NAT-11	*******	*******	35	32	59	77	4	28	TRNSCT-4, 100' NW OF PWR LINES (SOUTH OF 3)
NAT-12	*******	*******	35	33	1	77	4	23	TRNSCT-4, 100' NW OF PWR LINES (NORTH OF 3)
NAT-13	*******	*******	35	32	54	77	4	15	TRNSCT-5, ACROSS MTH OF K. CRK. (MIDDLE OF 3)
NAT-14	*******	*******	35	32	54	77	4	11	TRNSCT-5, NEAR MTH OF K. CRK. (EAST OF 3)
NAT-15	*******	*******	35	32	53	77	4	18	TRNSCT-5, @ MTH OF K. CRK. (WEST OF 3)
PAMV-2	27192.4	40121.5	35	24	31	76	46	0	1000' SOUTH OF COUM PT LIGHT "4"
PAMV-3	27234.0	40113.0	35	26	44	76	57	33	BLOUNTS BAY
PAM-1A	27268.6	40126.6	35	30	32	77	3	18	100' SE OF MOUTH OF SYDNEY CREEK
PAM-2	27258.9	40146.8	35	30	45	77	3	18	CHOCOWINITY BAY NEAR MOUTH OF SYDNEY CREEK
PAM-3	27259.0	40146.2	35	30	42	77	3	20	CHOCOWINITY BAY NEAR MOUTH OF TWIN LAKES CANAL
PAM-4	27258.8	40115.2	35	30	37	77	3	21	CHOCOWINITY AT MOUTH OF SYDNEY CREEK

CORE I.D.	LORAN S1	LORAN S2	LAT DEG	LAT MIN	LAT SEC	LONG DEG	LONG MIN	LONG SEC	LOCATION DESCRIPTION
PAM-5	27259.1	40134.1	35	30	34	77	3	18	JUST INSIDE MOUTH OF SYDNEY CREEK
PAM-6	27259.9	40143	35	30	30	77	3	40	AT SECOND BEND (SHOREWARD) INSIDE SYDNEY CREEK
PAM-7	27258.5	40163.7	35	32	8	77	2	31	50 YDS SW OF CITY PARK, WASHINGTON
PAM-8	*******	*******	35	31	51	77	2	42	OFF SOUTHERN TIP OF GRANPAP ISLAND
PAM-9	*******	*******	35	31	33	77	2	49	OFF RODMAN CREEK ENTRANCE
PAM-10	*******	*******	35	31	58	77	2	39	50 YRDS. NE OF GRANDPAP ISLAND
PAM-11	27249.6	40149.6	35	30	33	77	0	35	PAMT-1 NORTHERNMOST
PAM-12	27249.7	40143.6	35	30	0	77	0	46	MID CHAN ON PAMT-1 3/4 ML SE OF MKR #"16"
PAM-13	27249.6	40141.3	35	29	48	77	0	51	JUST ON NORTH SIDE OF SHOULDER OF FORK PT. SHORE
PAM-14	27249.1	40137.5	35	29	27	77	0	51	@ SE END OF FORK PT SHOAL (S. SIDE) ON PAMT-1
PAM-15	27248.9	40135.9	35	29	19	77	0	50	MID CHAN, MOUTH OF CHOCO BAY PAMT-1
PAM-16	27248.9	40133.2	35	29	9	77	0	52	100 YDS FRM S. SHR NR MTH CHOCO BAY (CREEK RM)
PAM-17	27236.1	40132.9	35	28	25	76	57	34	PAMT-2 NORTHERN MOST CORE
PAM-18	27235.4	40127.8	35	27	58	76	57	31	NRTH SPOIL PINE NRTH OF NAV CHAN @ DGLG IN BLNT BY
PAM-19	*******	*******	35	27	44	76	57	31	50YD NE OF MRKR "9" IN CHAN @ DOGLEG IN BLNT BAY
PAM-20	*******	*******	35	26	52	76	57	41	CENTRAL BLOUNT'S BAY
PAM-21	27206.0	40134.7	35	26	36	76	49	20	JUST OUTSIDE MOUTH OF BATH CREEK
PAM-22	27205.3	40130.0	35	26	9	76	49	14	MID CHAN NORTH SIDE OF PAMLICO RIVER
PAM-23	27204.3	40121.4	35	25	27	76	49	17	SOUTHSIDE OF BROAD SHOULDER OF CHANNEL
PAM-24	27202.3	40113.6	35	24	38	76	49	0	1/4 ML NE OF DURHAM CRK PT NE OF WRECK
PAM-25	27183.3	40111.6	35	23	8	76	44	4	1/2 ML NE OF FERRY CHAN MKR "1" WEST OF LONG PT
PAM-26	27183.5	40117.9	35	23	38	76	43	47	MID OF RIVER ABT 1 ML NE OF FERRY MARKER "1"
PAM-27	27183.1	40123.8	35	24	4	76	43	29	MID OF PAM RIVER 1.5 ML SOUTH OF REST HAVEN
PAM-28	27183.1	40128.4	35	24	28	76	43	21	1.1 ML S. OF REST HAVEN
PAM-29	27182.9	40140.6	35	25	24	76	42	45	JUST OFF MOUTH OF ST. CLAIR CREEK
PAM-30A	27187.5	40110.8	35	23	23	76	45	6	1/2 ML NW OF "1" FERRY CHAN ON SOUTH SHORE
PAM-30B	27187.5	40110.8	35	23	23	76	45	6	1/2 ML NW OF "1" FERRY CHAN NEAR TG
PAM-31	27193.4	40109.6	35	23	42	76	46	41	2000' NORTH OF YACHT BASIN AT TEXASGULF
PAM-32	27196.0	40106.7	35	23	42	76	47	35	1/4 ML OFFSHORE FROM TG EAST OF GARRISON POINT
PAM-33	27196.4	40114.4	35	24	20	76	47	20	1 ML NORTH OF SHORE AT TG
PAM-34	27196.4	40120.9	35	24	52	76	47	10	MIDDLE OF RIVER 1.5 ML SW OF GUM POINT
PAM-35	27195.5	40127.0	35	25	21	76	46	58	3/4 ML SW OF MIXON CRK ENTRANCE (DEEP CHANNEL)
PAM-36	27187.2	40124.6	35	24	28	76	44	33	1.3 ML SOUTH OF GAYLORD BAY FERRY LANDING
PAM-37	27130.6	40136.9	35	21	4	76	28	54	MOUTH OF PAMLICO RIVER NORTH OF PAMLICO PT.
PAM-38	27126.7	40124.4	35	19	49	76	28	3	1.2 ML NW OF PAMLICO POINT LIGHT
PAM-39	27151.3	40110.4	35	20	43	76	35	15	.5 ML NE OF ENTRANCE MKR TO GOOSE CRK "1" PAM RIVE
PAM-40	27151.4	40122.7	35	21	42	76	34	58	MID OF PAM RIVER SW OF WADE POINT
PAM-41	27152.9	40131.2	35	22	36	76	34	46	PAMLICO RIVER, 1 ML S OF WADES PT
PAM-42	27170.5	40112.0	35	22	11	76	40	16	900 YDS NE OF MRKR "1" AT ENTRANCE TO SOUTH CREEK
PAM-43	27170.2	40122.5	35	23	0	76	39	50	APPROX. MID CHAN BETWEEN REED PT & CHAMBERS PT

CORE I.D.	LORAN S1	LORAN S2	LAT DEG	LAT MIN	LAT SEC	LONG DEG	LONG MIN	LONG SEC	LOCATION DESCRIPTION
PAM-44	27170.2	40132.2	35	23	44	76	39	25	1500 YDS OFFSHORE BETWEEN CHAMBERS PT & MARE PT
PTG-1	*******	*******	35	32	30	76	38	9	200' SOUTH OF MIDDLE SPAN OF PANTEGO CRK BRIDGE
PTG-2	*******	*******	35	32	20	76	37	39	OFF END DCK FSH HSE NXT TO BLHVN MAR 100' E OF "9
PTG-3	*******	*******	35	32	1	76	37	30	50 YDS SW OF "9" SW OF NAV CHANNEL
PTG-4	*******	*******	35	31	54	76	37	37	SW SDE OF CHAN IN PANTEGO CRK ACROSS FROM FISH HOU
PTG-5	*******	*******	35	31	48	76	37	42	25' FRM MARSH ON S SHORE OF PTG CRK ACRS FRM FSHSE
PTG-6	*******	*******	35	31	42	76	37	0	JUST INSIDE ENTRANCE TO BELHAVEN HARBOR
PUN-1	*******	*******	35	33	11	76	27	16	JUNCTION OF PUTMAN & WILKERSON CRKS. MARKER "25"
PUN-2	*******	*******	35	33	21	76	28	6	JUST INSIDE MTH OF UPPER PUNGO 4 ML N OF "23"
PUN-3	*******	*******	35	34	4	76	28	54	IN UPPER PUNGO NEAR CONSTRUCTION BEFORE BRIDGE
PUN-4	*******	*******	35	34	20	76	29	37	UPPER PUNGO RIVER 1/4 DOWNSTREAM OF BRIDGE
PUN-5	*******	*******	35	33	1	76	27	48	ADJACENT TO ICW @ "24" OUTSIDE MTH OF WILKERSON CR
PUN-6	*******	*******	35	32	5	76	28	47	100 YDS SE OF "21" (SE SIDE ON NAV CHAN PUNGO RIV)
PUN-7	*******	*******	35	30	59	76	29	39	50 YDS SE OF "18" NEXT TO NAV CHANNEL
PUN-8	*******	*******	35	31	23	76	32	59	1000 YDS NORTH OF "14" NORTH OF NAV CHAN
PUN-9	*******	*******	35	31	25	76	35	59	50 YDS NORTH OF MARKER "2" CHAN INTO BELHAVEN
PUN-10	*******	*******	35	32	18	76	36	12	MOUTH OF BATTALINA CREEK
PUN-11	*******	*******	35	32	24	76	36	32	MTH CRK LONG TO SWGE OUTFLL FOR WWTP(BLHVN) BTL CK
PUN-12	27147.1	40143.1	35	22	49	76	32	26	CONFLUENCE OF PUNGO RVR W/ PAM 1 ML EST OF JUNC LT
PUN-13	27149.4	40160.9	35	24	58	76	33	59	PUNGO RVR EAST OF GRASSY PT (1.2 MILES)
PUN-14	27151.3	40169.4	35	25	26	76	33	13	PUNGO RVR .5 ML EAST OF "WR 2"
PUN-15	*******	*******	35	26	52	76	34	47	PUNGO RIVER 300' WEST OF "4" SANDY POINT
PUN-16	27164.0	40209.7	35	29	42	76	35	15	1 ML SOUTH OF DURANT PT ON PUNGO RIVER
PUN-17	27165.9	40203.7	35	29	30	76	35	57	.5 ML NORTH OF WOODSTOCK PT
PUN-18	27176.4	40215.3	35	30	57	76	38	25	JUST INSIDE MOUTH OF PUNGO CREEK
PUN-19	27171.4	*******	35	29	56	76	40	12	PUNGO CREEK 200' EAST OF BRIDGE
STHV-1	27191.1	40081.3	35	20	35	76	44	23	50' WEST OF MKR "9" SOUTH CREEK
STH-1	27169.8	40101.1	35	21	17	76	40	32	MTH OF SOUTH CRK 300 YDS OFF OF REED POINT
STH-2	27172.2	40091.7	35	20	46	76	41	32	MTH BOND CRK 10 YDS W OF MKR "2" BTWN FRK & GUM PT
STH-3	27185.4	40074.1	35	21	15	76	42	17	25 YDS SOUTH OF MRKR 7 IN SOUTH CREEK
STH-4	*******	*******	35	21	11	76	43	36	200 YDS W OF MPKER "8" BTWN SAGE & BUOY PT, STH CK
STH-5	*******	*******	35	20	37	76	44	29	200 YDS WST OF MRKR "9" IN PIPELINE AREA
STH-6	*******	*******	35	20	40	76	44	43	300 YDS EAST OF TOOLEY CRK POINT (NORTH)
STH-7	*******	*******	35	20	31	76	44	10	NEAR MOUTH OF LONG CREEK INSIDE SOUTH CREEK
STH-8	*******	*******	35	20	14	76	45	22	75 YDS EAST OF MRKR "10" SOUTH CREEK
STH-9	*******	*******	35	19	19	76	46	0	RNGE 1 ML LNE OFF 14/12 INTRCONG W/ LNE OFF 16/18
STH-10	*******	*******	35	18	4	76	46	33	25 MILES BELOW HWY 33 BRIDGE
TAR-1	*******	*******	35	33	35	77	6	30	MID-CHAN JUST DWN-STRM OF SMALL ISLET
TAR-2	*******	*******	35	33	36	77	6	29	JUST EAST (150 FT) OF ISLAND UPSTRM OF MARTIN BAY
TAR-3	*******	*******	35	33	3	77	5	60	JUST OFF PT (EAST) OFF MTH OF BEAR CK. (STHN OF 3)

CORE I.D.	LORAN S1	LORAN S2	LAT DEG	LAT MIN	LAT SEC	LONG DEG	LONG MIN	LONG SEC	LOCATION DESCRIPTION
TAR-4	*******	*******	35	33	5	77	5	58	NTH SHR OPP MTH OF BEAR CK. E OF PT (NTHNMST OF 3)
TAR-5	*******	*******	35	33	4	77	5	59	MID CHAN (TAR) JUST OSDE ENTR TO BRN CK. (MID OF 3
TAR-6	*******	*******	35	32	37	77	4	36	STH SHRE TAR ACRS FRM PRONG(C) 2000 UPSM FR PWR LN
TAR-7	*******	*******	35	32	49	77	4	32	NORTH SHORE OF TAR RIVER 150 YDS SOUTH FROM SHORE
TAR-8	*******	*******	35	32	51	77	4	27	25' FRM N SHR TAR, ON STVE'S 2ND TRNSCT NR PRONG C
TAR-9	*******	*******	35	33	9	77	5	0	NTH SHR TAR NR HUBBARD (C) 100' FRM SHORE
TAR-10	*******	*******	35	33	11	77	4	59	NRTH END OF TART-1 IN SMALL CREEK MOUTH
TAR-10-G	*******	*******	35	33	11	77	4	59	SAME AS TAR-10
TAR-11	*******	*******	35	33	8	77	5	2	SOUTH OF TAR 9 IN MAIN CHANNEL
TAR-12	*******	*******	35	33	2	77	0	8	100 YDS FRM S SHR/RANGE N PT S OF N END OF BRIDGE
TAR-13	*******	*******	35	33	0	77	5	10	ABT. 10 YARDS FROM SOUTH SHORE
TAR-14	*******	*******	35	32	58	77	4	59	END OF N. SPINNERY DISCHARGE PIPE NEAR MID CHAN
TAR-15	*******	*******	35	32	59	77	4	54	BELOW NAT SPIN DISCHARGE ON NORTH EDGE OF CHANNEL
TAR-16	*******	*******	35	32	59	77	4	57	APPROX. MID DISCHARGE NAT. SPINNING
TAR-17	*******	*******	35	33	1	77	4	54	APPROX. 30 YDS FRM SHR ALONG DSCHRGE FOR NAT SPIN
TAR-18	*******	*******	35	32	48	77	4	38	
TAR-19	*******	*******	35	32	37	77	4	2	STH SDE CHAN; RANGE - S PT AND EAST SDE OF PILINGS
TAR-20	*******	*******	35	32	33	77	4	4	TART-2 TRNSCT USTM 1/4 ML FRM US-17 BRG
TAR-21	*******	*******	35	32	29	77	4	6	TART-2 75 YDS FRM SOUTH SHORE OF TAR
TAR-22	*******	*******	35	32	41	77	4	1	MID CHAN (NAV) 1/4 ML USTM FRM US-17 BRDG TART-2
TAR-23	*******	*******	35	33	45	77	3	59	50' FRM WALL IN NORTH END OF TART-2
TG-1	27190.8	40104.6	35	23	6	76	46	12	75' FROM MOUTH OF OUTFALL CANAL
TG-2	27190.8	40104.7	35	23	8	76	46	11	150-200' NORTH OF OUTFALL CANAL
TG-3	27190.8	40104.7	35	23	8	76	46	11	AT EDGE OF SHELF ADJACENT TO CHANNEL
TG-4a	27191.3	40110.7	35	23	37	76	46	4	4TH CORE NORTHWARD ON TG-1 TRANSECT
TG-4b	27191.3	40110.7	35	23	37	76	46	4	MIDDLE OF CHANNEL
TG-5a	27192	40122.1	35	24	36	76	45	53	MIDDLE OF NAVIGATON CHANNEL
TG-5b	27192.1	40122.2	35	24	39	76	45	55	MIDDLE OF NAVIGATION CHANNEL NORTH OF TG
TG-V1	27190.9	40104.9	35	23	10	76	46	14	200' NE OF EASTERN PROMONTORY OF BARGE CANAL
TRA-1	*******	*******	35	33	33	77	5	27	TRANTER'S CRK. UPSTRM CHAN MAKES 90 DEG TURN WEST
TRA-2	*******	*******	35	33	33	77	5	26	MID-CHAN TRNTR'S CK. NR MTH OF SHOP COV (MID OF 3)
TRA-3	*******	*******	35	33	33	77	5	24	TRNTR'S CK. USTM FRM 90 DG TRN NR MTH OF SHOP COVE
WHD-1	*******	*******	35	30	10	77	1	25	EAST END OF WHICHARD'S MARINA ON NORTH SHORE
WHD-2	27241.9	40154.5	35	30	12	77	1	29	50 FT SW OF SLIP AT WHICHARD'S