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HEAVY METALS IN ORGANIC-RICH MUDS OF THE ALBEMARLE SOUND ESTUARINE SYSTEM

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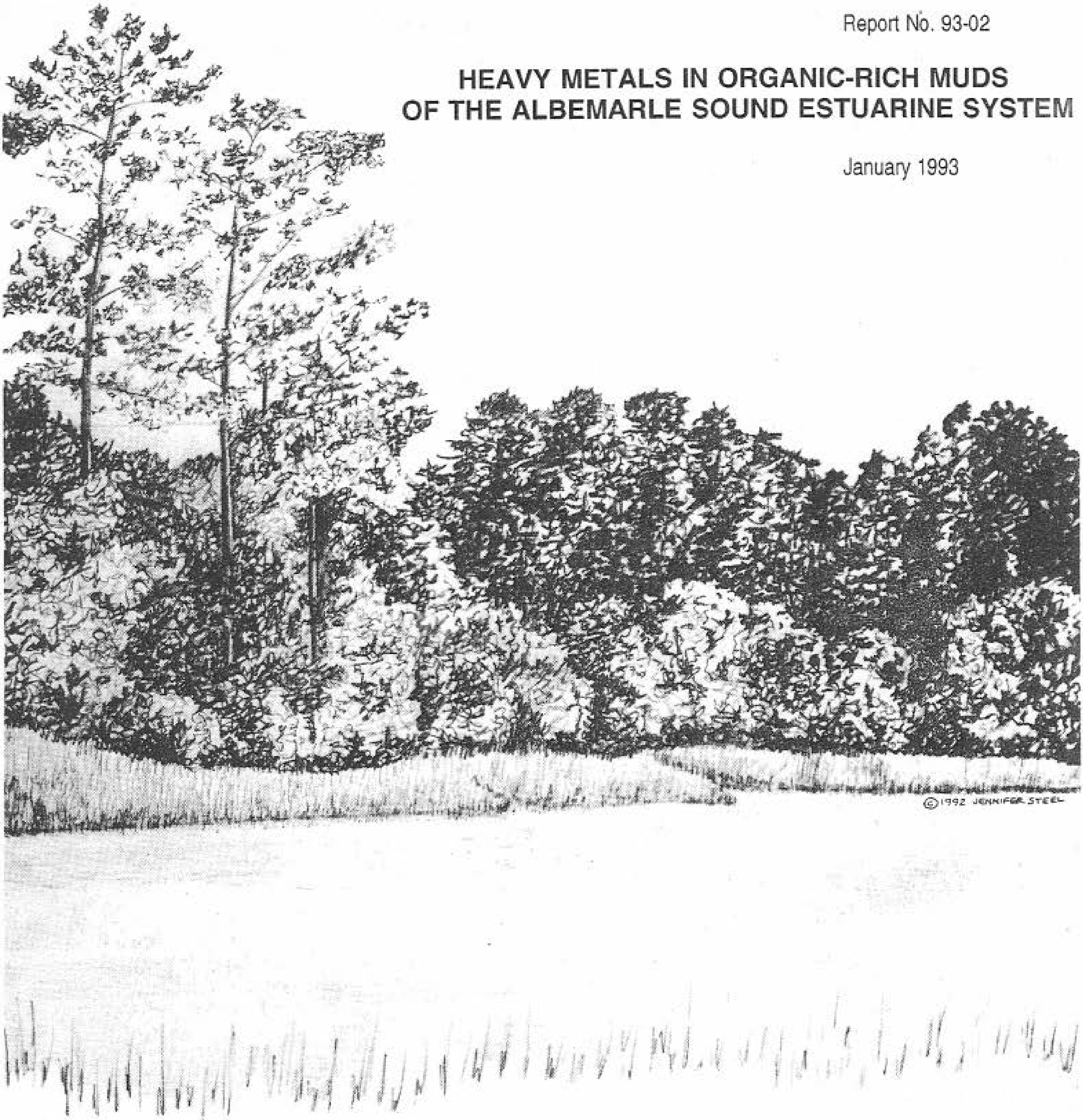

ALBEMARLE-PAMLICO ESTUARINE STUDY

NC Department of
Environment, Health,
and Natural Resources

Environmental
Protection Agency
National Estuary Program

HEAVY METALS IN ORGANIC-RICH MUDS OF THE ALBEMARLE SOUND ESTUARINE SYSTEM

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US Environmental Protection Agency, National Estuary Program
NC Department of Environment, Health, and Natural Resources

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TABLE OF CONTENTS

Page

TITLE PAGE i
TABLE OF CONTENTS ii
LIST OF FIGURES iv
LIST OF TABLES vi
LIST OF ABBREVIATIONS x

PART A: EXECUTIVE SUMMARY 1
  Heavy Metals in Organic-rich Muds of the Albemarle Sound Estuarine System 3
  Conclusions 8

PART B: INTRODUCTION 13
  Drainage Basins for the Albemarle Sound Estuarine System 15
    Morphological Setting 15
    Albemarle Sound Estuarine System 18
    Geologic Framework of the Roanoke River Basin 20
  Water Quality Status of the Albemarle Sound Estuarine System 21
  Objectives 25
  The Nature of Trace Elements 26
    Trace Elements and Health 26
    Trace Elements in the Estuarine Environment 27
    Potential Sources of Trace Element Contaminants 29
  Trace Elements in the Albemarle Sound Estuarine System 31
    Point and Nonpoint Source Discharges 31
    Trace Element Contaminants: Problems with Monitoring Water Quality 33

PART C: METHODOLOGY 37
  Field Sampling 39
    Delineation of the Albemarle Sound Study Area 39
    Design and Rationale 40
    Development of Base Maps 43
    Acquisition of Sediment Samples 43
  General Analytical Procedures 46
  Sediment Analyses 49
    Sediment Sub-Sampling 49
    Textural and Compositional Analyses of Sediment 49
  Chemical Analyses 50
    Rationale for Extraction Procedure Utilized 50
    Sample Pre-Treatment 53
    Extraction Procedures 53
    Comparison of Extraction Procedures 54
    ICAPES Analyses 56
    Control Samples 58
    Limit of Quantitation and Reproducibility 59
    Comments on Quality of Analytical Numbers 59
    AAS Mercury Analyses 62
    Electrochemical Fluorine Analyses 62

Data Analyses 63
    Data Management and Statistical Analyses 63
    Rationale and Definitions for Data Analyses 64
        Trimmed Means and Enrichment Factors 64
        Areas of Concern 69

PART D: RESULTS 71
Albemarle Sound Estuarine Sediments 73
    Morphology of the Estuarine System 73
    Sediment Composition and Distribution Patterns 75
    Organic-Rich Mud (ORM) Sediment 86
    Organic-Rich Mud and Heavy Metals 90
    Vertical Distribution of Trace Elements 91
    Comparison of Albemarle Sound to the Neuse and Pamlico River Systems 92

PART E: RESULTS 95
Areas of Concern in the Albemarle Sound Estuarine System 97
    Lower Roanoke River Area 97
        Welch Creek 97
        Lower Roanoke River 102
        Middle and Cashie Rivers 105
    Inner Albemarle Sound Area 105
        Lower Chowan River 108
        Edenton Bay 111
        Inner Albemarle Sound 113
    Middle Albemarle Sound Area............................... 113
        Yeopim River 113
        Perquimans River 116
        Little River 116
        Deep Creek 119
        Scuppernong River 119
        Middle Albemarle Sound 120
    Outer Albemarle Sound Area 123
        Pasquotank River 123
        North River 130
        Alligator and Little Alligator Rivers 130
        Outer Albemarle Sound 132
    Areas of Concern Summary 135
        Regional Patterns within Albemarle Sound System 135
        Comparison with Benkert Trace Metal Data 142
    North Landing River Area 143

PART F: REFERENCES CITED 147

PART G: APPENDIX 159
Summary of Sample Location Maps for Estuarine Areas............. 161
Sample Location Data for the Albemarle Sound Estuarine System 163

LIST OF FIGURES

FIGURE Page

A1. Map showing the major and minor contaminated and least contaminated areas of concern within the Albemarle Sound estuarine system.. 7

B1. Map of the three drainage basins for the Albemarle Sound estuarine system.. 16

B2. Location map of the Albemarle Sound estuarine system............ 19

C1. Map of the Albemarle Sound estuarine system showing the location of short core (< 0.6 m) sample sites for this study, excluding the North Landing River........................ 41

C2. Map of the North Landing River in Currituck Sound showing the location of short core (< 0.6 m) and vibracore (6 m) sample sites and bathymetric profiles utilized in this study..... 42

C3. Map of the Albemarle Sound estuarine system showing the location of vibracore (3 to 8 m) sample sites for this study, excluding the North Landing River........................ 44

C4. Map of the Albemarle Sound estuarine system showing the location of six bathymetric profiles with associated surface sample transects utilized in this study, excluding the North Landing River.............................. 45

C5. Laboratory flow sheet for sediment and chemical analyses......... 48

C6. Comparison of mean percent of various metals obtained by three partial extraction procedures used by the International Council for Exploration of the Sea (Loring and Rantala, 1988) and those produced by the 2N HNO_3 partial extraction procedure of Riggs et al. (1989) in the Pamlico River estuary. This 2N HNO_3 procedure is the same as that used in the Neuse River (Riggs et al., 1991) and present Albemarle Sound studies...................... 55

C7. Comparison of mean percent of various metals obtained by two partial extraction procedures in metal pollutant studies. The Los Angeles waste water treatment outfall (LAWTO) study utilized a 25% $HOAc/NH_2OHHCl$ + 30% H_2O_2 procedure (Bruland et al., 1974), whereas the National Institute of Standards and technology estuarine sediment (NISTES) was analyzed during the Pamlico River study (Riggs et al., 1989b) utilizing a 2N HNO_3 procedure.............. 57

D1. Depositional environments of the Albemarle Sound estuarine system.. 74

D2. Bathymetric profile A-A′ across the Lower Roanoke River showing the distribution of the four major sediment components and their relationship to bottom morphology........... 76

D3. Bathymetric profile B-B′ across Inner Albemarle Sound adjacent to the Highway 37 bridge, showing the distribution of the four major sediment components and their relationship to bottom morphology........................ 77

FIGURE Page
D4. Bathymetric profile C-C′ across Middle Albemarle Sound showing the distribution of the four major sediment components and their relationship to bottom morphology........... 78
D5. Bathymetric profile D-D′ across Outer Albemarle Sound showing the distribution of the four major sediment components and their relationship to bottom morphology........... 79
D6. Bathymetric profile E-E′ across the mouth of Outer Albemarle Sound showing the distribution of the four major sediment components and their relationship to bottom morphology.. 80
D7. Bathymetric profile F-F′ across the Alligator River adjacent to the Highway 64 bridge, showing the distribution of the four major sediment components and their relationship to bottom morphology........................... 81
D8. Schematic map of the upper transition zone of a drowned river estuarine system during the initial stages of flooding by rising sea level and showing the locations of two schematic cross-sections in Figure D9..................... 88
D9. Two schematic cross-sections of the upper transition zone of a drowned river estuarine system during the initial stages of flooding by rising sea level. The upper panel is across the riverine portion prior to flooding; the lower panel is across the estuarine portion as flooding begins.. 89

E1. Index map of the Albemarle Sound estuarine system showing the location of specific regions as discussed in the text......... 98
E2. Sample location map of the Lower Roanoke River Area.............. 100
E3. Downstream plot of maximum enrichment factors for Welch Creek.. 103
E4. Downstream plot of maximum enrichment factors for Welch Creek.. 103
E5. Sample location map of the Inner Albemarle Sound Area............ 107
E6. Sample location map of the Middle Albemarle Sound Area........... 115
E7. Sample location map of the Outer Albemarle Sound Area............ 124
E8. Sample location map of the Pasquotank River...................... 126
E9. Downstream plot of maximum enrichment factors for Newbegun Creek... 128
E10. Downstream plot of maximum enrichment factors for Pasquotank River... 129
E11. Downstream plot of mean enrichment factors for Albemarle Sound (Cu, Co, Mn, and Ti)............................ 137
E12. Downstream plot of mean enrichment factors for Albemarle Sound (As, Cd, Cr, Hg, Ni)............................. 137
E13. Downstream plot of mean enrichment factors for Albemarle Sound (P, Pb, V, Zn).................................. 138
E14. Downstream plot of mean enrichment factors for Albemarle Sound (Mo, Sn).. 138

G1. Map of the Albemarle Sound estuarine system showing the location of sampled regions and site abbreviations used for samples.. 162

LIST OF TABLES

TABLE Page
A1. Quantitative analysis for 22 elements on 360 sediment subsamples from 198 sample stations within the Albemarle Sound estuarine system.......... 4
A2. Classification of degree of contamination for each estuarine area of Albemarle Sound with respect to the 15 trace elements analyzed.......... 6

B1. Drainage basins of the Albemarle-Pamlico estuarine system.......... 15
B2. Land use within the Albemarle Sound estuarine system.......... 17
B3. Ability of the Roanoke River Basin in North Carolina to support the designated water quality uses along with source of contaminants for that 54% of the Roanoke River mileage classified as partially or totally degraded.......... 22
B4. List of pertinent water-quality and sediment-quality investigations for various portions of the Albemarle Sound estuarine system.......... 23
B5. Federal standards for elemental concentrations in drinking water.......... 27
B6. Concentrations of metals in sewage sludge.......... 29
B7. Concentrations of metals in urban storm-water runoff.......... 30
B8. Combined effluent flow and pollutant loads for 23 major waste water dischargers in the Neuse River drainage basin from 4/89 through 3/90.......... 33
B9. Comparison between detection limits for trace metal samples from North Carolina rivers and average metal concentrations in the Mississippi River.......... 34

C1. Distribution and numbers of sediment samples collected in the Albemarle Sound estuarine system for subsequent sediment and elemental analyses.......... 39
C2. Analytical data obtained for 30 elements in this study.......... 48
C3. Analytical wavelengths (in nm) for 21 elements analyzed by ICAPES and included in this report.......... 58
C4. Samples analyzed by ICAPES for Albemarle Sound and the North Landing River in Currituck Sound.......... 58
C5. Quality assurance data for ICAPES and AAS determinations for samples from the Albemarle Sound estuarine and North Landing River studies (this report) as compared to similar data from the Pamlico River (Riggs et al., 1989b) and Neuse River (Riggs et al., 1991) studies.......... 60
C6. Percent recovery of NIST SRM 1646 Estuarine Standard data for ICAPES and AAS determinations for samples from the Albemarle Sound estuarine and North Landing River studies (this report) as compared to similar data from the Pamlico River (Riggs et al., 1989b) and Neuse River (Riggs et al., 1991) studies.......... 61

TABLE Page

C7. Albemarle trimmed mean (ATM) data for all surface samples that are less than 2 standard deviations from the mean total population. The standard deviation, coefficient of variation, and the minimum and maximum concentration values used in this calculation for 22 elements (in μg/g or ppm) in surface sediments of the Albemarle Sound estuarine system, are also included.............................. 65

C8. Level of uncertainty for enrichment factors equal to 1 (or the ATM) as compared to the maximum enrichment factor (MEF) for each of the 15 trace elements utilized in the Albemarle and North Landing estuarine sediment studies....... 68

D1. Average composition of total sediment for the four major sediment types occurring within the Albemarle Sound estuarine system.. 82

D2. Summary of sediment particle size and the inorganic-organic composition of the total sediment for 356 samples of the Albemarle Sound estuarine system................................. 83

D3. Summary of 350 samples and their inorganic and organic composition within the Albemarle Sound estuarine system.......... 84

D4. Changing patterns of % sand, mud, and organic matter in samples through the Albemarle Sound estuarine system............. 85

D5. Comparison of organic and clay concentrations (in %) in all sediment samples (surface and deep) of the most and least contaminated portions of the Albemarle Sound estuarine system.. 90

D6. Comparison of mean concentrations for 15 trace elements (in μg/g or ppm) between surface and deep sediment samples in the Albemarle Sound estuarine system.......................... 91

D7. Average composition of total sediment for all samples collected within the entire Pamlico, Neuse, and Albemarle estuarine systems and within the respective trunk estuaries...... 93

D8. Comparison of trimmed mean concentrations for 22 elements (in μg/g or ppm) in surface sediments of Albemarle Sound (this study), the Neuse River (Riggs et al., 1991c), and Pamlico River (Riggs et al., 1989b) estuarine systems............ 94

E1. Outline of the regional areas of the Albemarle Sound estuarine system and associated figures and tables considered in the Results.. 99

E2. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in Welch Creek................................. 101

E3. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Lower Roanoke River.................... 104

E4. Summary of mean and maximum enrichment factors for 15 trace elements in surface sediments from Middle River and Cashie River, two tributary channels of the Lower Roanoke River......... 106

TABLE Page
E5. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Chowan River.............................. 109
E6. Relationship between trace element enrichment and sediment composition for selected samples in the Chowan River estuary.. 110
E7. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in Edenton Bay................................ 112
E8. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Inner Albemarle Sound.................. 114
E9. Summary of mean and maximum enrichment factors for 15 trace elements in surface sediments from Yeopim and Little Rivers, two tributary estuaries on the north side of Albemarle Sound and Deep Creek, a tributary estuary on the south side of Albemarle Sound.. 117
E10. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Perquimans River....................... 118
E11. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Scuppernong River...................... 121
E12. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Middle Albemarle Sound................. 122
E13. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Pasquotank River....................... 127
E14. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the North River............................ 131
E15. Summary of mean and maximum enrichment factors for 15 trace elements in surface sediments from the Alligator and Little Alligator Rivers, two tributary estuaries on the south side of Albemarle Sound... 133
E16. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Outer Albemarle Sound.................. 134
E17. Summary of mean concentrations of 15 trace elements and composition of associated sediments of surface samples as they change from the Lower Roanoke River systematically down the trunk of the Albemarle Sound estuarine system........... 136
E18. Maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas of concern in the Lower Roanoke River area................ 139
E19. Maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas of concern in the Albemarle Sound area.................... 140

TABLE Page

E20. Maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas of concern in the Pasquotank, Chowan, and Perquimans River areas, including the urban areas of Elizabeth City and Hertford 141
E21. Comparison of sediment analyses for metals that occur in concentrations considered to represent "polluted" sediments by the U.S. Fish and Wildlife Service (Benkert, 1992) 142
E22. Concentrations of 15 trace elements and enrichment factors for all surface and shallow subsurface samples collected in the North Landing River in Currituck Sound 144
E23. Number and percent of samples in the North Landing River that are substantially and slightly enriched in 7 trace elements above the trimmed mean for Albemarle Sound estuarine system 145
E24. Comparison of mean concentrations of enriched elements in the North Landing River with trimmed means for the Albemarle, Neuse, and Pamlico estuarine systems (in μg/g or ppm) 145

LIST OF ABBREVIATIONS USED IN THE ALBEMARLE SOUND REPORT

TERMS DEFINED IN THIS REPORT

ORM	Organic-rich Mud
EF	Enrichment Factor
MEF	Maximum Enrichment Factor
TM	Trimmed Mean
ATM	Albemarle Trimmed Mean
NRTM	Neuse River Trimmed Mean
PRTM	Pamlico River Trimmed Mean
AOC	Area of Concern
CAOC	Contaminated Area of Concern
NAOC	Noncontaminated Area of Concern

STANDARD ANALYTICAL TERMS

ICAPES	Inductively Coupled-Argon Plasma-Emission Spectrometry
AAS	Atomic Absorption Spectrometry
LLQ	Lower Limit of Quantification
NIST	National Institute of Standards and Technology
SRM	Standard Reference Material

STANDARD ENVIRONMENTAL TERMS

NPDES	National Pollution Disharge Elimination System
WWTP	Waste Water Treatment Plant
SIU	Significant Industrial User

GOVERNMENT OFFICES

A/P	Albemarle/Pamlico Estuarine Study
DEM	N.C. Division of Environmental Management
DEHNR	N.C. Department of Environment, Health and Natural Resources
DMF	N.C. Department of Marine Fisheries
EPA	U.S. Environmental Protection Agency

CHEMICAL ELEMENTS ANALYZED IN THIS STUDY

Al	Aluminum
As	Arsenic
Cd	Cadmium
Ca	Calcium
Cr	Chromium
Co	Cobalt
Cu	Copper
Fe	Iron
F	Fluorine
Pb	Lead
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Ni	Nickel
P	Phosphorus
K	Potassium
Si	Silica
Na	Sodium
Sn	Tin
Ti	Titanium
V	Vanadium
Zn	Zinc

PART A: EXECUTIVE SUMMARY

PART A: EXECUTIVE SUMMARY

HEAVY METALS IN ORGANIC-RICH MUDS OF THE ALBEMARLE SOUND ESTUARINE SYSTEM

Increased human activity contributes ever increasing amounts of suspended sediment and chemical contaminants to the estuarine system. Data from the N.C. Division of Environmental Management (DEM, pers. comm., 1992), suggest that municipal and industrial facilities are presently permitted to discharge waste water into the Albemarle Sound estuarine system and associated drainage basins as follows.

Roanoke River (below Lake Gaston)	261 permits	78 mgpd
Chowan and Pasquotank Rivers (in N.C.)	95	2
Albemarle and Pamlico Sounds	9	2
TOTAL	365 permits	82 mgpd

Permitted facilities include municipal waste water treatment plants (WWTP), large industrial facilities that discharge up to 55 million gallons per day, and numerous small municipal and industrial operations. Many of these facilities are permitted to discharge specific heavy metals; however, for many the concentration of heavy metal toxicants in their waste water discharge is poorly known.

Heavy metal contaminants may also come into the Albemarle Sound estuarine system from nonpoint source activities such as the use of pesticides, fertilizers, and soil conditioners in the extensive agriculture and forestry industries that occur within the drainage basins. Historical facilities such as old industrial and dump sites may contribute heavy metal contaminants, particularly those sites that occur in estuarine lowlands around urban centers and that received poorly known types of waste for decades.

Discharge of apparently low concentrations of heavy metals from both natural and anthropogenic point and non-point sources into estuarine environments dominated by organic-rich mud leads to potential sediment contamination problems. High adsorption capabilities of clay minerals coupled with high chemical reactivity of organic matter, continuously strip trace metals from the water column. Enrichment of trace metals in sediments continues through time as storms, biological processes, and man (i.e., fish trawling, dredging, etc.) routinely resuspend the mud sediments into the water column. Thus, the cumulative effect of large volumes of waste water discharge and runoff, with low metal concentrations, over long time periods can lead to substantial metal enrichment within the sediments. 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. Kimerle (1987) concluded that some chemicals tend to strongly partition to sediments becoming sinks that may be "acutely and chronically toxic to aquatic organisms".

Thus, analysis of the estuarine mud sediments represents a relatively easy and reliable approach to help establish environmental quality for several reasons. First, concentrations of toxic heavy metals are considerably enriched in sediments compared to their dilute character within the water column; therefore they can be analyzed and monitored with much more reliable results. Second, sediments represent a long-term average and a temporal record of assimilation that smooths out the short-term variability associated with collecting water samples; therefore they can readily indicate enrichment areas associated with various types of heavy metal sources. Third, information obtained from heavy metal analyses of a few samples can often be more useful in defining potential problem areas than many analyses of water samples taken over space and time. These problem areas may also be enriched in other chemical components such as organic toxicants, many of which are more difficult and costly to quantify. Thus, for many areas, sediment analyses for trace elements can be a much more cost effective means of identifying potential problem areas.

The major objective and sub-objectives for this study entitled "Heavy Metals in Organic-Rich Muds of the Albemarle Sound Estuarine System" are to:

> **Determine concentrations and distributions of specific trace elements (i.e., toxic heavy metals and phosphorus contaminants) associated with organic-rich mud within the Albemarle Sound estuarine system.**
>
> **a. Establish present contamination levels around known point and non-point sources,**
> **b. Identify "areas of concern" throughout the estuarine system,**
> **c. Define a basin wide framework for determining migration paths of contaminants, and**
> **d. Determine the pre-man or "natural background" levels of contaminants and establish changing impacts through time resulting from anthropogenic activities.**

A regional grid of 198 sites was sampled throughout the Albemarle Sound estuarine system representing most geographic and geologic conditions and anthropogenic sources of contaminants. From these sites, 360 subsamples were analyzed for sediment grain size, sediment composition, and chemistry including 7 major elements and 15 trace elements that include the EPA's priority pollutant metals (Table A1). Elemental analysis is based on a partial extraction procedure that may approximate "bioavailability" of the elements. Quantitative concentrations of 20 elements were determined utilizing an inductively coupled-argon plasma-emission spectrometer (ICAPES); mercury analyses were done utilizing atomic absorption spectrometry (AAS), and fluorine measurements utilized an electrometric method.

TABLE A1. Quantitative analysis for 22 elements on 360 sediment subsamples from 198 sample stations within the Albemarle Sound estuarine system.

TRACE ELEMENTS (15)				MAJOR ELEMENTS (7)	
Arsenic	(As)	Molybdenum	(Mo)	Aluminum	(Al)
Cadmium	(Cd)	Nickel	(Ni)	Calcium	(Ca)
Chromium	(Cr)	Phosphorus	(P)	Iron	(Fe)
Cobalt	(Co)	Tin	(Sn)	Magnesium	(Mg)
Copper	(Cu)	Titanium	(Ti)	Potassium	(K)
Lead	(Pb)	Vanadium	(V)	Silica	(Si)
Manganese	(Mn)	Zinc	(Zn)	Sodium	(Na)
Mercury	(Hg)				

The analytical data were entered into SYMPHONY worksheets, evaluated statistically utilizing SAS software, and stored in various data bases. An

Albemarle trimmed mean (ATM) was calculated for each element and used as the reference concentration for all subsequent data analyses. Enrichment factors (EF) were determined for each trace element in each sample by comparing the elemental concentration to the Albemarle trimmed mean (ATM) for surface samples.

The present report summarizes the sedimentological and chemical data for the Albemarle estuarine system. The raw data are not included in this report, but are permanently stored in PC computer data base spreadsheets and in Statistical Analysis System (SAS) data sets on the East Carolina University mainframe computer. All of the analytical data for the Pamlico, Neuse, and Albemarle estuarine systems are also on file in the Albemarle/Pamlico Estuarine Study data base established in the Center for Geographic Information Analysis, Office of State Planning, 115 Hillsborough St., Raleigh, NC 27607.

Analyses of analytical data for organic-rich muds within the Albemarle Sound estuarine system have documented specific lateral and vertical distribution patterns of elemental concentration throughout the basin. Anthropogenic sources are believed to be largely responsible for heavy metal enrichment within the Albemarle Sound estuarine system. Sediments in the vicinity of known point source discharges are often substantially enriched in specific metals compared to sediments in other portions of Albemarle Sound. Locally, surface sediments have been enriched orders of magnitude times elemental concentrations occurring either in surface sediments in pristine portions of the estuary or in sediments deeper in the cores that represent pre-man estuarine conditions.

Each estuarine area of Albemarle Sound has been classified with respect to the degree of contamination of the 15 trace elements analyzed (Table A2). This classification is based upon the percent of samples that contain enriched levels of the 15 contaminating trace elements within each estuarine area that are either substantially (= or >2 X the ATM) or slightly (= or >1.5 and <2 X the ATM) enriched over the Albemarle trimmed mean. Areas in which 20% or more of the analyses represent enriched trace element concentrations are considered to be <u>major contaminated areas of concern</u> (CAOC). Those areas in which 10% to 19% of the elemental analyses represent enriched trace elements are considered to be <u>minor contaminated areas of concern</u> (CAOC). Since no areas were found to be totally pristine and without contaminated sediments, a third category was designated <u>least contaminated areas of concern</u> (LCAOC) and includes those areas in which less than 10% of the analyses represent enriched trace element concentrations and that do not consist of the EPA "priority pollutant metals".

Eighteen contaminated areas of concern (CAOC) and four least contaminated areas of concern (LCAOC) have been identified with respect to the quality of bottom sediments of the Albemarle Sound estuarine system (Fig. A1 and Table A2). Ten of the 18 CAOCs have major levels of sediment contamination and 8 COACs have minor levels of sediment contamination. No areas within the entire Albemarle Sound estuarine system had totally noncontaminated or pristine surface sediments, even though some of tributary estuaries have very low levels of development.

TABLE A2. Classification of degree of contamination for each estuarine area of Albemarle Sound with respect to the 15 trace elements analyzed. Classification is based upon the percent of analyses that contain enriched levels of the 15 contaminating trace elements within samples from each estuarine area. Substantially enriched elements have values = or >2 X the Albemarle trimmed mean, whereas slightly enriched elements have values = or >1.5 X and <2 X the Albemarle trimmed mean.

ESTUARINE AREA	N	NUMBER TRACE ELEMENTS ANALYZED	NUMBER ENRICHED TRACE ELEMENTS	NUMBER SUBSTAN ENRICHED ANALYSES	NUMBER SLIGHTLY ENRICHED ANALYSES	TOTAL NUMBER ENRICHED ANALYSES	PERCENT ENRICHMENT
<u>MAJOR CONTAMINATED AREAS OF CONCERN</u>							
WELCH CREEK	10	150	14	68	15	83	55
ELIZABETH CITY	26	390	14	92	41	133	34
EDENTON BAY	13	195	12	36	28	64	33
INNER ALBEMARLE	42	630	13	96	107	203	32
ROANOKE RIVER	26	390	11	55	71	126	32
MIDDLE RIVER	6	90	7	12	15	27	30
CASHIE RIVER	4	60	7	6	12	18	30
LOWER CHOWAN RIV	20	300	13	34	39	73	24
HERTFORD	6	90	9	5	16	21	23
PASQUOTANK RIVER	24	360	12	42	31	73	20
<u>MINOR CONTAMINATED AREAS OF CONCERN</u>							
PERQUIMANS RIVER	10	150	10	14	15	29	19
COLUMBIA	8	120	8	10	10	20	17
LITTLE ALLIGATOR	4	60	8	6	3	9	15
MIDDLE ALBEMARLE	25	375	9	15	37	52	14
SCUPPERNONG RIV	12	180	9	15	10	25	14
DEEP CREEK	6	90	5	5	7	12	13
NORTH LANDING RI	56	840	6	30	62	92	11
NORTH RIVER	10	150	5	5	10	15	10
<u>LEAST CONTAMINATED AREAS OF CONCERN</u>							
LITTLE RIVER	8	120	4	0	11	11	9
OUTER ALBEMARLE	16	240	7	10	9	19	8
ALLIGATOR RIVER	21	315	7	7	12	19	6
YEOPIM RIVER	6	90	1	3	2	5	6

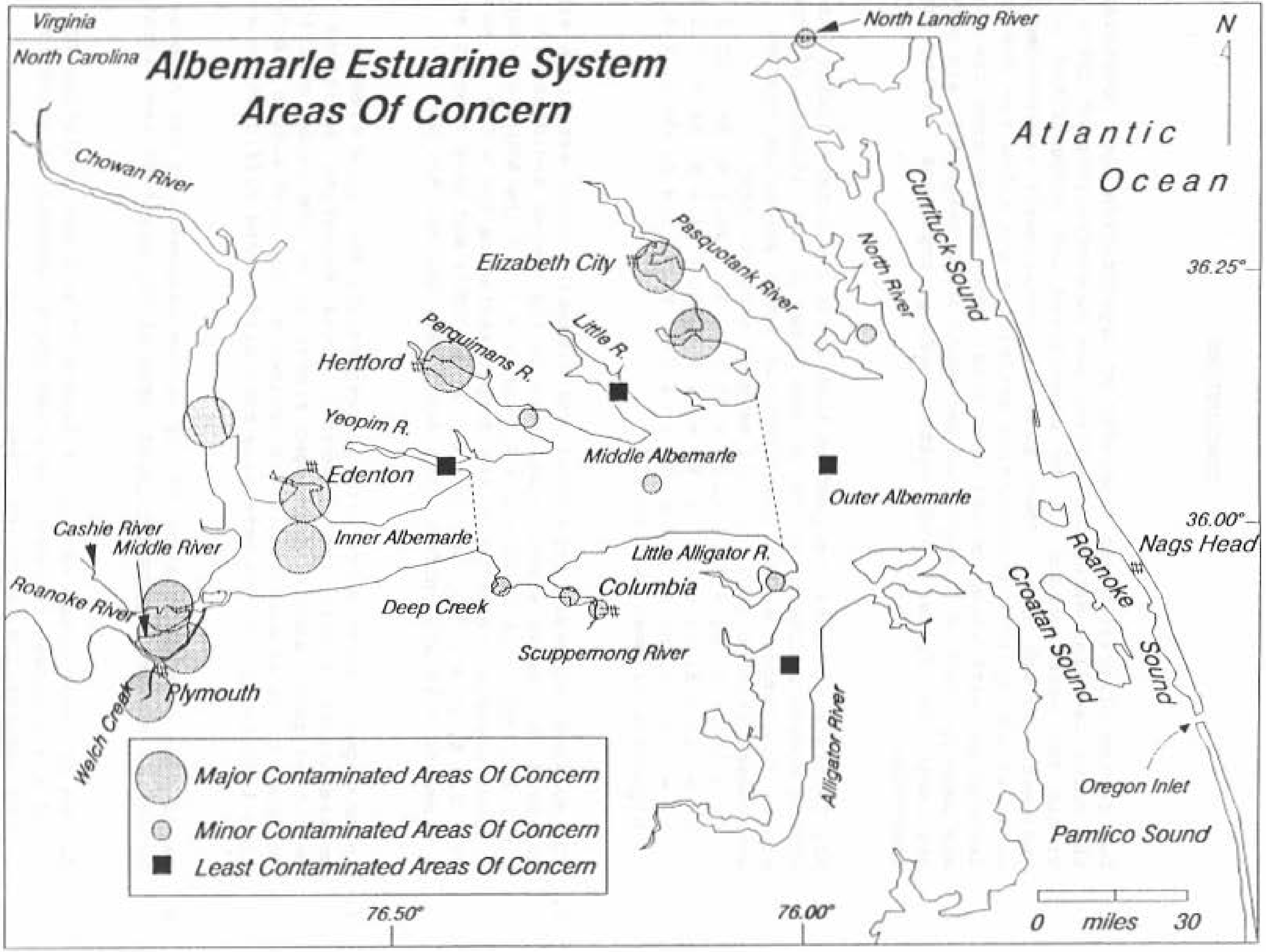


FIGURE A1. Map showing the location of major and minor contaminated areas of concern and the least contaminated areas of concern within the Albemarle Sound estuarine system.

CONCLUSIONS

1. Due to the mineralogy and chemistry of organic-rich muds occurring within the North Carolina estuarine system, low concentrations of trace elements within the water column can be sequestered and concentrated within the sediments through time. These muds are continuously resuspended into the water column by bottom disturbing activities and allow for the continued interaction with water column chemicals. Most sequestered trace elements are loosely bound to fine-grained sediments and consequently are potentially available to filter- and bottom-feeding organisms living in these ecosystems.

2. All 15 trace elements analyzed in this study are substantially enriched within bottom sediments at one or more sites in the vicinity of known point source discharges within the Albemarle Sound estuarine system. Maximum enrichment factors (MEF) for all samples analyzed are:
   Cr = 156.1 X, Hg = 72.9 X, Pb = 30.3 X, Ni = 20.5 X, Zn = 13.3 X,
   Cd = 12.9 X, Cu = 9.4 X, Mo = 5.6 X, Mn = 5.6 X, As = 5.1 X,
   V = 4.0 X, Sn = 3.9 X, P = 3.7 X, Ti = 3.4 X, Co = 2.8 X the
   Albemarle trimmed mean or ATM.

3. The surface sediments throughout the Albemarle Sound estuarine system are enriched in 5 trace elements relative to the deeper sediments (Pb = 1.7 X, P = 1.6 X, Cd = 1.4 X, Zn = 1.4 X, and Cu = 1.2 X the ATM); are depleted in 5 trace elements relative to the deeper sediments (Sn = 0.9 X, Mo = 0.8 X, Ni = 0.8 X, Ti = 0.7 X, and Cr = 0.6 X the ATM); and have concentra-tions of 5 elements that are uniform with depth (As, Co, Hg, Mn, and V).

4. Anthropogenic sources are largely responsible for trace element contamination within the Albemarle Sound estuarine sediments. NPDES permitted point source discharges appear to be the major contributors of enriched trace elements to bottom sediments. Nonpoint source discharges are also important, but are generally more diffuse and difficult to evaluate.

5. Based upon chemical quality of the bottom sediments of the Albemarle Sound estuarine system, <u>18 contaminated areas of concern</u> have been identified.

   A. Ten of these areas have major levels of sediment pollution (20% or more of the analyses represent enriched trace elements relative to the ATM and include the following areas.

REGION	NUMBER TRACE ELEMENTS ENRICHED	% ANALYSES ENRICHED
Welch Creek	14	55
Elizabeth City	14	34
Edenton Bay	12	33
Inner Albemarle	13	32
Roanoke River	11	32
Middle River	7	30
Cashie River	7	30
Lower Chowan River	13	24
Hertford	9	23
Pasquotank River	12	20

B. Eight of the contaminated areas of concern have minor levels of sediment pollution (10% to 19% of the analyses represent enriched trace elements relative to the ATM and include the following areas.

REGION	NUMBER TRACE ELEMENTS ENRICHED	% ANALYSES ENRICHED
Perquimans River	10	19
Columbia	8	17
Little Alligator River	8	15
Middle Albemarle Sound	9	14
Scuppernong River	9	14
Deep Creek	5	13
North Landing River	6	11
North River	5	10

6. Based upon chemical quality of the bottom sediments of the Albemarle Sound estuarine system, <u>4 least contaminated areas of concern</u> have been identified. These 4 areas are not pristine tributaries, however they do contain low levels of sediment contamination (less than 10% of the analyses) by generally non-EPA priority pollutant elements and include the following regions.

REGION	NUMBER TRACE ELEMENTS ENRICHED	% ANALYSES ENRICHED
Little River	4	9
Outer Albemarle Sound	7	8
Alligator River	7	6
Yeopim River	1	6

7. Industrial discharge from a large paper mill on the Roanoke River and Welch Creek, west of Plymouth has contributed the highest levels of trace elements to Albemarle estuarine sediments. The most contaminated sediments are in Welch Creek, where 13 trace elements are substantially enriched (MEF: Cr = 156.1 X, Hg = 72.9 X, Ni = 20.5 X, Cu = 9.4 X, Zn = 6.2 X, Mo = 4.5 X, Cd = 4.0 X, V = 4.0 X, Sn = 3.9 X, P = 3.7 X, Mn = 3.1 X, Ti = 2.4 X, Co = 2.0 X the ATM). Pb and As are slightly enriched within Welch Creek.

8. Based upon the present data base, the trace element contamination problem in Welch Creek appears to be relict and a result of former industrial discharge. It is not clear how much of the trace element contamination problem in the Lower Roanoke River and Inner Albemarle Sound is relict and due to historic processes and how much is a direct result of ongoing industrial and municipal discharge. Modern accumulation of metals is probably taking place in the surface sediments of both the Lower Roanoke River and Inner Albemarle Sound from ongoing NPDES permitted discharges; however, those enriched sediments within the River are probably ephemeral and end up being redeposited during periods of flood within Inner Albemarle Sound, where they contribute to the overall low-grade, regional contamination.

9. The amount of sediment contamination in urban regions is generally directly proportional to the size of that municipal area.

URBAN AREA	1970 POPULATION	NUMBER ENRICHED ELEMENTS	PERCENT ENRICHED ANALYSES
Elizabeth City	14,381	14	34%
Edenton	4,956	12	33
Hertford	2,023	9	23
Columbia	902	8	17

10. The second and third most contaminated sediment regions within the Albemarle estuarine system are the municipal areas of Elizabeth City and Edenton, respectively.

    A. Sediments in the Upper Pasquotank River adjacent to the large urban area and old industrial and port facilities at Elizabeth City are substantially enriched in eight trace elements (MEF: Pb = 30.3 X, Zn = 13.3 X, Cd = 8.8 X, Cu = 7.3 X, Hg = 4.4 X, P = 3.3 X, Sn = 2.3 X, Cr = 2.0 X the ATM). As, Co, and Ni are slightly enriched (1.7 X ATM).

    B. Sediments in Edenton Bay, adjacent to the intermediate size urban area and old port around the town of Edenton are substantially enriched in eight trace elements (MEF: Cu = 7.1 X, Cd = 3.3 X, Ni = 3.3 X, Sn = 3.0 X, Mn = 2.8 X, Pb = 2.6 X, P = 2.6 X, As = 2.5 X, Zn = 2.3 X, Hg = 2.2 X, Cr = 2.0 X ATM). Ti and Co are slightly enriched (1.8 X and 1.5 X ATM, respectively).

11. The waste water treatment plants at Elizabeth City and Columbia have contributed trace elements to the sediments around their discharges.

    A. The large WWTP at Elizabeth City has resulted in substantial sediment enrichment of 7 trace elements (MEF: Cd = 15.4 X, P = 3.5 X, Pb = 3.4 X, Hg = 3.3 X, Sn = 2.7 X, Zn = 2.3 X, Cu = 2.2 X the ATM) with 2 other elements being slightly enriched (Ni and Cr).

B. The much smaller WWTP at Columbia has resulted in substantial sediment enrichment in only 2 trace elements (MEF: Zn = 2.4 X and P = 2.3 X the ATM) with 5 other elements being slightly enriched (Cd, Sn, Zn, Cu, and Pb).

C. The WWTP at Plymouth, Edenton, and Hertford probably would display similar patterns, however, no samples from the vicinity of these WWTP were analyzed.

12. Marinas contribute substantial amounts of copper, and variable amounts of zinc, lead, and other trace elements to the surrounding sediments. The number of enriched trace elements and amount of enrichment appear to be direct functions of the size, age, and nature of the marina operation.

A. Edenton marina: large, established marina with major boatyard; 6 enriched elements; MEF: Cu = 7.1, Sn = 2.8, Cd = 2.4, Zn = 2.3 X, Pb = 1.8, and Ni = 1.5 X the ATM

B. Scuppernong marina: small, established marina with small boatyard; 1 enriched element; MEF: Cu = 5.4 X the ATM

C. Alligator River marina: small, relatively new, transient harbor with no boatyard facilities; no elements enriched

13. Ever increasing amounts of discharged waste water into the Albemarle Sound estuarine system will continue the systematic enrichment of trace elements within the sediments. North Carolina should require waste water treatment plants for industries and government agencies to design and incorporate more efficient treatment systems and not allow the discharge of any potentially toxic elements into "Public Trust Waters". The resulting increased costs are essential to maintain a viable ecosystem and ensure long-term protection of environmental quality.

PART B: INTRODUCTION

PART B: INTRODUCTION

DRAINAGE BASINS FOR THE ALBEMARLE SOUND ESTUARINE SYSTEM

Morphological Setting

The Albemarle estuarine system acts as a large settling basin for sediments, organic matter, heavy metals, and other contaminants resulting from agriculture, urbanization, and industrialization within the drainage basin (Copeland et al., 1983, 1984). The Albemarle Sound drainage system (Fig. B1) is the largest drainage system in North Carolina and encompasses about 17,500 square miles within the Piedmont and Coastal Plain Provinces of both Virginia and North Carolina. This drainage system encompasses several different drainage basins as outlined in Table B1.

TABLE B1. Drainage basins of the Albemarle-Pamlico estuarine system (Giese et al., 1985).

DRAINAGE BASIN	SQUARE MILES
Roanoke River Basin	9,700
Chowan River Basin	4,900
Albemarle Sound Basin	
Pamlico-Albemarle Penn.	1,100
Northern Albemarle Penn.	1,700
Outer Banks	100
ALBEMARLE SOUND SYSTEM	17,500
TAR-PAMLICO RIVER SYSTEM	4,300
NEUSE RIVER SYSTEM	5,600

The Upper Roanoke River drainage system constitutes about 55% of the entire Albemarle drainage and carries more water than any other river in North Carolina with a daily average of about 8,500 ft^3/sec (Moody et al., 1985). The Roanoke and its tributaries have had a series of six dams constructed between 1950 and 1963 for hydroelectric power, flood control, and recreation and include Philpott Lake, Smith Mountain Lake, Leesville Lake, John H. Kerr Reservoir, Lake Gaston, and Roanoke Rapids Lake (Manooch and Rulifson, 1989). The most important of these reservoirs to the Lower Roanoke River and Albemarle Sound is Kerr Lake because of its large storage capacity and direct influence on operation of two downstream dams. Below the lowermost dam at Roanoke Rapids, the River elevation is 50 feet above mean sea level and drops to sea level where it enters Albemarle Sound. The River flows over a distance of 137 miles through an extensive, five mile wide swamp forest floodplain considered to be the largest intact, and least disturbed bottomland forest ecosystem remaining in the mid-Atlantic region (NC Natural Heritage Program, 1988).

Prior to construction of the dams, the lower portion of the Roanoke River was characterized by extreme variability of water level and flow in response to seasonal variations and individual storms. Today, water discharge is controlled at the dams to eliminate the extremes of floods and droughts and approach a more

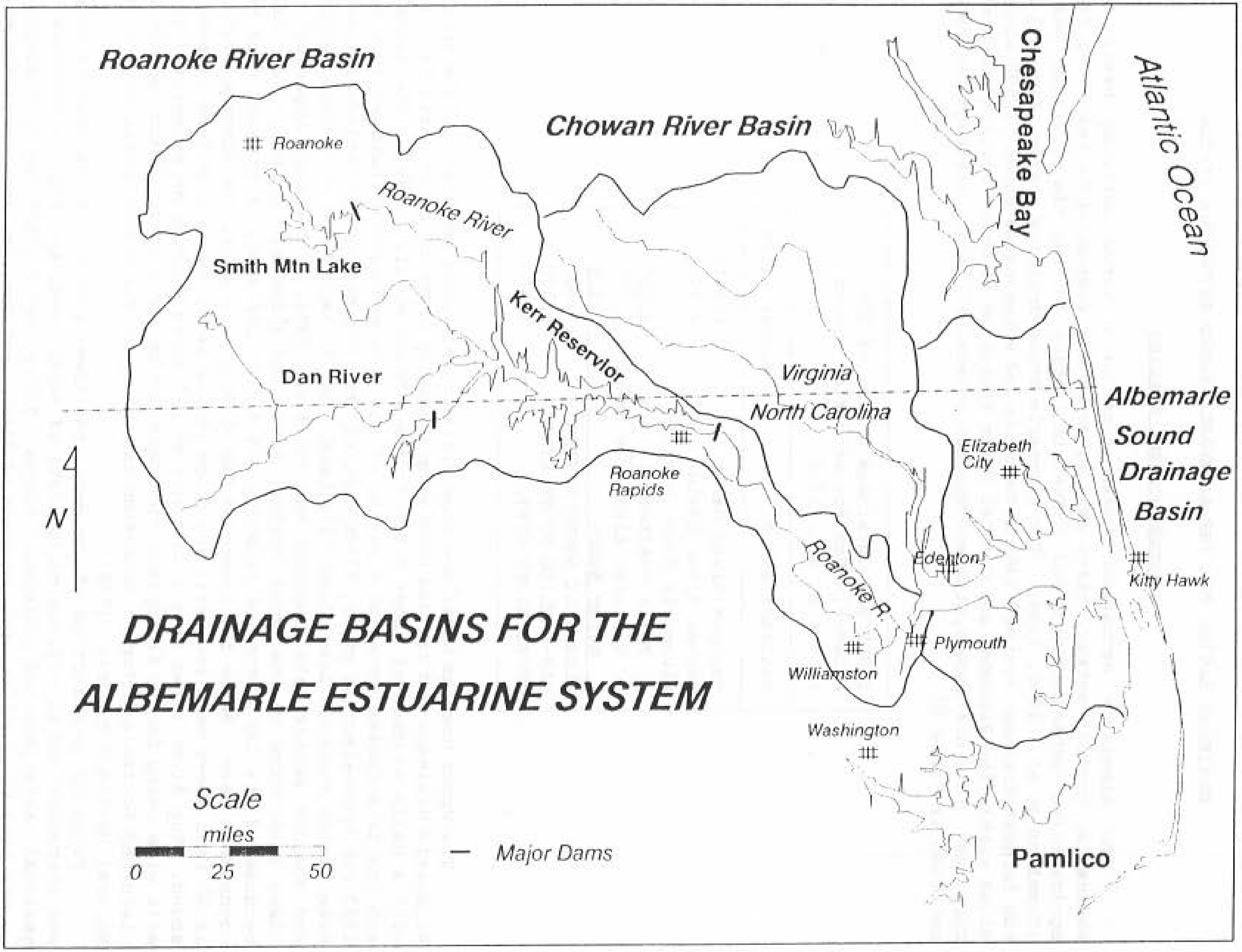


FIGURE B1. Map of the three major drainage basins supplying water, sediments, and contaminants to the Albemarle Sound estuarine system.

uniform year-round flow; however, there are still fluctuations in water levels and flow rates, but they are significantly modified from the natural processes operating on the River during pre-dam conditions. Simmons (1988) concluded that the combined effects of the reservoirs on the Roanoke River trap an estimated 90% of the River's suspended load sediment and 100% of the bed load sediment.

The majority of people living in the Roanoke River drainage basin live either in the vicinity of major reservoirs or in the towns of Gaston, Roanoke Rapids, Weldon, Halifax, Scotland Neck, Williamston, Jamesville, and Plymouth with an estimated population of about 30,000 in 1970 (Manooch and Rulifson, 1989). The upper Chowan River had an estimated population of 26,000 in 1970, about 80% of which is rural with small population centers in the towns of Emporia and Franklin, Virginia (NCDNRCD, 1979). Tschetter (1989) determined the population within the estuarine portion of the Albemarle Sound drainage system to be 107,224 in 1980, up from 101,094 in 1960, with the major population centers being Elizabeth City, Edenton, Hertford, and Columbia. The region is dominantly rural with forestry and agriculture being the major land-use activities; in addition there are some large industries including paper mills at Roanoke Rapids, Plymouth, and Franklin. Land use within the Albemarle Sound estuarine system is generally similar to that in the Tar-Pamlico and Neuse Rivers with the land-use as outlined in Table B2 (Harned and Davenport, 1990).

TABLE B2. Land use within the Albemarle Sound estuarine system (from Harned and Davenport, 1990).

CATEGORY	PERCENT
Forest land	38.7%
Forested wetlands	24.2%
Cropland/pasture	20.9%
Nonforested wetlands	10.3%
Urban	4.1%
Other	1.8%

In terms of discussing the geologic setting, the Roanoke-Albemarle system can be divided into three distinctive parts: the upper Roanoke and upper Chowan Rivers, lower Roanoke and lower Chowan Rivers, and Albemarle Sound estuarine system. The upper Roanoke and upper Chowan Rivers occur west of the Fall Line (Fig. B1), constitute about 87% of the two river drainage systems, and are located within the Piedmont Province. The lower Roanoke and lower Chowan Rivers occur east of the Fall Line (Fig. B1), extend southeast to about 5 miles east of Plymouth in the Roanoke River and to Holiday Island in the Chowan River, respectively. A much smaller portion (about 13%) of these two river drainage basins occur totally within the Coastal Plain Province. Both Rivers drain into the western end of Albemarle Sound, an extensive complex of fresh to low-brackish water estuaries.

The Coastal Plain portion of the Roanoke-Chowan-Albemarle drainage systems can be further subdivided into two main geographic sections by the Suffolk Scarp (Fig. B2). The Suffolk Scarp is a fossil barrier island complex formed by an ocean shoreline during a previous interglacial period when sea level was considerably higher than present. This series of high sand ridges extend southward from Suffolk, Virginia, west of the Dismal Swamp southward to the southeastern corner of the Chowan River. The upland area west of this Scarp is significantly higher than the upland area to the east. This higher terrace to the west results in the spectacular bluff shorelines that occur along the Chowan River and Batchelor Bay in western-most Albemarle Sound. The Scarp complex has been eroded from the Roanoke River floodplain, but it reoccurs in the Plymouth area where it continues southward along Highway 32 towards Washington, North Carolina.

The Coastal Plain region west of the Suffolk Scarp is geomorphically much older than the Suffolk Scarp itself and the surface morphology to the east. Consequently, the western area has higher elevations with slightly rolling topography and moderately well-drained soils with a generally sandy texture. Thus, natural soil drainage is generally good west of the Scarp with many small farms growing crops like tobacco, where the relative net income per acre is high. East of the Scarp, elevations range from maximums of 15 to 20 feet above sea level along the base of the Scarp, with the low, flat surface sloping gently eastward to the eastern end of the mainland with elevations of about 1 to 2 feet above sea level. The flat, poorly drained topography contains extensive swamps and pocosins composed of organic peat soils that generally thicken eastward. Nonswamp areas generally have fine-grained sandy soils with high organic and clay contents. Consequently, artificial drainage is universally required throughout this outer portion of the Coastal Plain. Resulting agriculture is characterized by large, row crop operations of mainly corn, wheat and soybeans. Production of such crops is highly mechanized with relative low net income per acre.

Albemarle Sound Estuarine System

Within the Coastal Plain, the Roanoke and Chowan Rivers operate as rivers with abundant meanders that are incised into broad swampforest floodplains. The eastern-most end of these rivers have been drowned by the present level of the sea and constitute the Albemarle Sound estuarine system (Fig. B2). From the point of initial drowning eastward, Albemarle Sound becomes wider, deeper, and along with the associated drowned tributaries, operate as a drowned river estuarine system. Albemarle Sound itself is that portion of the Roanoke River that has been flooded by the present level of the sea.

The Albemarle Sound estuarine system contains approximately 900 square miles of water, includes seven major embayed tributary estuaries and numerous small embayed lateral streams (Fig. B2). These tributary streams drain the low, flat, swampy Coastal Plain and discharge acidic blackwater and relatively small amounts of sediment into the Sound. Albemarle Sound is not directly connected to the ocean due to North Carolina's Outer Banks, a continuous barrier island without an ocean inlet in the Albemarle area.

Mean annual precipitation is about 50 in/yr with variabilities that range from 35 to 80 in/yr. The greatest monthly precipitation is during the period of October to April and least is from July to September (Wilder et al., 1978). According to Harned and Davenport (1990), Albemarle Sound receives an average of 13,500 ft^3/sec of freshwater inflow; approximately 8,900 ft^3/sec of freshwater is from the Roanoke River and 4,600 ft^3/sec is from the Chowan River. This does not include the freshwater inflow from the remaining Coastal Plain streams; however, it still represents the greatest amount of inflow in the entire North Carolina estuarine system.

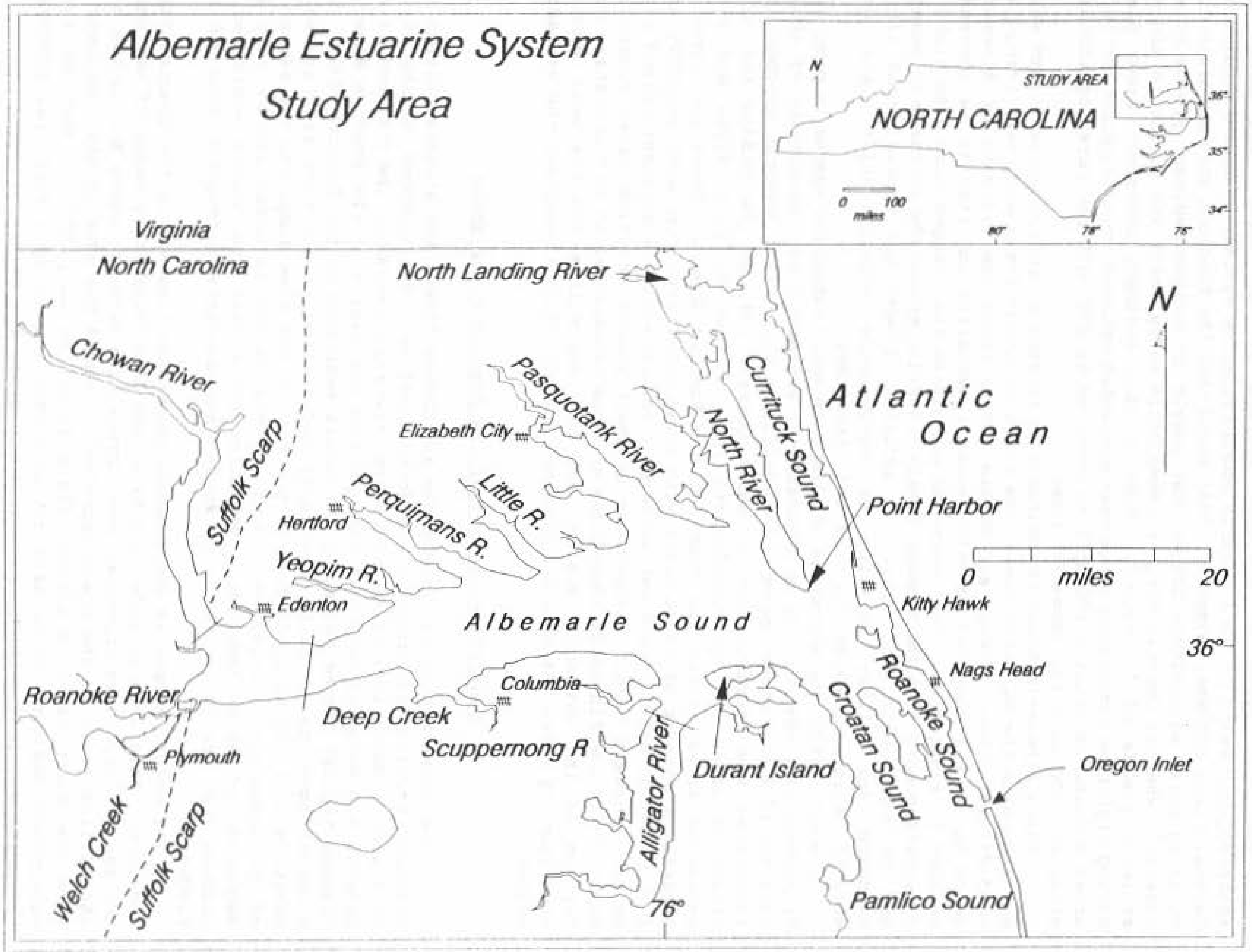


FIGURE B2. Location map of the Albemarle Sound estuarine system.

Two main types of drainage systems deliver water, sediments, and anthropogenic waste to the Albemarle Sound estuarine system: Piedmont streams and Coastal Plain streams. Simmons (1988) found that the Piedmont streams drain clay soils in rural agriculture basins that result in maximum sediment yields of 470 tons/mi^2, whereas Coastal Plain streams drain sandy soils and result in minimum sediment yields of 7 tons/mi^2. Most of this sediment transport takes place during high flow conditions where mean suspended sediment concentration for large urban streams is about 1,600 mg/L as compared to 870 mg/L for rural agriculture sites and 100 mg/L for forested sites.

Since Albemarle Sound is dominated by freshwater inflow and no direct water exchange with the Atlantic Ocean, the Sound is mostly fresh with only irregular, wind-driven tides. Bowden and Hobbie (1977) found the salinity of Albemarle Sound to be low compared to other coastal estuaries and that it is inversely related to river flow. They measured salinities that ranged from 0 to highs of 7 parts/thousand with the highest levels occurring around the entrance to Roanoke and Croatan Sounds (Fig. B2). In addition, Bowden and Hobbie found little evidence for either salinity or temperature stratification, and what stratification did exist was weak and transitory.

About 38% of the shoreline of Albemarle Sound estuarine system is dominated by vegetation, whereas 62% is dominated by sediment banks consisting of strata that are of Pleistocene age or older (Bellis et al., 1975). Vegetation-dominated shorelines are characterized by marsh grasses (8%) in the middle and outer estuarine areas and by swampforests (30%) in lateral tributaries and inner estuarine areas around the mouth of the Roanoke River. These two types of shorelines consist of thick peats with erosional scarps that drop abruptly into 1 to 6 feet of water on the estuarine side and lap onto the adjacent upland areas on the landward side. Pleistocene sediment bluffs and high banks constitute about 19% of the Albemarle shorelines with the highest relief in the western-most portion of the estuarine system; low bank shorelines are the most common, constituting about 43% of all shorelines and occurring throughout the estuarine system.

Geologic Framework of the Roanoke River Basin

The upper basins of the Roanoke and Chowan Rivers are situated within the Piedmont Province of Virginia and North Carolina. The Piedmont begins at the Fall Line, a broad transition zone where crystalline rocks of the Piedmont (i.e., igneous and metamorphic rocks that produce the rapids in the Roanoke River at Roanoke Rapids) become buried by the marine sediments of the Coastal Plain. The Piedmont consists of hilly topography and rolling ridges that rise gradually westward to 1,500 to 2,000 feet at the foot of the Blue Ridge and the beginning of the Appalachian Province. Most of this region is underlain by very old sequences of NE-SW trending crystalline rocks that are highly weathered to produce the orange to red clay soils that dominate throughout much of the Piedmont.

The entire Albemarle Sound estuarine system lies within the Coastal Plain Province. This area is underlain by an eastward thickening wedge of sediments and sedimentary rocks deposited over crystalline basement rocks during the past 150 million years as the ocean repeatedly flooded the edge of the continent to form the North Carolina Coastal Plain (Brown et al., 1972). Most of these subsurface sediment units have little direct effect upon surficial processes operating within the modern Albemarle estuarine system.

Thinner beds of Pliocene and Pleistocene sediments were deposited on the surface of the Coastal Plain during the past 5 million years (Blackwelder, 1981; Riggs and Belknap, 1988; Ward et al., 1991). This later history produced the surface veneer of unconsolidated sediments that directly dictates the Coastal Plain characteristics including regional morphology of the drainage systems and flooded estuaries, soil types, and potential land use. Plio-Pleistocene sediments were deposited by coastal systems that migrated rapidly back and forth across the Coastal Plain-Continental Shelf as sea-level fluctuated in response to repeated episodes of glaciation and deglaciation. Within this rapidly changing coastal system, extremely varied sediments (including gravels, sands, clays, and peats in all possible combinations) were deposited in river, estuarine, barrier island, and continental shelf environments. The Pleistocene sediments range from a few meters in thickness in places along the lower Roanoke River, up to 70 meters in the outer Albemarle area (Riggs et al., 1992).

WATER QUALITY STATUS OF THE ALBEMARLE SOUND ESTUARINE SYSTEM

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 by 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. Man's activities in the Albemarle Sound estuarine system contribute ever increasing amounts of suspended sediment and trace elements. The quality of water within the estuarine system is intrinsically related to development and utilization of waters within the basin upstream from and surrounding the estuary.

In North Carolina, NCDEM (1990) classifies all waterbodies according to designated uses. All waters must, at a minimum, be suitable for aquatic life propagation and maintenance, wildlife, and secondary recreational uses including boating and wading. Additional and more stringent standards are applied to waters with classifications more protective than the general Freshwater Class C or Saltwater Class SC. The more stringent categories include Class B (freshwater for primary recreation), Class WS (water supply), Class SB (saltwater for primary recreation), Class SA (saltwater for shellfishing), and Class HQW (high quality waters). Any source of water pollution that precludes any designated uses is considered to be in violation of water quality standards.

The Lower Roanoke River is classified as a C stream by NCDEM and receives wastewater from 13 large and many small NPDES discharge permits that have a potential flow up to 92 million gallons/day (Manooch and Rulifson, 1989). Briggs (1991) found that in 1990, 25% of the NPDES discharge permits to the Lower Roanoke River Basin, were in significant noncompliance with the conditions of their permits. In addition, 10% were experiencing difficulty in meeting effluent toxicity limits. Harned and Davenport (1990) demonstrated that the amount of wastewater discharged into the Lower Roanoke River (below Lake Gaston) has increased significantly from 1958 to 1988; however, due to the small population base and the large river flow for this drainage system, wastewater discharge only represents approximately 11% of the 7-day, 10-year flow at Roanoke Rapids. Table B3 outlines the water quality characteristics for that portion of the Roanoke River that is in North Carolina (Briggs, 1991).

TABLE B3. Ability of the Roanoke River Basin in North Carolina to support the designated water quality uses along with source of contaminants for that 54% of the Roanoke River mileage classified as partially or totally degraded (estimates from Briggs, 1991).

% OF RIVER MILAGE THAT SUPPORTS THE USE DESIGNATION	
33% full support 46% partial support 9% does not support 12% not evaluated	
NONPOINT RUNOFF (85%)	POINT SOURCE DISCHARGE (15%)
51% agriculture	8% schools
25% construction	5% nonmunicipal
4% forestry	2% municipal
4% urban	

There have been numerous water-quality investigations, but only a few sediment-quality studies within parts of the Albemarle Sound estuarine system over the years. Some of the more pertinent studies are listed in Table B4.

Beginning in the 1960's and extending through the 1970's, the Chowan River estuary experienced nuisance algal blooms that were symptomatic of advanced eutrophication and clear evidence that excessive concentrations of nutrients were present in the River (NCDNRCD, 1979). In addition, the State described a bacterial infection of fish that reached epidemic proportions in 1979, which the State believed was probably linked to deteriorating water quality in the River. An extensive series of monitoring programs and scientific studies were initiated to understand the dynamics of the Chowan River system and the nature of point and nonpoint waste being discharged into the River. The Chowan River system was given a permanent Nutrient Sensitive Water classification in 1979 and a management plan was developed by NCDEM to limit nutrient releases to the River.

Due to the well mixed character and general lack of either salinity or temperature stratification within the Albemarle Sound estuarine system, Bowden and Hobbie (1977) believed that oxygen was always present within the water column with aerobic organisms thriving down to the bottom and aerobic decomposition proceeding to quickly regenerate nutrients. They concluded that at the time of their study, Albemarle Sound was biologically healthy with few signs of cultural eutrophication, but was relatively unproductive. However, the Lower Roanoke River was somewhat different based upon the NCDEM ambient monitoring program, which had seven locations from the Roanoke Rapids dam to the River mouth at Batchelor Bay in Albemarle Sound (Mulligan, 1991). The most recent water column data suggested "consistently good water quality with the noteworthy exception of dissolved oxygen. In late spring, summer, and early fall, dissolved oxygen levels drop below the swamp water standards for significant periods of time in the lower River" (Mulligan, 1991). NCDEM has assigned a "water quality limited" category to the Lower Roanoke River due to dissolved oxygen levels below the 5.0 mg/L limit, especially near the paper mill west of Plymouth. This lead Manooch and Rulifson (1989) to conclude that "continued growth in water withdrawals and wastewater discharges will exacerbate existing water quality problems and causes concern regarding the ability of the Lower Roanoke to assimilate additional waste loadings".

TABLE B4. List of pertinent water-quality and sediment-quality investigations for various portions of the Albemarle Sound estuarine system. See REFERENCES CITED for complete citations.

AUTHOR	DATE	REGION
WATER QUALITY		
Rulifson	1990	Lower Roanoke River
Harned and Davenport	1990	Albemarle-Pamlico Estuarine System
NCDEM	1990	Albemarle-Pamlico Estuarine System
Manooch and Rulifson	1989	Lower Roanoke River
Craig and Kuenzler	1983	Chowan River
Paerl	1982	Chowan River
NCDNRCD	1979	Chowan River
Bowden and Hobbie	1977	Albemarle Sound
Stanley and Hobbie	1976	Chowan River
NCDNER	1975	Chowan River and Albemarle Sound
NCSSSC	1960	Pasquotank River
NCSSSC	1956	Roanoke River
NCSSSC	1955	Chowan River
SEDIMENT QUALITY		
Riggs et al.	This Report	Albemarle Estuarine System
Riggs et al.	1993	North Landing River
Benkert	1992	Albemarle-Pamlico Estuarine System
Riggs and Bray	1991	Lower Roanoke River
Evans et al.	1984	Albemarle-Pamlico Estuarine System

Fluctuations in Roanoke River flow in response to the dams cause certain types of water quality problems in the downstream portion of the River. Manooch and Rulifson (1989) summarize these concerns as follows. Some NPDES permits are independent of flow. Sometimes this results in inadequate dilution and flushing of wastewater from the River during low flow conditions (<2,700 cfs). Some discharges into tributary creeks end up with areas of standing waste and some operations have to temporarily shut down because water flow is actually in an upstream direction. Excessive discharge from the reservoirs places other burdens on wastewater facilities susceptible to flooding. This requires building of protective dikes, pumping facilities, and results in serious leakage problems in antiquated sewer systems which end up exceeding plant capacities.

NCDEM (1990) concluded from their synoptic survey that "the upper or western Albemarle Sound, near the mouth of the Chowan River, is experiencing eutrophication as evidenced by elevated chlorophyll-a concentrations and phytoplankton populations. Dissolved oxygen concentrations and pH values were high reflecting the increased algal activity in this area of the Sound." No water samples taken in Albemarle Sound or associated tributaries were above state standards in metal concentrations; however, there were positive analyses (above reporting level) for zinc, copper, iron, and manganese within these samples. The Alligator River, which is designated as Outstanding Resource Waters, had no apparent water quality problems (NCDEM, 1990).

The water quality report of Harned and Davenport (1990), outlined the following trends within the Albemarle estuarine system during the period between 1970 to 1988, and including some data from as early as 1945.

1. Numbers of farms have decreased about 60% from the 1950's to 1982; fertilizer sales increased from 1958 to about 1975 and then declined; manufacturing employment has increased and agricultural employment has decreased since the 1950's; and population has generally increased since 1910.
2. Suspended-sediment concentrations decreased throughout the Albemarle system, probably because of the effect of upstream reservoirs and improved agricultural soil management.
3. Dissolved oxygen concentrations increased throughout the Albemarle system, except in the Chowan River where levels decreased slightly.
4. Significant trends of increasing alkalinity were detected for the Roanoke River at Roanoke Rapids; alkalinity decreased in the Chowan River.
5. Total ammonia plus organic nitrogen concentrations decreased significantly throughout the Albemarle estuarine system.
6. Total phosphorus concentrations generally decreased throughout the Albemarle system with phosphorus being the limiting nutrient.
7. Chlorophyll-a concentrations increased in a portion of Albemarle Sound and decreased in a portion of the Chowan River.

NCDEM (1991) carried out a baseline study of fish tissue collected in 1989 throughout the Albemarle-Pamlico estuarine system. Within the Albemarle Sound estuarine system, they sampled 13 stations and analyzed 244 samples for metals, and 38 samples for selected synthetic organic chemicals. They found the highest mean concentration of mercury in the Chowan River (0.73 mg/kg with 4 of six samples contaminated) and in Kendricks Creek (0.56 mg/kg) on the southern shore of Inner Albemarle Sound. Both of these sites had fillet samples above the 1.0 mg/kg Food and Drug Administration (FDA) action level for mercury. The remainder of the samples in the Albemarle Sound system were below the FDA action level for mercury, which is the only metal with an FDA action level. The highest mean concentration of copper (0.62 gr/kg) was in the Scuppernong River near Columbia. No detectable lead was found in any fillet samples; however, lead was detected in 15% of the 102 tissue samples analyzed as whole fish. Only three of the thirteen main pesticides were detected, all at levels below the FDA action levels: 29 of the 38 samples contained DDT metabolites, 4 contained dieldrin, and 4 samples contained chlordane metabolites.

Low concentrations of toxic heavy metals in discharge waters or in estuarine water columns are not necessarily indications that the estuaries are free from metal 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 within the sediments can continue as storms, biological processes, and man routinely resuspend the muds into the water column where they can chemically react with low concentrations of dissolved substances. Consequently, the cumulative effect of large discharge volumes with very low elemental concentrations over long time periods allows for continuous interaction with and significant enrichment of concentrations in the inorganic and organic sediment components. Thus, elemental enrichment within surficial sediments may become a factor in long-term, potential bioavailability of trace metals. As trace metal concentrations increase within surficial sediments, they potentially become more available to the food chain through abundant filter and detritus feeding organisms living within the organic-rich mud environments.

Site specific and regional baseline sediment data obtained for the Albemarle Sound estuarine system represent an important first step. From this point, we can begin to determine if causal relationships exist between toxic trace metal sediment contamination, water quality, and the resultant health of the biological components of the estuary (i.e. shellfish, finfish, etc.). Only when these causal relationships are understood can effective management plans be developed to optimize the estuarine resources and minimize the potential detrimental impacts of increasing concentrations of metals in sediments 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 sub-objectives for this study entitled "Heavy Metals in Organic-Rich Muds of the Albemarle Sound Estuarine System" are to:

> **Determine concentrations and distributions of specific trace elements (i.e., toxic heavy metals and phosphorus contaminants) associated with organic-rich mud within the Albemarle Sound estuarine system.**

- **a. Establish present contamination levels around known point and non-point sources,**
- **b. Identify "areas of concern" within the estuarine system,**
- **c. Define a basin wide framework for determining migration paths of contaminants, and**
- **d. Determine the pre-man or "natural background" levels of contaminants and establish changing impacts through time resulting from anthropogenic activities.**

This report presents the results from the last portion of a research project to consider the main estuarine systems of North Carolina (i.e., Pamlico River, Neuse River, and Albemarle Sound estuaries, respectively). This study presents the baseline information that is essential for generating a management plan concerning toxic metal contamination within the estuarine system and lays the groundwork necessary to address 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 contaminants upon the North Carolina estuarine system?**

THE NATURE OF TRACE ELEMENTS

Trace Elements and Health

Heavy metals and other trace elements are normal constituents of most ecosystems. However, natural concentrations are often being supplemented by, 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 (National Academy of Sciences, 1974; 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 may have measurable health effects on organisms as demonstrated by the National Academy of Sciences report on Geochemistry and the Environment (1974) and the NOAA National Status and Trends Program report on The Potential for Biological Effects of Sediment-Sorbed Contaminants (Long and Morgan, 1990). 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 a very important, but poorly understood consideration. The bioavailability of any given element depends upon a host of complex factors. 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, many of which have been summarized in Long and Morgan (1990). For example, mercury, cadmium, arsenic, and lead are toxic to man and to other living things in various chemical forms. In most cases threshold limits for long-term, toxic effects are poorly understood, 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" (NCDEM, 1983). USEPA (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). The importance of trace metals to human health concerns is reflected by the Federal standards for drinking water (USEPA, 1986). The standards include 8 heavy metals in the primary restrictions, which have critical health effects, and five elements in the secondary restrictions, which are less critical to health (Table B5).

TABLE B5. Federal standards for elemental concentrations in drinking water (U.S. EPA, 1986).

PRIMARY RESTRICTIONS µg/L	SECONDARY RESTRICTIONS µg/L
As = 50	Cl = 250,000
Ba = 1,000	Cu = 1,000
Cd = 10	Fe = 300
Cr = 50	Mn = 50
Pb = 50	Zn = 5,000
Hg = 2	
Se = 10	
Ag = 50	

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 and other trace elements can become incorporated into sediments by several different mechanisms and can be partitioned among a variety of sedimentary phases as follows:

1. Dissolved in interstitial pore waters;
2. Adsorbed or chelated by organic matter (often 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., hydroxides, 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 many 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 uncontaminated 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 metals from industry and that the primary mode of concentration and transportation within the estuarine zone is via sediment 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 suspended and bottom sediments, obviously has the potential of conveying large quantities 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.

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 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-Neuse 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 contaminants 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 waste water treatment plants (WWTP). 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 Contaminants

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, raw municipal waste water generally contains concentrations of many heavy metals that are lower than the EPA drinking water standards (Crites et al., 1979). However, sewage sludge generally contains high metal contents as indicated in Table B6. Actual concentrations for any sewage treatment plant are extremely variable and depend upon the amount and composition of industrial waste that is treated. All too often, during peak use periods, mechanical breakdowns, and periods of storms and high rainfall runoff, untreated effluent is discharged directly into the environment from waste water treatment plants. Two recent reports indicate that this type of discharge is common within the Neuse and Pamlico River systems (Clean Water Fund-NC, 1990; EDF and PTRF, 1989).

TABLE B6. Concentration of metals in sewage sludge (Regan and Peters, 1970).

ELEMENT	CONCENTRATION RANGE
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 ppm
Ni	790 to 1,200 ppm
Pb	650 to 1,100 ppm
Cd	290 to 520 ppm

The shorelines along North Carolina's estuaries contain a few major industrial plants such as pulp and paper mills, metal plating operations, chemical plants, textile mills, synthetic fiber plants, and mining operations. Some of these industrial facilities have large waste-water discharges that contain varying amounts of different heavy metals. In addition, many small industrial municipal operations have point source discharges with potential for containing specific trace elements and producing localized or cumulative impacts upon the estuarine system.

A poorly known, but potentially important contributor of heavy metals to the estuaries are the many historic waste disposal and industrial sites scattered through the marshes and lowlands of eastern North Carolina. Since these waste facilities and dump sites generally predate the time of environmental awareness, their locations and the chemicals dispensed into them are also poorly known.

A major source of lead in the environment has been 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 adsorption. Carr et al. (1983) found storm water runoff from seven storms in three different urban settings had the ranges of concentrations of dissolved heavy metals presented in Table B7.

TABLE B7. Concentrations of metals in urban storm-water runoff (Carr et al., 1983).

ELEMENT	CONCENTRATION RANGE μg/L
Hg	<0.3 to 5
As	<5 to 90
Cd	<10 to 950
Ni	30 to 5,900
Cr	25 to 8,470
Cu	100 to 20,100
Pb	250 to 64,600
Zn	130 to 37,600
Fe	61,302 to 970,000

Use of heavy metal pesticides has generally increased with the decline in use of 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 fluxes 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 in the Pungo River. Nine percent of 368 water samples obtained with the Ambient Water Monitoring Program (AWMP) from 1979 through 1981 contained detectable mercury (N.C. 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 an important 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."

TRACE ELEMENTS IN THE ALBEMARLE SOUND ESTUARINE SYSTEM

Point and Nonpoint Source Discharges

Pollution and population are wed in an intimate relationship. Demographic increases generally lead to increases in man-produced waste, much of which is discharged into our rivers. Although the Albemarle region was the first portion of North Carolina to be settled, today it has the lowest level of urbanization of all North Carolina's estuaries. At this time there are about 356 NPDES (National Pollution Discharge Elimination System) industrial and municipal discharge permits for the Albemarle Sound estuarine system with a design flow of about 80 million gallons of waste water per day (pers. comm. Albemarle-Pamlico Estuarine Study). This known discharge represents approximately 35% (67% municipal and other domestic point sources and 33% industrial point sources) of the total pollution load to the Albemarle Sound estuarine system. The largest source of contaminants into the Albemarle Sound system is the additional 65% that comes from non-point sources (NCDEM, 1987).

The U.S. Fish and Wildlife Service (Benkert, 1992) studied the contaminant levels in biota and sediments at sites in the Pasquotank, Perquimans, Chowan, Roanoke, Scuppernong, and Alligator Rivers. Sediments from several stations in the Lower Roanoke River exceeded pollution guidelines for mercury, copper, chromium, and zinc concentrations. Metal concentrations in Rangia clams were generally low overall; however, mercury levels were comparatively greater in clams from drainages on the south side of Albemarle Sound. Metal residues were low in all three fish species analyzed and typical of background conditions, except for slightly elevated cadmium residues in shad from the Perquimans and Pasquotank Rivers.

Evans et al. (1984) analyzed mercury concentrations in subsurface peat samples, exposed in drainage ditches, bottom sediments of drainage ditches, and in the clam Rangia cuneata. They found negligible mercury in the water-soluble and ion-exchangeable fractions of peat and no methylmercury was detected in peat above the analytical detection limits of 25 ng/g. Mercury concentrations in bottom sediments of drainage canals and the Pungo River were lower than those measured in peat due to the lower organic content of the sediments. Total mercury concentrations in the waters of Pungo River and in drainage waters of the Pamlico-Albemarle Peninsula were universally low (<2 ng/L to 23 ng/L) and mercury concentrations in Rangia ranged from 25 to 32 ng/g wet weight in the Pungo River with no methalmercury above the detection limit (25 ng/g). Thus, Evans et al. suggest that mercury concentrations in the peat and peatland drainage systems of eastern North Carolina are low and therefore represent a minor, long-term and low-grade source of mercury to the estuarine system, even if peat mining increases the potential for mobilizing this mercury supply.

Chemical composition of permitted discharge waters for anything other than basic nutrients, oxygen, suspended solids, and a few other parameters, is poorly known. For example, only a very few of the permitted dischargers are required to monitor their waste water for other parameters such as a few heavy metals or toxic organic compounds. These NPDES permits are the sole source for the limited information that does exist from monitoring data. These data are gathered to fulfill individual permit requirements concerning chemical compositions of effluent from specific discharges.

The Clean Water Fund-NC (1990) studied the performance record of 23 of the largest dischargers to the Neuse River for a one year period during 1989-1990. These 23 plants had NPDES permits with a total design flow of about 179 million gallons of waste water per day and an actual flow of about 115 million gallons per day into the Neuse River drainage basin. Following is a partial summary of the conclusions of this study on these 23 plants.

1. Twelve plants reported problems regularly meeting their permit limits for flow.
2. Seventeen of the plants had maximum monthly flows that significantly exceeded their design capacity by amounts up to 235%.
3. Eight plants reported bypassing raw sewage.
4. Most plants had virtually no limits on the heavy metals they could discharge into their receiving waters. Since the majority of plants were not even required to test for heavy metals, their heavy metal load to the river cannot be determined.
5. Fifteen municipal WWTP's have pretreatment programs that monitor and regulate the discharges of 117 industries; the most recent semi-annual pretreatment reports show that 40% of these industries had permit violations.

The average concentration of toxic metals within any discharged waste water is generally very low. However, when the total volume of discharge is considered during a day, month or year, the total volume of metals delivered to the estuarine system can be quite large. For example, Table B8 summarizes data collected for 23 waste water dischargers that suggest significant volumes of heavy metals are contributed to the Neuse River system each year when the combined concentrations are considered.

Little is known about nonpoint source discharges into the Albemarle Sound estuarine 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. In addition, there are numerous impoundment projects and various types of channel alterations and stream modifications, all of which directly impact the sediment characteristics of the downstream estuarine system. For example, during the 1960's and 70's many coastal plain tributaries were channelized by the U.S. Soil Conservation Service and many miles of channel modification projects were carried out by the U.S. Army Corps of Engineers.

TABLE B8. Combined effluent flow and pollutant loads for 23 major waste water dischargers in the Neuse River drainage basin from 4/89 through 3/90. Data are from the Clean Water Fund-NC, 1990.

ELEMENT	NO. OF PLANTS	DAILY AVERAGE	YEARLY AVERAGE
Cadmium	7	0.69 lbs	252 lbs
Chromium	13	3.28 lbs	1,197 lbs
Copper	11	8.61 lbs	3,143 lbs
Lead	10	3.02 lbs	1,102 lbs
Mercury	4	0.11 lbs	40 lbs
Nickel	7	4.00 lbs	1,460 lbs
Silver	4	0.72 lbs	263 lbs
Zinc	10	27.20 lbs	9,928 lbs

Trace Element Contaminants: Problems with Monitoring Water Quality

The EPA STORET Data Base System for the North Carolina estuaries and associated drainage basins contain information from monitoring sites for the Ambient Water Monitoring Program administered by the N.C. DEM. Measured monthly, data at each site consist of chemical and physical parameters for water samples including heavy metals. In 1987, a North Carolina state agency (NCDEM) concluded that heavy metals were not a problem in the Pamlico River estuary. The main basis for their heavy metal conclusion was that most water analyses within the STORET data base 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 B9 compares analytical detection limits for 5 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). Analytical detection limits for these five metals in N.C. are significantly higher than ambient concentrations in the Mississippi, a river heavily influenced by anthropogenic input of heavy metals. However, the high detection limits used in analyses for the North Carolina data base have lead to misinterpretations. Cadmium for example, may be 500 times higher in concentration compared to background or non-contaminated waters; however, this would not be detected using the present techniques in North Carolina.

Two possible explanations for the use of the high detection limits depicted in Table B9 are: 1) the methods used routinely by many labs studying North Carolina waters are not adequate for determining ambient trace metal concentrations, or 2) some State agencies set analytical detection limits for heavy metal concentrations in ambient water at fairly high levels only to detect violation of standards and keep analytical costs low. In either case, using these types of data to conclude that water quality problems do not exist because metal concentrations in water samples are below analytical detection limits are misleading.

TABLE B9. 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

Also, such analyses do not address the potential concentration and toxicity of metals that might occur within the riverine and estuarine sediments. Due to rapid changes in estuarine water chemistry and high chemical reactivity of the sediments, many metals 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 the mud sediments are routinely resuspended into the water column. Consequently, the cumulative effect of large discharge volumes over long time periods and continuous interaction with inorganic and organic sediment components are important factors 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.

Long and Morgan (1990) summarized the biological studies "to assess the relative likelihood or potential for adverse biological effects occurring due to exposure of biota to toxicants in sediments sampled and analyzed by the NOAA National Status and Trends Program". In this study they determined the apparent ranges in concentrations of individual chemicals in sediments in which various biological effects are likely to occur. Kimerle (1987) concluded that some chemicals tend to partition strongly to sediments becoming sinks that "are acutely and chronically toxic to aquatic organisms". Gilford and Zeller (1987) have found that polluted sediments have negatively impacted benthic organisms in areas where water column criteria were not violated.

Analysis of the estuarine mud sediments represents a screening tool that is an easy and reliable approach to determining general problem areas within the estuarine system for several reasons.

1. Concentrations of heavy metals are considerably enriched in the sediments compared to their dilute character within the water column; therefore they can be analyzed and monitored with much more reliable results.

2. Sediments represent a long-term average and a temporal record of assimilation that smooths out the extreme short-term variability associated with collecting water samples; therefore they can readily pinpoint problem areas associated with various types of heavy metal sources.
3. Problem areas defined by heavy metal enrichment have high potentials for being enriched in other chemical components that may cause more serious water quality problems (e.g., organic toxicants, many of which are difficult and costly to quantify). Thus, sediment analyses for trace elements may be a much less expensive, more cost effective means of identifying potential problem areas.

Long and Morgan (1990) conclude that chemical data provide indications of the relative degrees of contamination among the sampling sites, but alone they provide neither a measure of adverse biological effects nor an estimate of the potential for effects. From chemical/sediment data bases, such as is presented in this study of the Albemarle Sound estuarine system, it is now critical to determine the effects of increasing heavy metal contamination in estuarine sediments upon the general health of biological systems within the North Carolina estuaries.

PART C: METHODOLOGY

PART C: METHODOLOGY

FIELD SAMPLING

Delineation of the Albemarle Sound Study Area

The study area includes the lower Roanoke River and the entire Albemarle Sound estuarine system. It extends from approximately 2 miles west of Plymouth on the Roanoke River, eastward to Point Harbor in Currituck County and Durants Island in Dare County (Fig. B2). All major tributary estuaries to the trunk estuary as outlined in Table C1 were included within the present study.

TABLE C1. Distribution and numbers of sediment samples collected in the Albemarle Sound estuarine system for subsequent sediment and elemental analyses. Sample areas are listed from west to east within each category.

SAMPLE AREAS	AREA NAME	SHORT CORES	NO. SUB-SAMPLES	VIBRA-CORES	SURFACE SAMPLES
ALBEMARLE SOUND TRUNK SYSTEM		60	119	11	60
Lower Roanoke River	RKE	13	26	2	9
Middle River	MID	3	6	0	0
Cashie River	CHS	2	4	0	0
Inner Albemarle Sound	ALBI/ALBW	21	42	7	14
Middle Albemarle Sound	ALBW/ALBE	13	25	1	15
Outer Albemarle Sound	ALBE	8	16	1	22
TRIBUTARIES--NORTH SIDE		65	123	3	0
Lower Chowan River	CHW	10	20	1	0
Edenton Bay	EDN	7	13	0	0
Yeopim River	YEO	3	6	0	0
Perquimans River	PER	8	16	0	0
Little River	LIT	4	8	1	0
Pasquotank River	PAS	28	50	1	0
North River	NTH	5	10	0	0
TRIBUTARIES--SOUTH SIDE		31	61	4	14
Welch Creek	WEL	5	10	0	0
Deep Creek	DEP	3	6	0	0
Scuppernong River	SCP	10	20	1	0
Little Alligator River	LALG	2	4	0	0
Alligator River	ALG	11	21	3	14
CURRITUCK SOUND		42	57	1	0
North Landing River	CTK	42	57	1	0
TOTALS:		**198**	**360**	**19**	**74**

The outermost estuaries that extend north and south off the eastern end of Albemarle Sound (Currituck, Roanoke, and Croatan Sounds) were not included in the present study due to financial limitations. A small portion on the northern end of Currituck Sound, referred to as the North Landing River (Fig. B2) was studied as part of a different project. However, the chemical data for the North Landing River is only summarized in the present report and is discussed in detail in the report entitled Sediment Quality and Dredging Effects in the North Landing River, Currituck Sound Estuarine System, North Carolina (Riggs et al., 1992a).

Design and Rationale

The general location and distribution of shallow-core sample sites and vibracore sites within the Albemarle Sound estuarine system are presented in Figures C1 and C2. We did not follow a purely randomized sampling scheme. Since the purpose of the study was to identify and delineate potentially contaminated areas and because the types and sources of trace element contaminants are highly varied, the sampling scheme reflects our attempt to describe as many of these variable conditions as possible. These include:

1. Areas that have high levels of both modern and relict man-influenced point source discharges, including industrial sites and municipal facilities such as waste water treatment plants;
2. Areas that have high levels of man-influenced nonpoint source discharges such as marinas and surrounding areas of intense boating activity, urban areas and associated runoff, and agricultural farming and feed-lot operations and resulting runoff;
3. Areas that appear fairly pristine with limited man-influenced development, runoff, and discharges; and
4. Samples from deeper in the cores that contain sediment that is pre-anthropogenic and below the man-influenced surface sediment.

The last two sample types provide two different "background" values for metals in the estuarine system while the first two sample types define the types and levels of heavy metal contaminants in the organic-rich estuarine muds. The research design specifically addressed the need to distinguish between these four types of areas and their respective levels of contamination within the estuarine sediments.

Regional sample sites were systematically located along the entire length of the trunk estuary and in all major tributaries within the Albemarle Sound estuarine system. These sample sites provided the regional patterns of elemental distributions. Denser sampling grids were established around known sources of chemical contamination in the sediments. Location of these sites was based upon the distribution of known point and nonpoint discharges as determined from surveying the literature and the NPDES waste water discharge permits within Albemarle Sound drainage system. The regions with denser sampling grids provide information on the types and volumes of contaminants contributed by specific sources for comparison to the background contaminant levels within the sediments of the Albemarle Sound estuarine system.

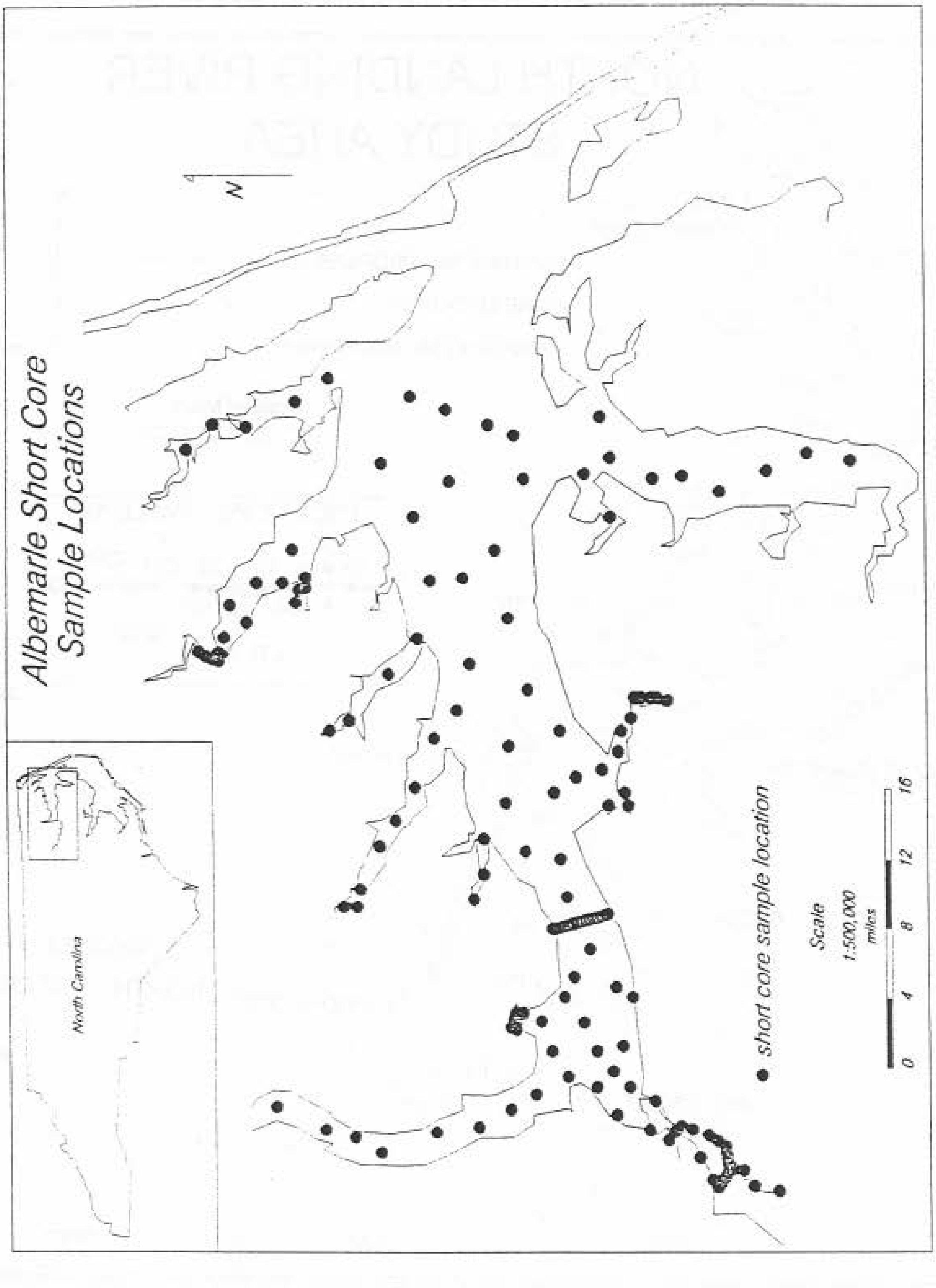


FIGURE C1. Map of the Albemarle Sound estuarine system showing the location of short core (< 0.6 m) sample sites for this study, excluding the North Landing River. See Figures E2, E5, E6, E7, E8, and the Appendix for detailed locations.

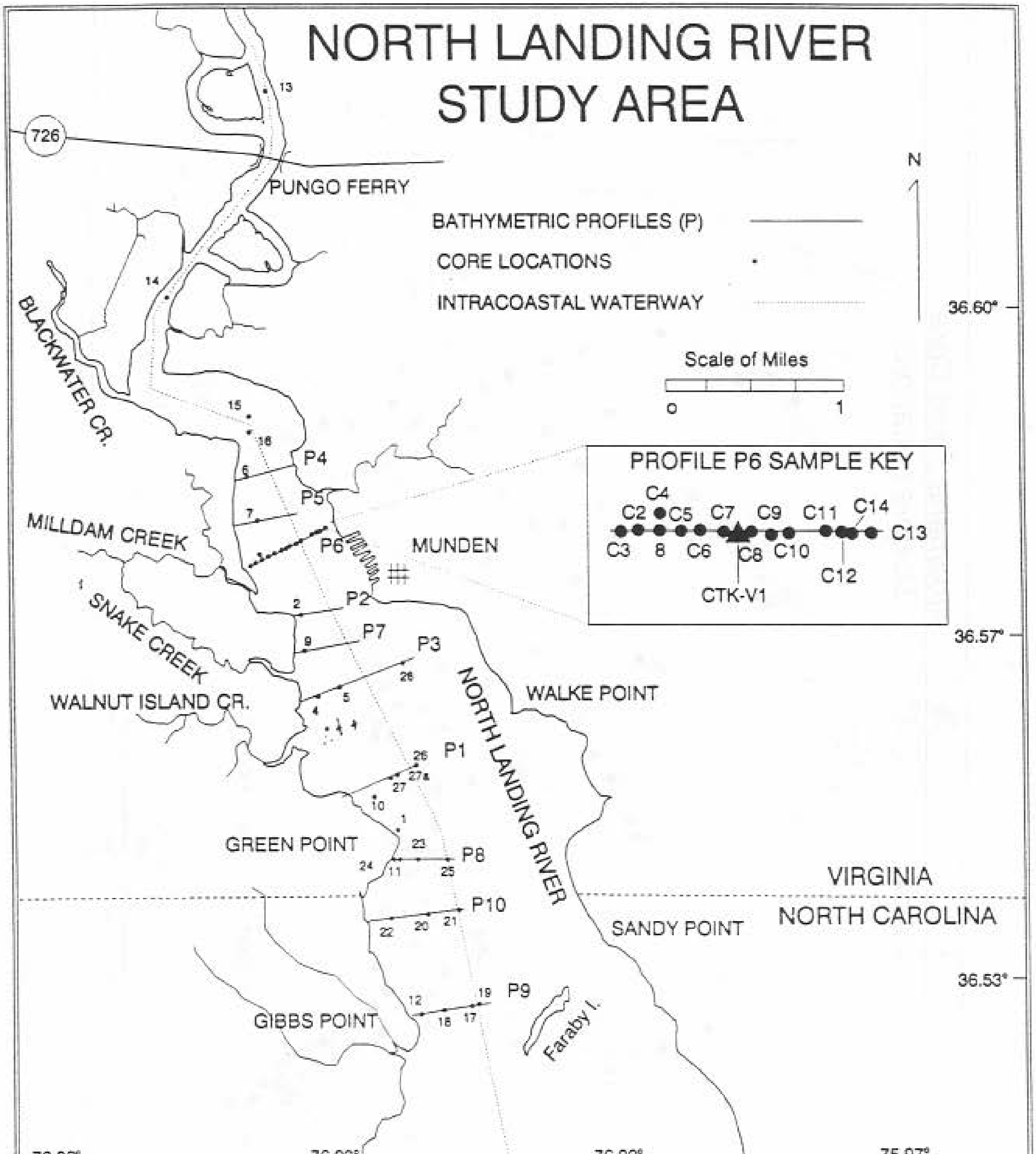


FIGURE C2. Map of the North Landing River in Currituck Sound showing the location of short core (< 0.6 m) and vibracore (6 m) sample sites and bathymetric profiles utilized in this study.

Development of Base Maps

Digital base maps were generated for the entire Albemarle Sound 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 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 the map. 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 Sediment Samples

Three different types of samples were acquired during this sampling period and included the following:

1. 198 short cores (< 0.6 m in length) utilized for sediment and geochemical analyses (Figs. C1 and C2);
2. 19 vibracores (3 to 8 m in length) utilized for sedimentological and stratigraphic analyses (Figs. C2 and C3); and
3. 74 surface sediment grab samples obtained along bathymetric profiles across specific water bodies for sedimentological analyses (Fig. C4).

Only one core or sample was obtained at each sample site. Table C1 summarizes the number and distribution of core and sample sites within the Albemarle Sound estuarine system. Appendix A presents location data for all core and samples acquired for the present study.

Each sample site was occupied on only one occasion. Most sampling for the Albemarle estuarine system was done during the summer of 1990 with minor additional profiling and surface sampling done during the summer of 1991. All field work in the North Landing River was done during February, March, and June of 1991. All samples were collected from 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 217 core sites:

1. Station number;
2. Location: LORAN-C coordinates or compass bearings and descriptive landmarks;
3. Water depth;
4. Bottom sediment description;
5. Bottom core and associated samples with assigned numbers and size.

Short sediment cores were collected at the 198 sites and ranged from 7 cm up to 60 cm in length. These diver-collected cores, obtained by free diving, were collected by hand-forcing a 9 cm diameter, clear polybuterate pipe into the sediment. The ends of the core pipe and included sediment were covered with plastic caps, the core pipe withdrawn, and returned to the surface in a vertical position. As soon as the core was onboard the boat, it was measured, trimmed,

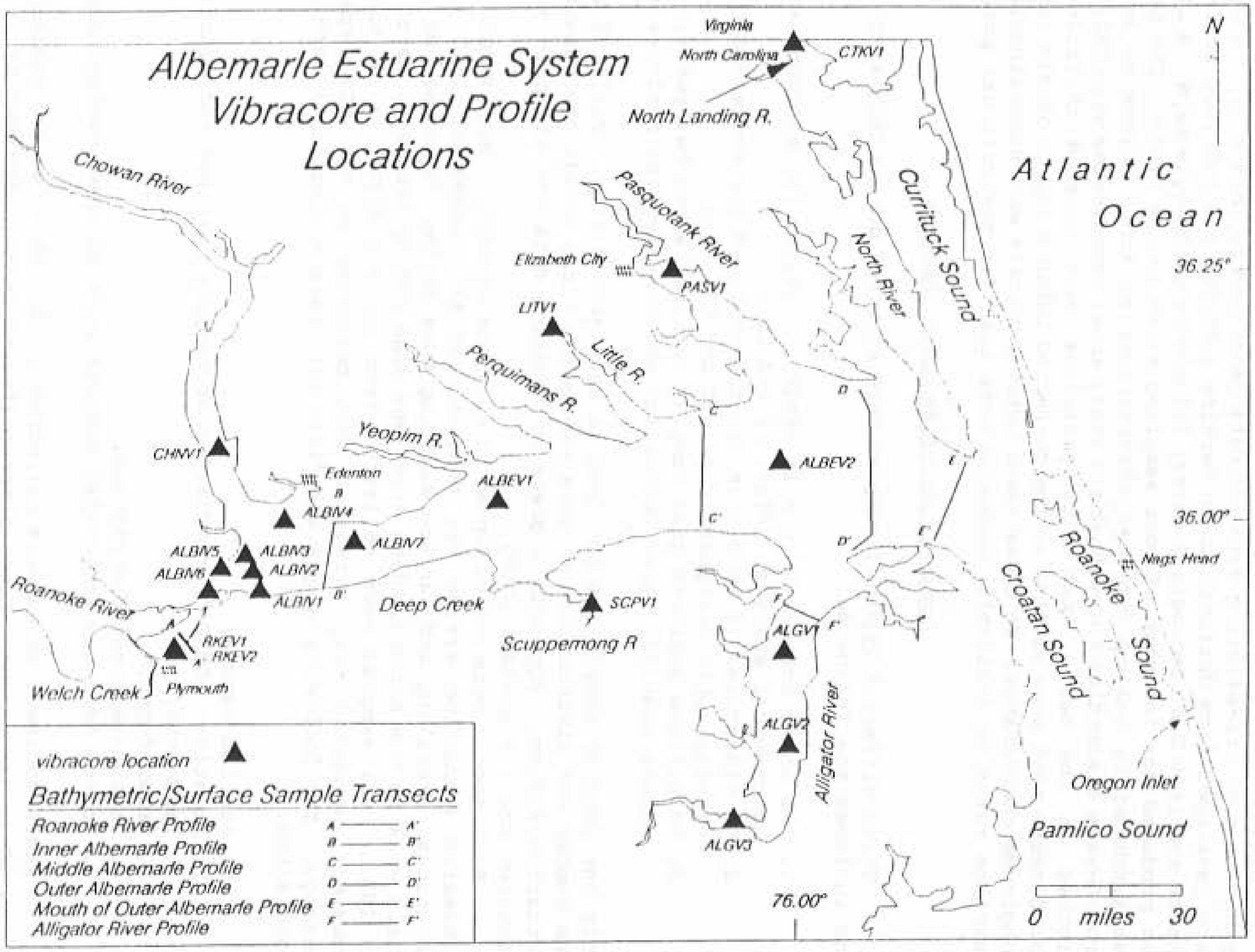


FIGURE C3. Map of the Albemarle Sound estuarine system showing the location of vibracore (3 to 8 m) sample sites utilized for this study.

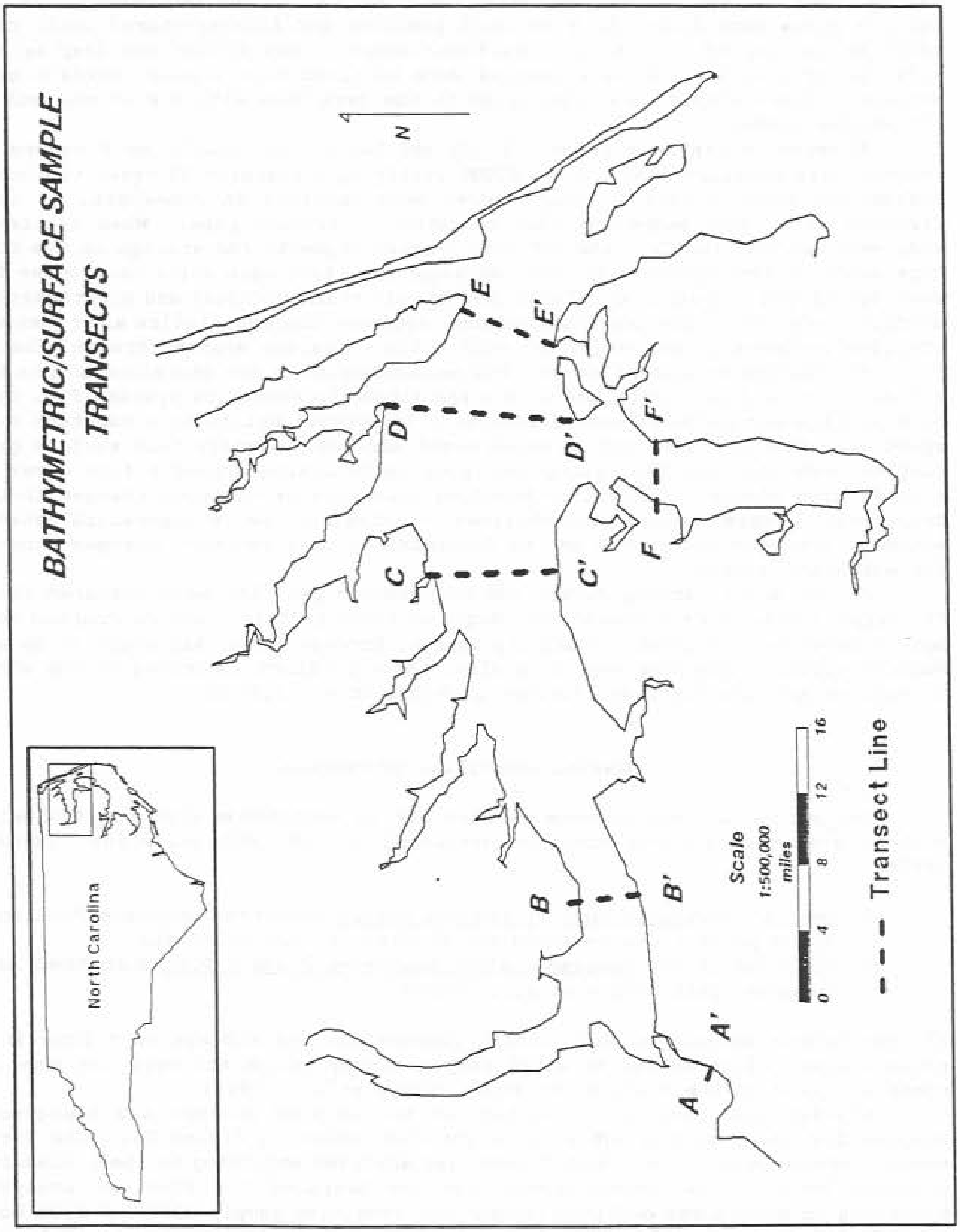


FIGURE C4. Map of the Albemarle Sound estuarine system showing the location of six bathymetric profiles with associated surface sample transects utilized in this study, excluding the North Landing River. Profiles are presented on Figures D2 through D7.

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. In a few locations, where it was either too deep or not safe for free diving, surface samples were obtained with a ponar surface grab sampler. These samples are identified in the data base with a P at the end of the sample number.

Nineteen vibracores (Figs. C2, C3 and Table C1), from 3 to 8 meters in length, were obtained from the R/V NITRO utilizing a standard 10 meter vibracore system and SCUBA divers. These cores were obtained in commercial (3 inch diameter by 30 foot segments) aluminum water irrigation pipe. When retrieved they were sealed, labeled, and cut into 3 meter segments for storage in the ECU, Department of Geology core library. Subsequently, they were split lengthwise for description and subsampling and utilized for all sedimentologic and stratigraphic studies to determine the pre-anthropogenic sediment characteristics and rates and changing patterns of sedimentation within the estuarine system through time.

Six bathymetric profiles were run perpendicular to the shoreline across the estuaries at critical locations within the Albemarle estuarine system (Fig. C4). Each profile was produced with a recording fathometer utilizing a constant boat speed with specific time and location event markers. Seventy four surface grab samples were then obtained along each profile utilizing either a free diver or a ponar grab sampler at specific sampling intervals or at major changes in the bathymetry. These samples were obtained to establish the relationships between sediment type and bathymetry and to determine lateral sediment changes through the estuarine system.

In the North Landing River, ten bathymetric profiles were measured (Fig. C2) perpendicular to the shoreline. Eight of these profiles were reoccupied four months later to determine approximate changes through time. All short cores and surface sediment sampling were done along these profiles according to the above procedures and are discussed further in Riggs et al. (1992a).

GENERAL ANALYTICAL PROCEDURES

Analytical procedures were carried out in accordance with the following quality assurance reports prepared according to U.S. EPA guidelines (Werme, 1985):

1. Quality Assurance/Quality Control Report submitted when the Pamlico River project was accepted for funding in June 1987; and
2. Upgraded in the Revised Quality Assurance Project Plan submitted in December 1989 (Riggs et al., 1989a).

All procedures associated with sample preparation and storage were done in a trace-element clean manner to avoid sample contamination and were the same as those utilized in the Neuse River study (Riggs et al., 1991).

Sub-sampling involved production of two sets of uniform and homogenous samples for the purposes outlined in the flow sheet in Figure C5. The first sample set was used for sedimentological lab analyses according to the procedures outlined below. The second sample set was prepared for chemical analyses according to procedures outlined below. All remaining sample material from both sample sets were archived for future reference and subsequent analyses. Following sub-sampling, remaining core material was not saved due to lack of

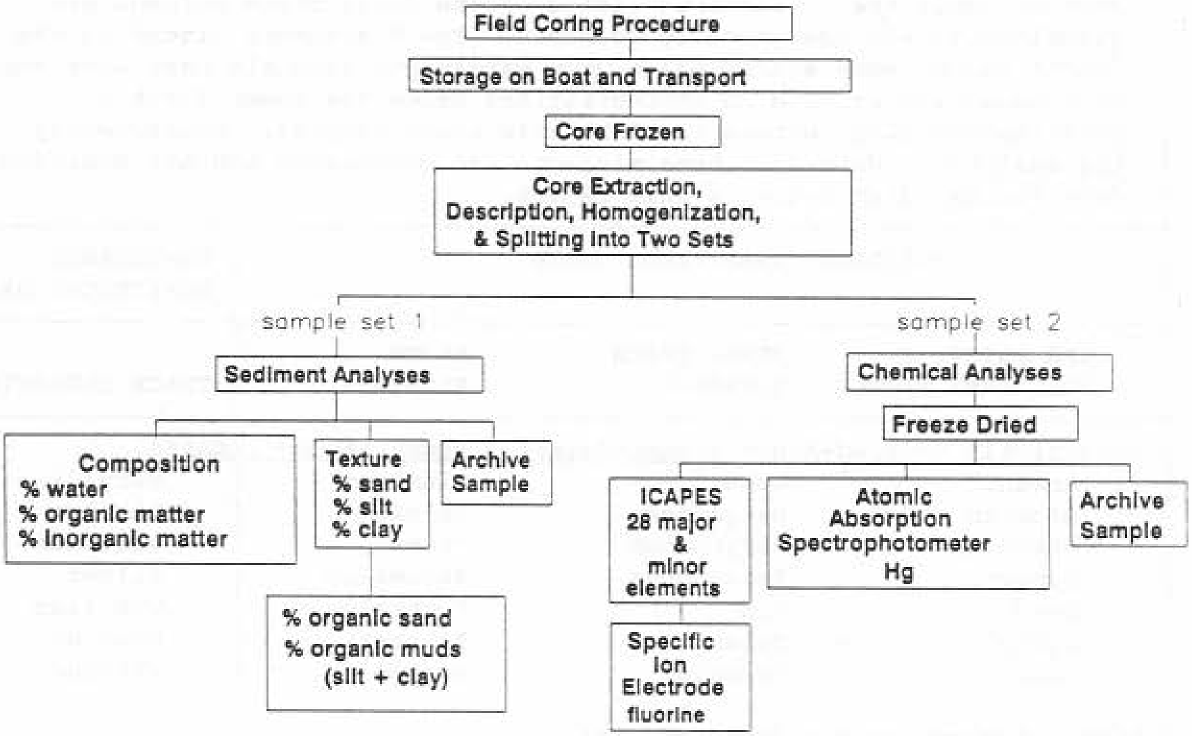


FIGURE C5. Laboratory flow sheet for sediment and chemical analyses.

storage facilities.

A total of 198 short cores (Figs. C1 and C2) were described and subsampled. This resulted in 360 subsamples distributed regionally as outlined in Table C1. These 360 subsamples were analyzed as outlined in Figure C5 and included:

1. Core and sediment descriptions;
2. Sediment compositions (% water, % organic, % inorganic, % organic in mud (silt plus clay) fraction, and % organic in sand fraction);
3. Grain size analysis (% sand, % silt, and % clay); and
4. Chemical analyses for 30 elements (Table C2).

TABLE C2. Analytical data were obtained for 30 elements in this study. However, only the 22 elements listed in the first three columns are quantitative and analytically reliable. The 8 elements listed in the fourth column were either based upon wavelength channels that were not very sensitive or were in concentrations below the lower limit of quantitation (LLQ) within the Albemarle Sound samples. Consequently, the analytical data for these elements are unreliable and are excluded from further discussion in this report.

RELIABLE ANALYTICAL DATA			UNRELIABLE ANALYTICAL DATA
EPA PRIORITY POLLUTANT METALS	OTHER TRACE ELEMENTS	MAJOR ELEMENTS	TRACE ELEMENTS
Inductively Coupled-Argon Plasma-Emission Spectroscopy (ICAPES)			
Arsenic	Cobalt	Aluminum	Beryllium
Cadmium	Manganese	Calcium	Lithium
Chromium	Molybdenum	Iron	Selenium
Copper	Phosphorus	Magnesium	Silver
Lead	Tin	Potassium	Thallium
Nickel	Titanium	Silica	Uranium
Zinc	Vanadium	Sodium	Yttrium
Atomic Absorption Spectrometry (AAS)			
Mercury			
Specific Ion Electrode			
			Fluorine

Thirty elements (Table C2) were chemically analyzed on the 360 subsamples according to the following procedures:

1. Mild acid leach (2 N HNO_3 for 48 hours) extract of all sediment samples:
    a. Inductively coupled-argon plasma-emission spectroscopy (ICAPES) determinations were made for 28 elements on the acid leachate. Due to particular instrumental conditions (e.g., available wavelength, type of photo-multiplier tube, the ability to identify

    and appropriately correct for inter-element interferences, as well as the order of magnitude of actual concentrations encountered) reliable results (based on acceptable lower limits of quantitation and reproducibility) were obtained for only 21 of the 28 elements examined.

  b. Electrometric techniques (specific ion electrode) were utilized to determine the concentration of extractable fluorine in all surface sediment samples. Because of the necessity to dilute out interfering effects of high levels of acid, iron, and aluminum prior to actual electrode measurement, the resultant lower limit of quantitation (LLQ) for fluorine is unusually high. Consequently, no samples from Albemarle Sound exhibited extractable fluorine levels above the LLQ. This is in great contrast to many sediment samples from the Pamlico River estuary that had enriched fluorine concentrations resulting from waste discharges from a phosphate mining and processing facility (Riggs et al., 1989b).

2. Autoclave digestion and mercury analysis (USEPA, 1979) of sediment samples was performed utilizing a cold vapor atomic absorption spectrometric (AAS) technique.

SEDIMENT ANALYSES

Sediment Sub-Sampling

Sub-sampling of sediment cores was done according to the following routine. 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 sub-samples of 7 cm thickness were obtained, at the top and bottom of the core if the core was longer than 20 cm; cores less than 20 cm long had only a top sample. Samples from each interval were homogenized using a plastic spatula and divided into two plastic containers for sedimentological and chemical analyses.

Textural and Compositional Analyses of Sediment

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 in a warm oven (20° to 25° C) for at least 6 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 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 remaining sediment mixture 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 the oxalate residue was used to correct 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 correcting for oxalate residues.

The sand and mud (silt plus clay) fractions were then microscopically inspected for mineralogic descriptions. Percent organic content in the sand fraction was determined by placing the weighed dried sand 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 sand fraction. The concentration of combustible organic matter in the mud fraction (silt plus clay) was calculated by subtracting the amount of organic matter in the sand fraction from the total amount of organic matter previously determined in the total sediment.

CHEMICAL ANALYSES

Rationale for Extraction Procedure Utilized

Numerous attempts have been made to approximate "bioavailability" by identifying relationships between whole body or organ specific trace metal levels in biota and 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 solubilize all residual metals bound within the crystal lattice of minerals.

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, and
4. Capability for determining the
    a. Anthropogenic derived fraction and
    b. "Bioavailable" fraction.

This study is not the first to investigate heavy metals in the Albemarle-Pamlico-Neuse 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 so that it can be readily applied in more than the rare "research" setting. No sequential extraction procedure can satisfy these two criteria; every added extraction step requires an added analysis step with its associated costs in personnel, 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 inputs (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 susceptible to pH conditions both in the environment and in digestive tracts of organisms), chelated surface organic coatings, and 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 but with 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. A detailed description of procedures utilized for sample pre-treatment and elemental extraction, as well as comparison of various extraction procedures follow in the subsequent sections.

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 taken place from the freezing process had already occurred. 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. Frozen subsamples were then 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 inductively coupled-argon plasma-emission spectrometry (ICAPES) and fluorine analyses were processed utilizing a mild extraction technique similar to that delineated by W.S. Boothman of the U.S. EPA ERLN facilities at Narragansett, R.I. (pers. comm., Jan. 1988). A 2N HNO_3 extraction procedure was utilized for chemical analysis of all 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 extractions is an important requirement that can only be achieved with close adherence to 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 (a source of metal contamination, especially Zn).
   b. While keeping the barrel vertical, carefully insert the syringe tip into 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 solution and 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 solution through the filter. Discard the first 2 to 3-mL and collect the rest in a 50-mL plastic, centrifuge tube appropriately labeled. In order to speed up the filtering process and minimize strain to operator's hands, it is recommended that some type of syringe filtering aide be used at this step (e.g. "Main Squeeze" from Scientific Technologies of Raleigh, N.C.).
   e. Cap the tube, mix by inversion 2 to 3 times, and save until analysis.
   f. Rinse out and air dry the 50-mL syringes for future use but discard the filter.
6. Note: Laboratory temperatures where the extraction are performed over the period of work varied from 19° to 24° C.

Comparison of Extraction Procedures

The study of trace metals in Albemarle Sound 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 C6 compares the means of results obtained by the various partial extraction procedures obtained by ICES and the samples from the Pamlico River study of Riggs et al. (1989b). The Pamlico River study was identical to those of the Neuse River (Riggs et al., 1991) and the present Albemarle Sound estuarine study. These comparisons indicate that procedures used in all of the North Carolina estuarine heavy metal studies are most similar to extraction procedure

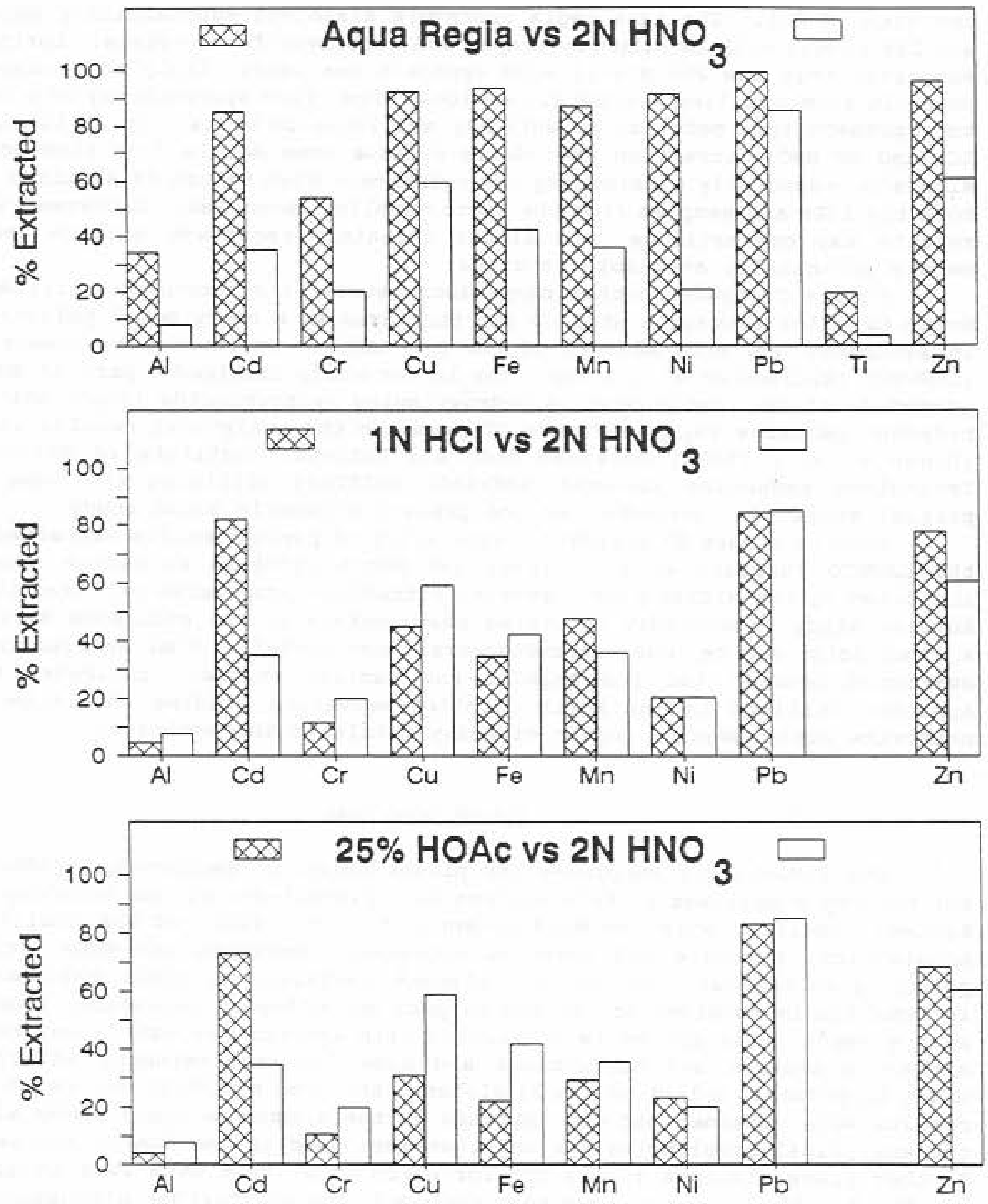


FIGURE C6. Comparison of mean percent of various metals obtained by three partial extraction procedures used by the International Council for Exploration of the Sea (Loring and Rantala, 1988) and those produced by the 2N HNO_3 partial extraction procedure of Riggs et al. (1989) in the Pamlico River estuary. This 2N HNO_3 procedure is the same as that used in the Neuse River (Riggs et al., 1991) and present Albemarle Sound studies.

two with 1N HCl. The aqua regia procedure dissolves substantially more metals and 25% acetic acid is slightly weaker and dissolves fewer metals. Loring (1981) suggested that the 25% acetic acid approach was least likely to release metals bound in aluminosilicate mineral lattices; thus, this approach may be more likely to represent only material potentially available to biota. It is likely the 1N 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 samples from the North Carolina estuaries. Consequently, these results may overestimate, and almost certainly represent maximum amounts of metals potentially available to biota.

Figure C7 shows another comparison between the technique utilized in the North Carolina estuarine studies 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 C7 presents the analytical results for metals (Riggs et al., 1989b) obtained from the National Institute of Standards and Technology estuarine sediment SRM-1646 (NISTES) utilizing the same 2N HNO_3 partial extraction procedure as the present Albemarle Sound study.

Data in Figure C7 indicate a similarity in percent metals extracted between the LAWWTO (Bruland et al., 1974) and North Carolina estuarine studies, as indicated by the NISTES 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 North Carolina estuarine studies 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 Acquisition) hardware and software upgrades. Analyses are made with a five point, simultaneous 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 C3 presents a list of the 21 elements analyzed by ICAPES for which reliable results were obtained and are reported in the Albemarle Sound study along with the analytical wavelengths (in nm) that were used in the ICAPES analyses. The 7 other trace elements (Table C2) for which unreliable data were obtained (Be, Li, Se, Ag, Tl, U, and Y) have been excluded from any further discussion in this report. ICAPES analyses were carried out on the samples for the Albemarle Sound and North Landing River estuarine systems as summarized in Table C4.

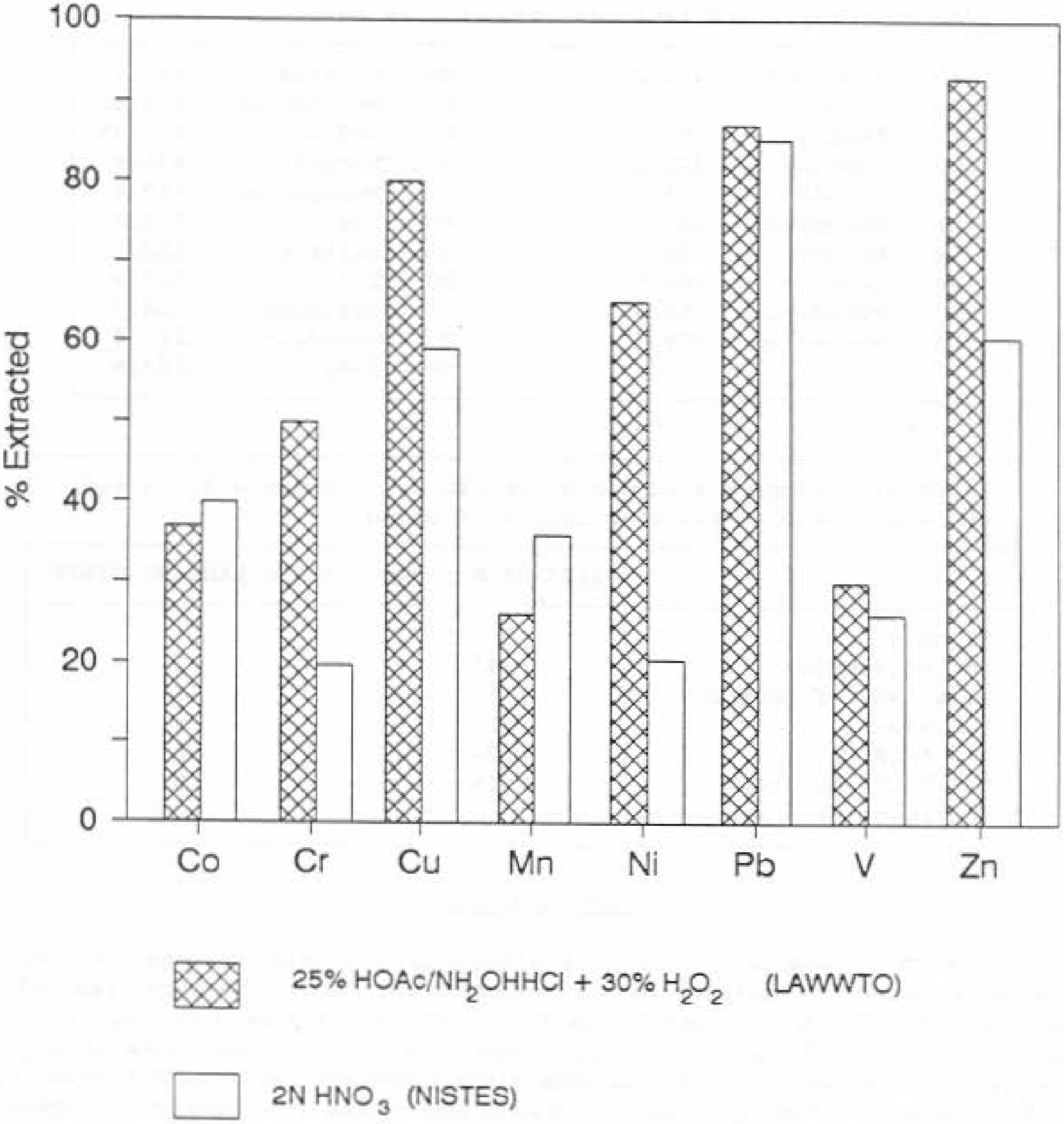


FIGURE C7. Comparison of mean percent of various metals obtained by two partial extraction procedures in metal pollutant studies. The Los Angeles waste water treatment outfall (LAWTO) study utilized a 25% HOAc/NH$_2$OHHCl + 30% H$_2$O$_2$ procedure (Bruland et al., 1974), whereas the National Institute of Standards and technology estuarine sediment (NISTES) was analyzed during the Pamlico River study (Riggs et al., 1989b) utilizing a 2N HNO$_3$ procedure.

TABLE C3. Analytical wavelengths (in nm) for 21 elements analyzed by ICAPES and included in this report.

Al	Aluminum	308.21	Mn	Manganese	257.6
As	Arsenic	193.6	Mo	Molybdenum	202.0
Ca	Calcium	317.9	Na	Sodium	588.99
Cd	Cadmium	228.8	Ni	Nickel	231.6
Co	Cobalt	228.6	P	Phosphorus	213.6
Cr	Chromium	267.7	Pb	Lead	220.3
Cu	Copper	324.7	Si	Silicon	288.1
Fe	Iron	259.9	Sn	Tin	283.9
K	Potassium	766.5	Ti	Titanium	334.9
Mg	Magnesium	279.5	V	Vanadium	292.4
			Zn	Zinc	213.8

TABLE C4. Samples analyzed by ICAPES for Albemarle Sound and the North Landing River in Currituck Sound.

	ALBEMARLE SOUND	NORTH LANDING RIVER
Batches	6	1
No. of Samples	243	56
Total No. of Controls	65	18
Blanks	27	6
APES D	24	6
NIST SRM 1646 (estuarine sediment)	14	6

Control Samples

The APES D internal control is a composite sample of organic-rich muds collected at several locations in the Pamlico River during the first year of this investigation. The APES D sample 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 APES D, was intended to last through the completion of all phases of this project. In order to provide information on more accessible and universal standards, two standard reference materials (SRM) from the National Institute of Standards and Technology (NIST) were utilized. The Pamlico River study utilized sediment standards SRM 1645 (River Sediments) and SRM 1646 (Estuarine Sediments). Throughout the Pamlico study (Riggs et al., 1989b) it became apparent that SRM 1645 (River Sediment) was inappropriate because of its trace element composition. Consequently only SRM 1646 (Estuarine Sediment) was used as a reference control in the Neuse River (Riggs et al., 1991) and the Albemarle Sound and North Landing River estuarine studies (this report).

Limit of Quantitation and Reproducibility

The instrumental lower limit of quantitation (LLQ), or lower limit of detection, is defined for purposes of this study as three times the standard deviation about the process blanks, expressed in the same concentration terms as the samples (viz., μg/g extractable). Process blanks are taken through the complete extraction, filtration and analytical process. 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 three replicate samples of APES D with each analytical batch. Fourteen replicates of SRM 1646 (Estuarine Sediments) were run randomly throughout the entire Albemarle Sound study and at least three blanks were run with each batch. Six replicates each of blanks, APES D, and NIST SRM 1646 were carried through with the single batch of 56 samples for the North Landing River study. Table C5 presents the estimate for the lower limit of quantitation as well as both the mean and two times the standard deviation about the means for APES D controls for the Pamlico, Neuse, Albemarle, and North Landing River studies. Table C6 presents the means of element concentrations extracted from the NIST Standard Reference Material expressed as a percent of the total value reported on the NIST certificate.

Comments on the Quality of Analytical Numbers

Due to the nature of the mild extraction procedure prior to ICAPES analyses, 100% recovery of all elements is highly unlikely. However, Table C6 does demonstrate a general agreement between the percent recoveries for each element within each of the four study areas. Substantial discrepancies between the Pamlico results and all others do exist for As, Cd, and Pb. The As and Pb discrepancies result from additional inter-element interference corrections that were applied to these elements in all post-Pamlico River studies. The discrepancy for Cd is due to the fact that absolute concentrations for Cd in the standard are below the limit of quantitation (.36 = ± 0.07 μg/g). Consequently, any slight variation results in a large relative difference.

It should be noted that there are variable LLQ's for Al, Ca, Fe, Na and Si especially in comparing all other studies to those of the Pamlico River study (Table C5). Very high concentrations of these elements caused the emission signals to go off-scale for nearly every sample during the Pamlico River study; this required a dilution and second analysis with appropriate recalibration for all samples. For all subsequent studies, analytical sensitivities for these five elements were reduced by changing the electrical resistance in the photomultiplier circuit. This resulted in greater analytical efficiency but in higher LLQ's for these elements. Nothing was lost, however, since at no time did the values for any of these elements approach the detection limit. The apparently anomalous values for the North Landing study result from far fewer blank replicates. This often lessens the full range of variability or analytical "noise" about the detection limit and can result in apparently lower LLQ's.

Reproducibility is defined as two times the standard deviation about all of the replicate APES D internal control samples processed through the entire analytical procedure (Table C5). In general, excellent agreement occurs in reproducibility for the control samples, both within runs and between runs, which is indicative of the excellent reproducibility of the extraction procedure. Studies on inter-element interferences for As and Pb resulted in greater

TABLE C5. Quality assurance data for ICAPES and AAS determinations for samples from the Albemarle Sound estuarine and North Landing River studies (this report) as compared to similar data from the Pamlico River (Riggs et al., 1989b) and Neuse River (Riggs et al., 1991) studies.

	LOWER LIMIT OF QUANTITATION LLQ = 3 x s.d. of Blanks (μg/g)				REPRODUCIBILITY ON APES-D CONTROL SAMPLES Mean = ± 2 x s.d. in μg/g			
REGION	<u>Pamlico</u>	<u>Neuse</u>	<u>Albemarle</u>	<u>N.Landing</u>	<u>Pamlico</u>	<u>Neuse</u>	<u>Albemarle</u>	<u>N Landing</u>
N =	27	47	27	6	15	36	24	6
ELEMENT								
Al	9.8	33.0	26.5	3.5	3808 ± 243	3906 ± 235	4163 ± 217	4308 ± 250
As	2.3	1.4	1.8	2.3	8.8 ± 5.2	2.4 ± 3.2	1.7 ± 2.5	0.7 ± 4.8
Ca	19.6	44.3	68.9	11.4	5815 ± 352	6060 ± 240	6142 ± 223	6287 ± 244
Cd	0.5	0.4	0.3	0.4	0.4 ± 0.3	0.4 ± 0.2	0.3 ± 0.1	0.4 ± 0.1
Co	0.2	0.4	0.4	0.3	4.0 ± 0.3	4.2 ± 0.3	4.4 ± 0.2	4.3 ± 0.2
Cr	0.2	0.3	0.4	0.3	6.7 ± 0.4	6.8 ± 0.4	7.2 ± 0.3	7.3 ± 0.4
Cu	0.3	0.3	0.4	0.6	9.2 ± 0.7	8.8 ± 0.6	9.0 ± 0.8	8.5 ± 0.5
Fe	4.7	119.9	124.0	31.1	8927 ± 456	9651 ± 542	10108 ± 491	10737 ± 529
K	45.1	51.3	52.9	104.8	463 ± 178	496 ± 76	558 ± 35	567 ± 58
Mg	35.7	33.3	43.4	21.4	1312 ± 91.3	1309 ± 88	1355 ± 81	1401 ± 102
Mn	0.9	1.1	1.2	0.4	77.0 ± 4.2	79.2 ± 4.4	81.6 ± 3.5	81.3 ± 4.4
Mo	0.3	0.5	0.5	0.1	0.4 ± 0.7	0.4 ± 0.1	0.4 ± 0.1	0.6 ± 0.1
Na	9.8	16.6	11.2	3.6	1985 ± 126	1955 ± 120	2110 ± 118	2102 ± 90
Ni	1.1	1.0	0.6	0.1	0.9 ± 0.7	1.8 ± 0.4	2.2 ± 0.4	1.9 ± 0.2
P	18.0	21.4	10.9	10.8	598 ± 110	514 ± 30	538 ± 28	554 ± 25
Pb	1.6	0.9	0.7	0.8	28.1 ± 4.0	22.9 ± 1.6	23.2 ± 1.8	23.3 ± 5.3
Si	26.2	40.2	11.0	20.5	1109 ± 60.5	1053 ± 91	1144 ± 52	2030 ± 92
Sn	*	3.7	2.2	0.5	*	9.1 ± 3.6	7.1 ± 3.2	0 ± 0.5
Ti	0.4	0.6	0.5	0.2	30.0 ± 1.7	29.5 ± 1.3	30.2 ± 1.3	29.0 ± 1.2
V	0.2	0.3	0.3	0.2	15.3 ± 1.0	15.0 ± 0.8	15.5 ± 0.8	15.2 ± 0.6
Zn	1.2	1.8	5.3	9.6	54.3 ± 3.2	53.3 ± 3.9	53.5 ± 5.9	52.8 ± 6.4
Hg					0.12 ± 0.03′ n = 26	0.11 ± 0.04 n = 36	0.14 ± 0.02′ n = 20	*

* = Elements were not analyzed
′ = Elements analyzed by the Modified Autoclave Procedure described in Riggs et al., 1991.

TABLE C6. Percent recovery of NIST SRM 1646 Estuarine Standard data for ICAPES and AAS determinations for samples from the Albemarle Sound estuarine and North Landing River studies (this report) as compared to similar data from the Pamlico River (Riggs et al., 1989b) and Neuse River (Riggs et al., 1991) studies.

	RECOVERY OF NIST SRM 1646 ESTUARINE SEDIMENT STANDARD Mean Recovery = % Certified Value (in percent)			
REGION	PAMLICO RIVER	NEUSE RIVER	ALBEMARLE SOUND	N. LANDING RIVER
N =	6	14	14	6
ELEMENT				
Al	8	8	8	9
As	120	72	66	54
Ca	38	39	39	40
Cd	28	83	86	93
Co	40	45	46	48
Cr	20	20	21	22
Cu	59	60	60	58
Fe	42	45	47	50
K	14	15	16	16
Mg	47	46	48	51
Mn	36	37	38	38
Mo	40	45	39	55
Na	48	49	50	52
Ni	21	29	32	33
P	65	59	60	63
Pb	86	65	64	63
Si	0.4	0.4	0.4	0.8
Sn	*	NR	NR	NR
Ti	4	4	4	4
V	27	27	27	27
Zn	61	62	61	63
Hg	116′ (n=3)	108′ (n=5)	107′ (n=14)	*
	83″ (n=4)		84″ (n=14)	*

* = Elements were not analyzed
NR = Elements were not reported
′ = NIST Estuarine Sediment Standard by Modified Autoclave Procedure
″ = NIST River Sediment Standard by Modified Autoclave Procedure

correction factors being applied to all post-Pamlico River study samples. This caused not only the discrepancies in percent recovery of these two elements between the studies, but also caused the LLQ's and reproducibilities on As and Pb to be different as well.

AAS Mercury Analyses

Atomic absorption spectrometry (AAS) was utilized for the mercury analyses. The analytical technique is EPA's Method 245.5 outlined in "Methods for the Chemical Analysis of Water and Wastes" Procedural Manual (USEPA, 1979) with slight modifications. This is a manual cold vapor technique for mercury in sediments and includes the alternate autoclave digestion procedure. The modifications involved 1) use of a commercially available cold vapor generator (IL model AVA 440), 2) use of one gram samples due to the low concentrations of Hg expected, and 3) an increase in the volume of the $KMnO_4$ reagent to 25 ml deemed necessary due to the increase in sample size. These differences in procedure as compared with the procedure originally applied to the Pamlico River samples (Riggs et al., 1989b) was not only more efficient but provided much better quality data for all post-Pamlico River samples.

With an appropriate autoclave, up to 100 samples could be digested simultaneously to permit processing a large number of samples. The reproducibility obtained on 20 replicates of the APES D internal control sample, which is comparatively low in Hg concentration, is .14 ± 0.02 $\mu g/g$ (Table C5). The mean recovery on 14 replicates of the NIST SRM 1646 (Estuarine Sediment) is 107% (Table C6). Because the estuarine sediment standard has even lower concentrations of Hg than the internal control, five replicate determinations were also run on the NIST SRM 1645 (River Sediment) sample. The mean and 2 x s.d. for those determinations were 1.38 ± 0.30 $\mu g/g$ for a mean recovery of 96%.

Additional quality control-quality assurance measurements were made along with a complete redetermination of all Pamlico River samples (Riggs et al., 1989b) by the method outlined above for the Neuse River and Albemarle samples. An addendum to the Pamlico River report detailing this work (Riggs et al., 1989b) will be published providing better analyses of the Hg concentrations. Mercury analyses were not performed on any of the North Landing River samples.

Electrochemical Fluorine Analyses

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 and for buffering purposes; consequently, the lower limit of quantitation is at about 30 $\mu g/g$ extractable. In all post-Pamlico studies, only surface sediment samples were subjected to fluoride analysis with no samples exhibiting extractable fluorine concentrations above this limit. Therefore, no deep samples were analyzed for fluorine.

DATA ANALYSES

Data Management and Statistical Analyses

All field, sedimentological and chemical data are permanently stored in two formats: 1) in data base spreadsheets using SYMPHONY software that are compatible with IBM PC type computers and 2) in Statistical Analysis System software (SAS) data sets on the East Carolina University 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. Formatting is flexible so that selected portions of the total data base can be separated and printed. All of the analytical data for the Pamlico, Neuse, and Albemarle estuarine systems are also on file in the Albemarle/Pamlico Estuarine Study data base established in the Center for Geographic Information Analysis, Office of State Planning, 115 Hillsborough St., Raleigh, NC 27607.

Data transcriptions were routinely triple checked. The chemical data were first checked by J.T. Bray and J.C. Hamilton in the laboratory generating the data. The second check was by D.V. Ames and K.L. Owens who had the primary responsibility for data transcription and manipulation. The final check was by S.R. Riggs who had the primary responsibility for data interpretation. The sedimentological data were first checked by R.A. Wyrick and C.R. Klingman in the laboratory generating the data. The second check was by D.V. Ames who had the primary responsibility for data transcription. The final check was by S.R. Riggs who had the primary responsibility for sediment interpretation.

All field, sedimentological and chemical data were compiled and merged using a combination of SAS programs and SYMPHONY worksheets and data bases. The data matrix consists of sample identifiers listed against all parameters measured on each sample. Each sample number had a location with respect to latitude and longitude, LORAN-C coordinates, and name of water body (Table C1 and Appendix A). Additional information assigned to each sample number includes depth below sediment/water interface, water depth, concentrations of major, minor and trace elements in μg/g extractable, % organic content, and concentrations of sediment size components (% sand, % silt, and % clay).

Data manipulations were accomplished on the IBM 4381 mainframe computer using SAS software. Simple statistics (mean, standard deviation, maximum and minimum values, etc.) were calculated for the following categories:

1. All samples,
2. Surface versus subsurface samples,
3. Specific sediment types,
4. Groups of samples within specific tributaries and river segments, and
5. Specific types of point and non-point source areas (i.e., urban regions, marinas, waste water treatment facilities, agricultural regions, etc.).

These analyses provide for stratigraphic, sedimentologic, and regional comparisons of both sediment characteristics and elemental concentrations. Results of these analyses are presented and discussed in subsequent sections.

Rationale and Definitions for Data Analyses

Trimmed Means and Enrichment Factors

Fifteen trace elements were utilized in this study (Table C7) and include the 8 U.S. EPA "priority pollutant metals" plus seven other environmentally important trace elements. An estimate of background levels was determined for each of the 15 trace elements within the Albemarle sediments. This estimate was derived by the following procedure and results in values hereafter referred to as the Albemarle trimmed mean (ATM) (Table C7).

1. Mean concentrations and standard deviations were computed for each trace element in all surface samples within the Albemarle Sound estuarine system.
2. Those samples with values greater than two standard deviations from this original mean were then excluded. These 'outliers' were assumed to represent either anthropogenically contaminated sediments or depleted relict sediments and should not be incorporated into any process intended to derive a general background value.
3. Mean values were then calculated for these trimmed data sets resulting in the ATM for each element (Table C7).
4. The ATM for each element serves as a reference point against which every sample, including the surface outliers excluded from the trimmed data set and samples from depth, were compared.
5. This comparison represents the enrichment factor (EF) for each element in each sample (EF is the ratio of actual concentration for the sample to the ATM). This provides a measure of either excess or depletion compared to an approximate 'background' level. It also provides a convenient and uniform method to graphically depict spatial distributions of concentrations of the elements.
6. The following definitions with respect to enrichment factors (EF) will be utilized in the remainder of this report:
    - a. EF = 1 is equal to the ATM,
    - b. EF < 1 is depleted relative to the ATM,
    - c. EF > 1 is enriched relative to the ATM,
    - d. EF between 1.5 X and 1.99 X is "slightly enriched" relative to the ATM,
    - e. EF = 2 X or greater is "substantially enriched" relative to the ATM.

The term enrichment factor is often used differently in the geochemical literature. For example, Zoller et al. (1974), Bruland et al. (1974), and Schropp et al. (1990) develop enrichment factors by calculating the ratio of 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 and Brown (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

TABLE C7. Albemarle trimmed mean (ATM) data for all surface samples that are less than 2 standard deviations from the mean total population. The standard deviation, coefficient of variation, and the minimum and maximum concentration values used in this calculation for 22 elements (in μg/g or ppm) in surface sediments of the Albemarle Sound estuarine system, are also included.

		ALBEMARLE TRIMMED DATA				
ELEMENT	N	TRIMMED MEAN μg/g	COEFFICIENT OF VARIATION %	STANDARD DEVIATION μg/g	MINIMUM VALUE μg/g	MAXIMUM VALUE μg/g
TRACE ELEMENTS						
As *	184	3.95	73.7	2.77	0.75	10.4
Cd	184	0.22	69.7	0.16	0.15	0.72
Cr	175	10.7	38.0	4.04	2.30	21.8
Co	175	6.67	44.9	3.00	1.78	13.2
Cu	175	10.8	53.7	5.80	2.03	33.3
Hg	149	0.14	88.1	0.12	0.02	0.63
Ni	175	4.28	36.1	1.54	0.67	7.31
Pb	175	21.7	62.0	13.5	3.62	69.3
Mn	175	329.	100.7	331.	30.4	1227.
Mo	183	0.29	31.8	0.09	0.25	0.60
P	175	401.	52.1	209.	92.1	1109.
Sn *	182	5.64	73.7	4.16	0.20	13.2
Ti	175	75.2	42.3	31.8	19.9	148.
V	175	23.4	47.5	11.1	4.39	47.7
Zn	175	50.4	48.5	24.4	10.9	114.
MAJOR ELEMENTS						
Al	175	5088.	34.7	1766.	1373.	8804.
Ca	175	2340.	43.9	1027.	775.	5103.
Fe	175	13340.	33.5	4466.	2699.	21256.
K	175	555.	38.1	211.	129.	952.
Mg	175	1713.	39.7	680.	361.	3029.
Na	175	609.	69.2	421.	51.	1633.
Si	175	1533.	29.7	456.	694.	2592.

* Analyses have poor reproducibility, hence somewhat less reliability.

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.

Application of general normalization or correction factors based upon metal/iron and metal/aluminum ratios, similar to Zoller et al. (1974), Bruland et al. (1974), and Schropp et al. (1990) is not appropriate for this study. In these cited studies, enrichment factors were calculated with concentrations obtained by total digestion techniques. However, the present study utilized a partial extraction procedure and it is not known how consistent the percent extraction for each metal is for different sediment types. In addition, the sedimentological data suggest the following:

1. Different parts of Albemarle Sound 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, the criteria used within this study suggest that if a specific trace element has relatively high concentrations within the natural system and is released by the partial digestion procedure used in this study, it is equally 'bioavailable' and represents the same potential problem as its anthropogenic counterpart.

The uncertainty surrounding the EF values for the 15 trace elements was explored by techniques comparable to those used to examine the propagation of errors (Daniels et al., 1962; Caulcutt and Boddy, 1983; Miller and Miller, 1984). For this discussion, several definitions, assumptions, and clarifications are in order.

The term 'uncertainty' is used to clearly distinguish this entity from rigorous statistical terms such as variance, standard deviation, and confidence interval. Similarly, the ATM, though arrived at in a semi-statistical fashion, is not used as a statistical parameter; it is merely a reference point against which to compare all other sediment concentrations. A median value of all the data or of the trimmed set of data could just as easily have been selected. Since a) the sampling scheme was setup to encounter areas likely to be anthropogenically altered and b) the trimmed data set still included some of these elevated values, the ATM reference value is probably relatively 'high' in comparison to values derived by a totally random sampling pattern and a weighted mean based on volume of sediment type. Therefore, the EF's utilized in this report are very conservative estimates of enrichment over 'background' conditions.

In this report, the Albemarle and North Landing surface sediment data were combined in the determinations and discussion of enrichment factors. For this reason the APES D reproducibility data, from Table C5, for the Albemarle and North Landing studies were also combined for each of the 15 trace elements receiving further discussion here. This was necessary to arrive at an overall reproducibility estimate for the combined studies.

The uncertainty about the measured sample concentrations is defined as two times the standard deviation about the mean of all replicate APES-D internal controls run throughout the various analytical batches. This value is a conservative estimate in that most often in the analysis of propagation of errors, simple single standard deviation is used. Since the ATM is not a true statistical parameter, the uncertainty about this value was taken to be the same value as the measurement uncertainty. This is likewise a very conservative estimate. Because of the way it is used in the calculations, it could be considered a constant, in which case there would actually be no uncertainty ascribed to it. Using δ as the symbol for uncertainty and treating this quantity the same as a true standard deviation of replicate measurements in determining the propagation of random errors, the equations used to calculate the percent uncertainty in EF, are as follows.

1. $EF = C/ATM$
2. $\%\delta(EF) = \delta(EF)/EF \times 100 = \{[\delta(C)/C]^2 + [\delta(ATM)/ATM]^2\}^{1/2} \times 100$

Where: EF = enrichment factor
C = extractable concentration in the sample
ATM = Albemarle trimmed mean
δ = uncertainty

The level of uncertainty is dependent on the actual EF value. For example, the uncertainty is 5.0% when the EF of Cr = 1 (Cr concentration = ATM = 10.7 μg/g). However, the uncertainty is only 3.9% for the maximum enrichment factor (MEF) of Cr = 21.8 (Cr concentration = 233 μg/g). Of course, as the measured concentration decreases, uncertainty increases so that for the very low values, those approaching the lower limit of quantitation, uncertainties over 100% are common. However, EF values below 1 are not so critical since the main objective is to identify anthropogenic sources (i.e., concentrations elevated over background). The enrichment factor uncertainties when EF = 1 and for the maximum enrichment factor (MEF) for the 15 trace elements are presented in Table C8. Note that the uncertainties for As, Cd, Mo, P, and Sn are relatively high, reflecting the poor reproducibility of these concentration measurements in the Albemarle samples.

TABLE C8. Level of uncertainty for enrichment factors equal to 1 (or the ATM) as compared to the maximum enrichment factor (MEF) for each of the 15 trace elements utilized in the Albemarle and North Landing estuarine sediment studies.

TRACE ELEMENT	REPRODUCIBILITY ESTIMATE (TABLE C5) N = 30 μg/g	PERCENT UNCERTAINTY	
		EF = 1	MEF
As	3.1	113.	85.6
Cd	0.1	65.2	48.2
Co	0.2	4.3	3.4
Cr	0.4	5.0	3.9
Cu	0.8	11.2	8.3
Hg	0.1	1.4	1.0
Mn	3.6	1.5	1.1
Mo	0.2	102.	79.8
Ni	0.4	13.3	10.9
P	181.	63.7	47.9
Pb	2.1	14.0	10.4
Sn	6.9	173.	133.
Ti	1.5	2.9	2.3
V	0.8	4.8	3.8
Zn	5.9	16.5	12.8

Areas of Concern

With respect to estuarine sediment quality, there are two types of areas of concern (AOC). The following definitions will be used to characterize the level of sediment contamination within the Albemarle estuarine system. Portions of the Albemarle estuarine system that contain multiple sample sites with trace elements that have enrichment factors between 1.5 X and 1.99 X the Albemarle trimmed mean (ATM), are considered to be "slightly enriched". Considering the conservative nature of the above definitions and calculations, it is appropriate that an EF of 2 X the ATM be achieved or surpassed in multiple sample sites in order to be defined as "substantially enriched" and a contaminated area of concern (CAOC). Also, we believe that it is equally as important to recognize those estuarine areas that are still relatively pristine as it is to define those areas in which the sediments are contaminated in response to long-term, cumulative impacts of man's waste discharges. These pristine or 'noncontaminated' areas of concern (NAOC) are just beginning to feel major development pressures and have high potentials for becoming contaminated if proper management procedures are not implemented.

1. Contaminated Areas of Concern (CAOC) are those portions of the estuarine system that contain substantially elevated levels of trace element contaminants associated with known anthropogenic point or nonpoint sources. CAOCs are those areas containing multiple sample sites with one or more trace element that are substantially enriched (EFs that are = or > 2 X the ATM).
   a. Major Contaminated Areas of Concern: CAOCs with major levels of sediment contamination (multiple sample sites that are substantially enriched in 3 or more trace elements. EFs that are = to or > 2 X the ATM).
   b. Minor Contaminated Areas of Concern: CAOCs with minor levels of sediment contamination (multiple sample sites that are substantially enriched in less than 3 trace elements. EFs that are = to or > 2 X ATM).
2. Noncontaminated Areas of Concern (NAOC) are those portions of the estuarine system that are relatively free of trace element loading within the sediments. NAOCs are those areas in which mean concentrations for all trace elements are near or below the ATM. NAOCs may have an occasional sample with anomalous concentrations of one or more trace elements; however, such anomalies could be due to laboratory or analytical error or due to minor spurious character of an individual sample (i.e., presence of a nail, fishing weight, or trash within or adjacent to the sample).

Thus, based upon the chemical quality of bottom sediments in the Albemarle estuarine system, the present study has identified 18 CAOCs and 4 NAOCs (Table A2 and Fig. A1). Ten of the 18 CAOCs have major levels of sediment contamination that are listed in Table A2 and located with large circles in Figure A1. Eight CAOCs have minor levels of sediment contamination that are listed in Table A2 and located with small circles in Figure A1. The 4 identified NAOCs are free of substantial levels of enrichment of all trace elements, listed in Table A2, and located with small squares in Figure A1.

PART D: RESULTS

ALBEMARLE SOUND ESTUARINE SEDIMENTS

PART D: RESULTS

ALBEMARLE SOUND ESTUARINE SEDIMENTS

Two important factors dictate the level of heavy metal contamination in the North Carolina estuarine sediments. First, there must be a source for trace metals and second, there must be fine-grained sediments that are chemically able to sequester the metals from the water and concentrate them within the sediment system. The source factor was discussed in an earlier section of the report. In the present section, we will first consider the morphology of the estuarine system and then the sediments filling this depositional basin.

The distribution, concentration, and composition of inorganic clay minerals and organic components are extremely variable throughout the Albemarle Sound estuarine system. However, there are some patterns that probably have significant effects upon determining a) which trace elements are concentrated in the sediment, b) their specific levels of enrichment and chemical state, and c) their potential availability to the biological system. These factors are poorly understood at present and are a major part of ongoing research efforts.

Morphology of the Estuarine System

The Albemarle estuarine system can be subdivided into a group of geographic components that to a large extent determine the physical, chemical, and biological processes operating within the system. First, the estuarine system can be divided into the trunk and tributary estuaries (Fig. D1). The trunk estuary is the flooded portion of the main channel of the Roanoke River; it is a major river that drains off the Appalachian Blue Ridge and a significant portion of the Virginia and North Carolina Piedmont with their red clayey soils before entering the North Carolina Coastal Plain. The tributary estuaries are smaller, black water Coastal Plain streams that have also been flooded by a rising sea level and flow into the flooded trunk estuary.

Second, the Albemarle trunk estuary can be subdivided along its length into the following depositional environments depicted in Figure D1. The riverine zone is that portion of any river (i.e., the Roanoke and Upper Chowan Rivers) with a narrow water body characterized by river flow conditions, bounded by fresh water swamp forest floodplains, and dominated by fresh water. This zone occurs both on the western end of the estuarine system and in the upper-reaches of tributary estuaries. The transitional zone is slightly wider and represents that portion of the Roanoke River or tributary estuaries that are dominated by rapidly eroding swampforest shorelines as the broad floodplains are being permanently drowned. The transitional zone is characterized by fresh water and fluctuating water flow in response to river flooding and coastal wind tides. The inner estuarine zone has an intermediate width, but is still somewhat protected from the higher wave energies that characterize the Middle and Outer Albemarle Sound due to the geographic shape of Albemarle Sound (Fig. D1). Shorelines in this zone are dominated by high to low sediment banks that are being actively eroded by wave energy. The water is fresh and variations in water level are primarily a function of wind tides. The middle and outer estuarine zones are the very wide, east-trending portion of Albemarle Sound. Albemarle Sound is connected to the Atlantic Ocean through Oregon Inlet, Pamlico Sound, and the narrow Roanoke and Croatan Sounds on its southeastern end (Fig. D1). This very high wave energy portion of Albemarle Sound is dominated by very rapidly eroding low sediment bank shorelines, low brackish water conditions, and irregular wind tides.

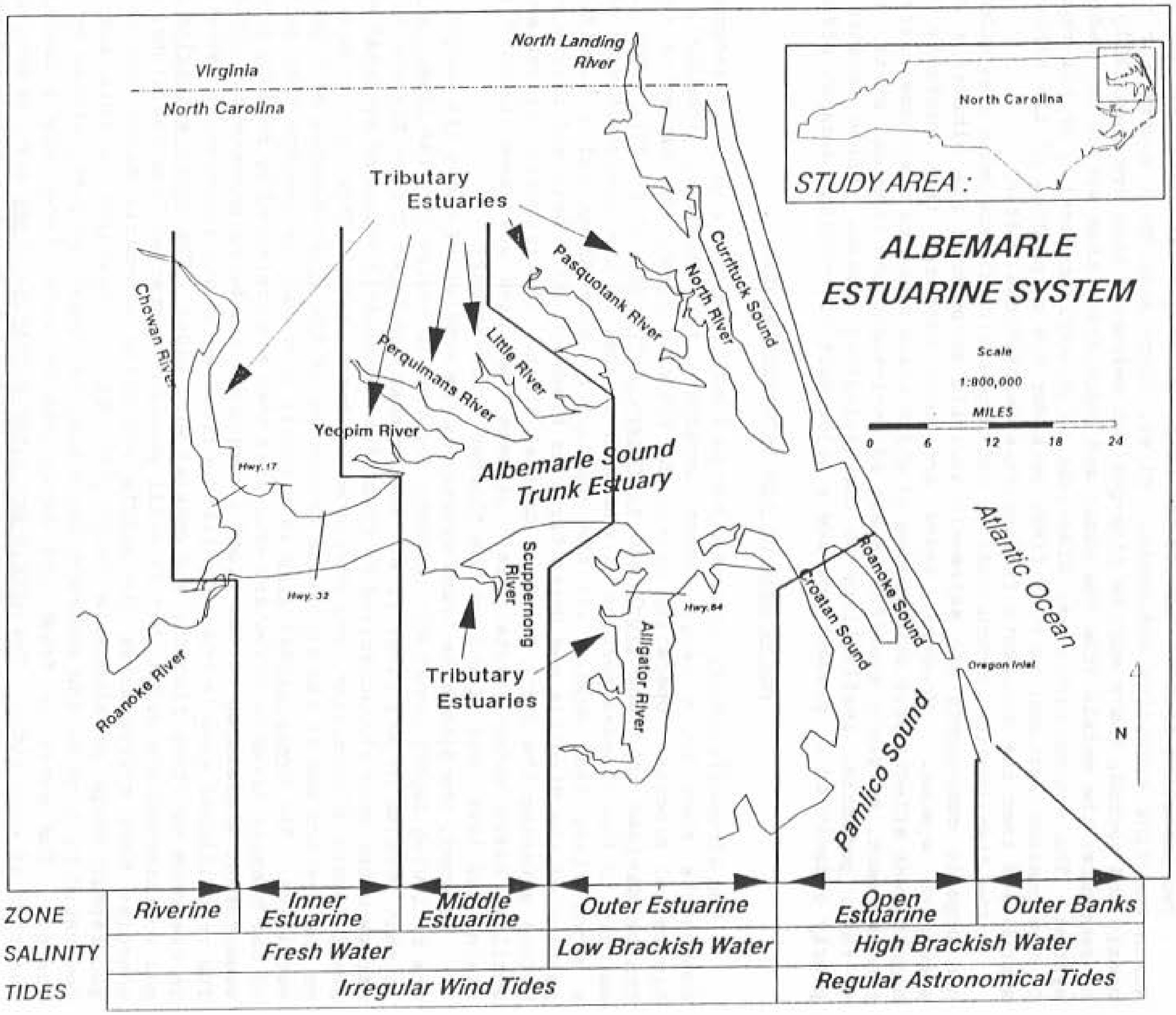


FIGURE D1. Depositional environments and operating processes within the Albemarle Sound estuarine system.

Six bathymetric profiles were produced across various portions of the estuarine system (Fig. C4). A suite of surface samples collected along each profile correlates distribution of sediment type to estuarine morphology. Figures D2 through D7 present the bathymetric profiles and associated sediment compositions. The cross-sectional morphology of the Roanoke River (Fig. D2), along a straight portion of the River, has a major mid-river channel dominated by sands. The channel flanks, occurring in less than 10 foot water depths, are dominated by mud.

The cross-sectional morphology throughout Albemarle Sound is like a shallow dish (Figs. D3 through D7). The shoreline perimeter has a narrow, shallow platform that slopes gradually down to depths of 4 to 6 feet and then slopes more abruptly to the broad, flat floor of the basin which occurs between 15 and 20 feet below MSL. The entire trunk estuary has this same basic cross-sectional morphology except that the flat basin floor gradually deepens from about 15 to 18 feet below MSL in the inner estuary to about 18 to 20 feet in the outer estuary. The easternmost portion of the Sound shallows to 15 to 17 feet as demonstrated in profile E-E' (Fig. D6). The bottom in this area is dominated everywhere by fine sand and large sand waves and continues to shallow eastward towards the sand flats around Kitty Hawk Bay and Colington Island. These sands are obviously filling Albemarle Sound from the east and result from flood-tide delta processes of ancient inlets and eolian processes associated with the Outer Banks.

Sediment Composition and Distribution Patterns

The composition and distribution patterns of sediment types within the Albemarle Sound estuarine system are directly related to basin morphology and associated estuarine processes. Sediments presently being deposited within the estuarine system are generally derived from four sources.

1. The dominant sediment component is inorganic clay that comes from the suspended sediment load in the Roanoke River during periods of high water flow.
2. Organic matter is an important secondary component (up to 20%) in some of the extensive mud deposits; it is derived from storm flushing of the swampforests and erosion of marsh and swamp forest shorelines that occur throughout the estuarine system.
3. Most of the sand and some of the clay comes from erosion of Pliocene and Quaternary sediment units that form all sediment bank shorelines and underlie the shallow platform flanks throughout the estuarine area.
4. The outermost portion of Albemarle Sound contains fine sands that are derived from the barrier islands by wind and storm overwash or have been transported into the estuary through former inlets in the barrier islands.

Surface distribution of the sand, silt, and clay within the Albemarle Sound estuarine system are displayed along the bathymetric profiles in Figures D2 through D7. Notice that within the estuarine area, the shoreline platforms are dominated by sand with little silt and clay present. As the profile drops into the central basin, the sand content decreases as silt, clay, and organic contents increase. The gradual decrease in sand content from both shorelines to a minimum within the estuarine center demonstrates that most of this sand is being derived

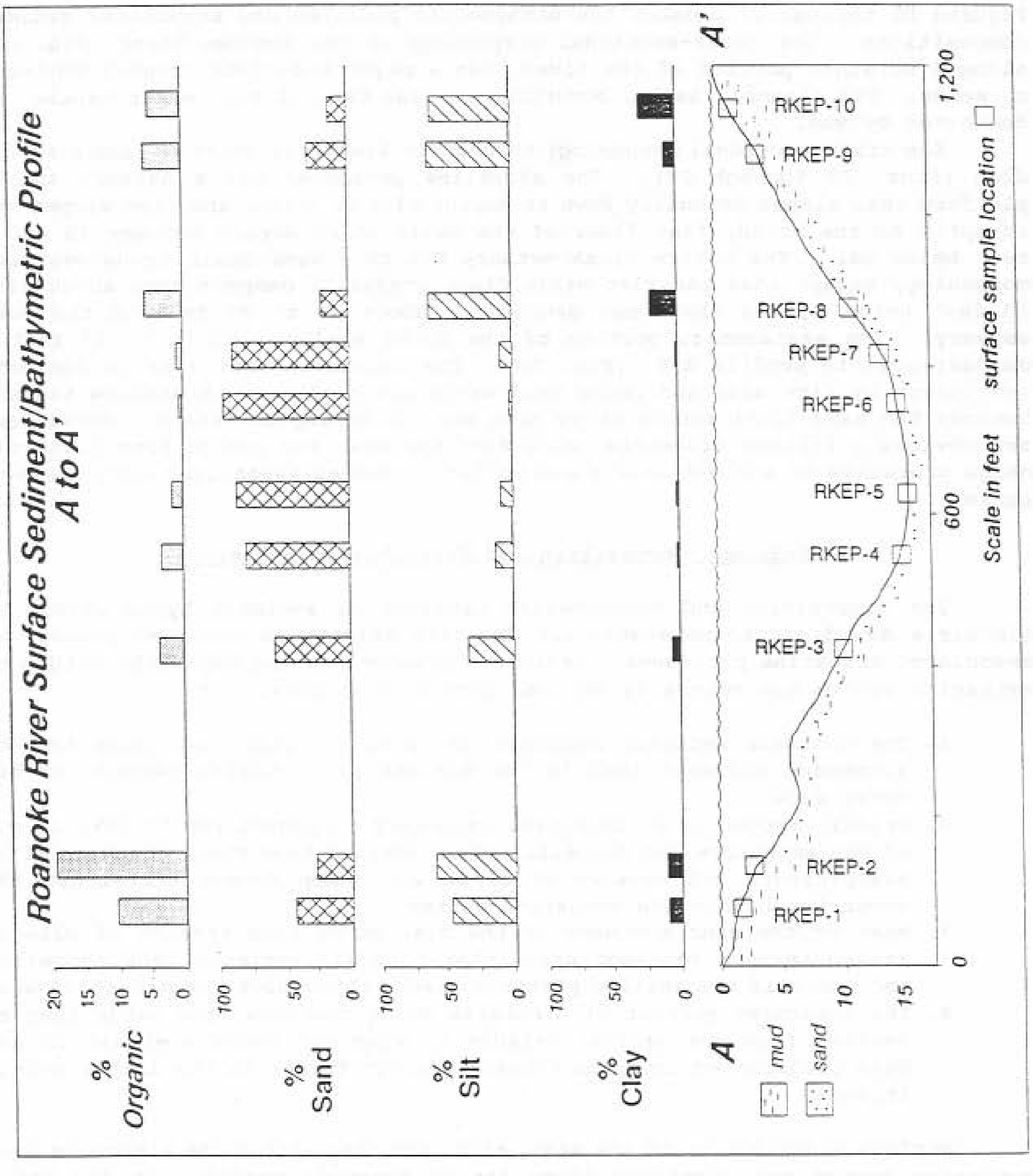


FIGURE D2. Bathymetric profile A-A' across the Lower Roanoke River showing the distribution of four major sediment components and demonstrating their relationship to bottom morphology. Location of profile A-A' is on Figure C5.

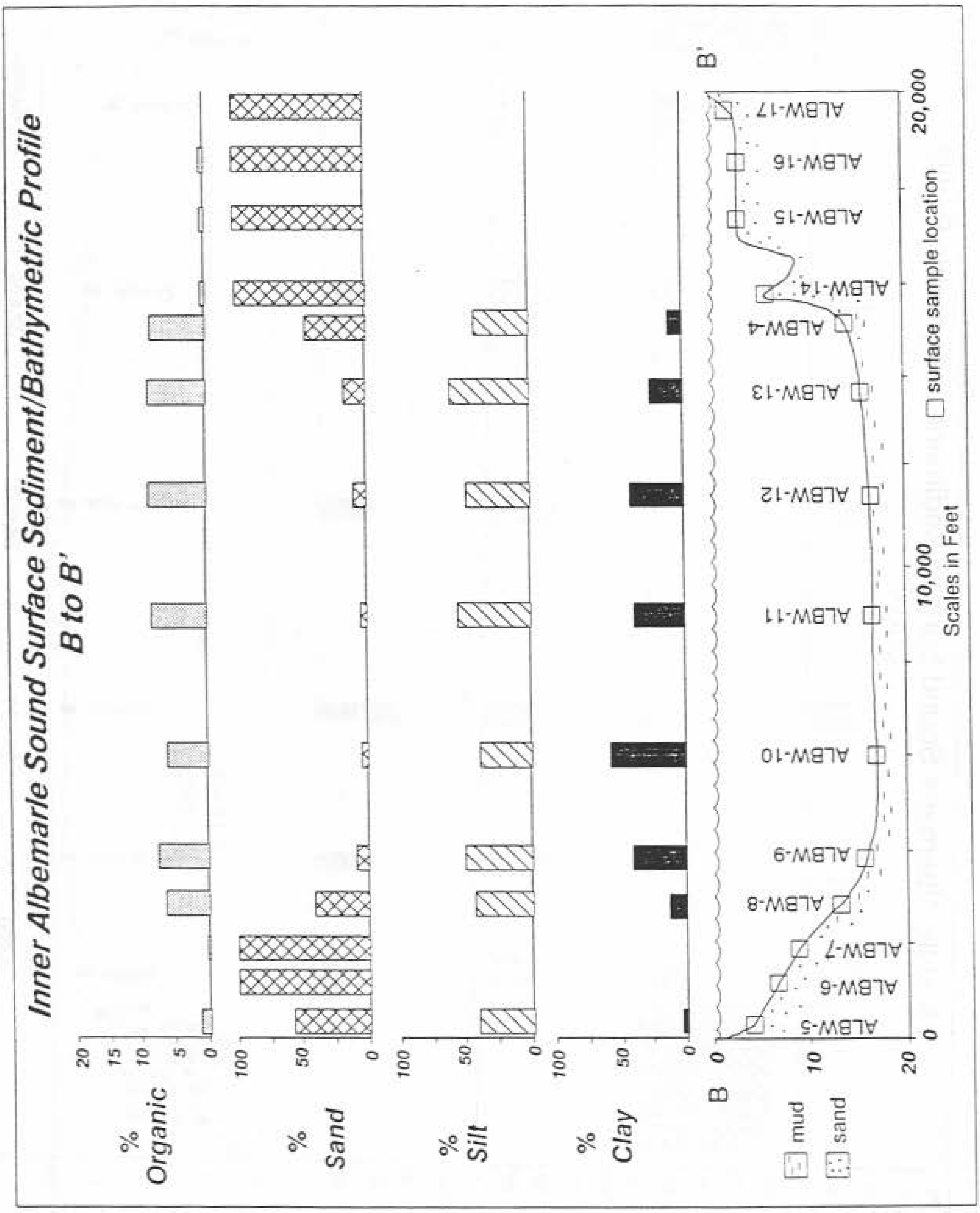


FIGURE D3. Bathymetric profile B-B' across Inner Albemarle Sound adjacent to the Highway 37 bridge showing the distribution of four major sediment components and demonstrating their relationship to bottom morphology. Location of profile B-B' is on Figure C5.

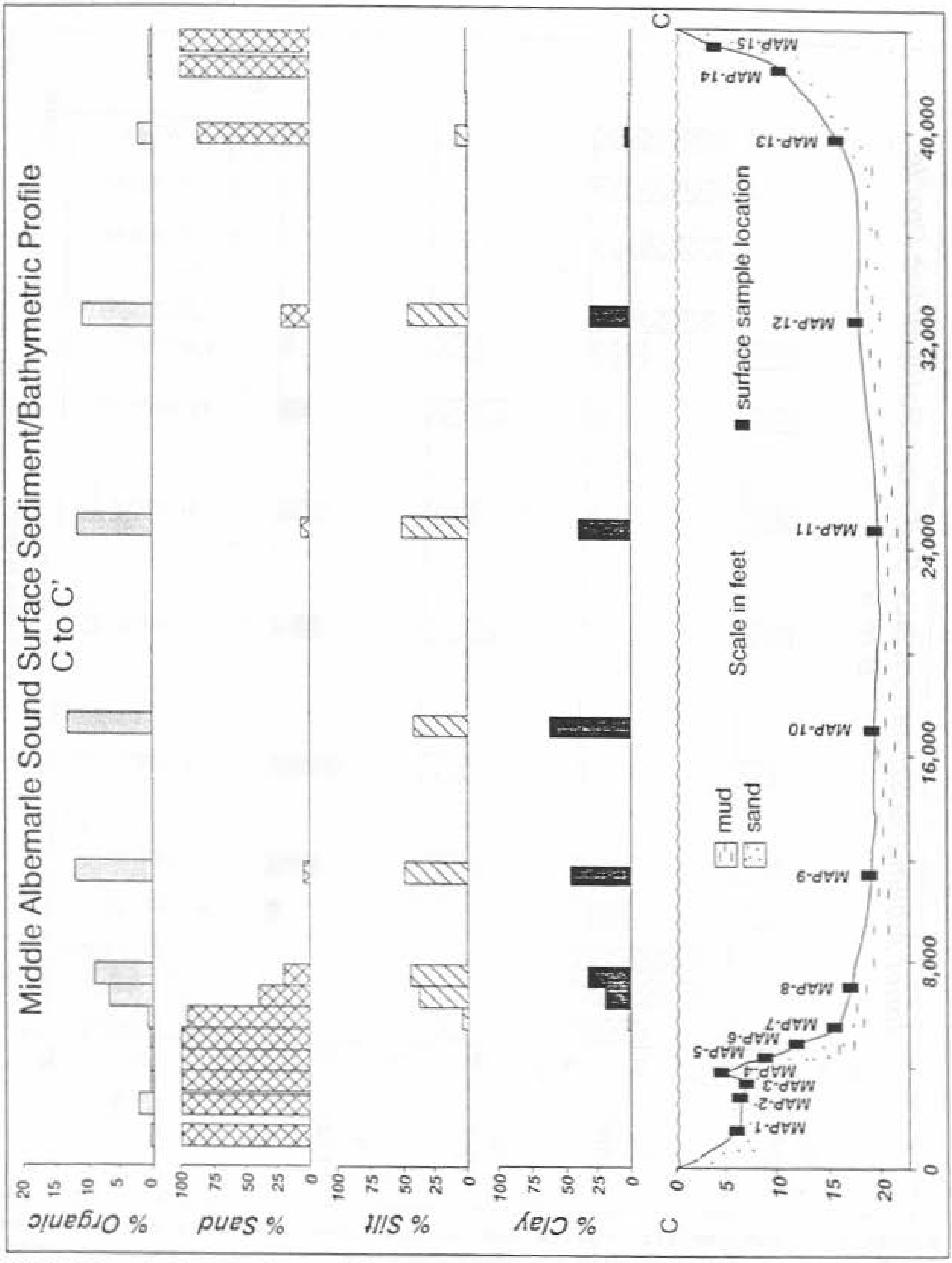


FIGURE D4. Bathymetric profile C-C' across Middle Albemarle Sound showing the distribution of four major sediment components and demonstrating their relationship to bottom morphology. Location of profile C-C' is on Figure C5.

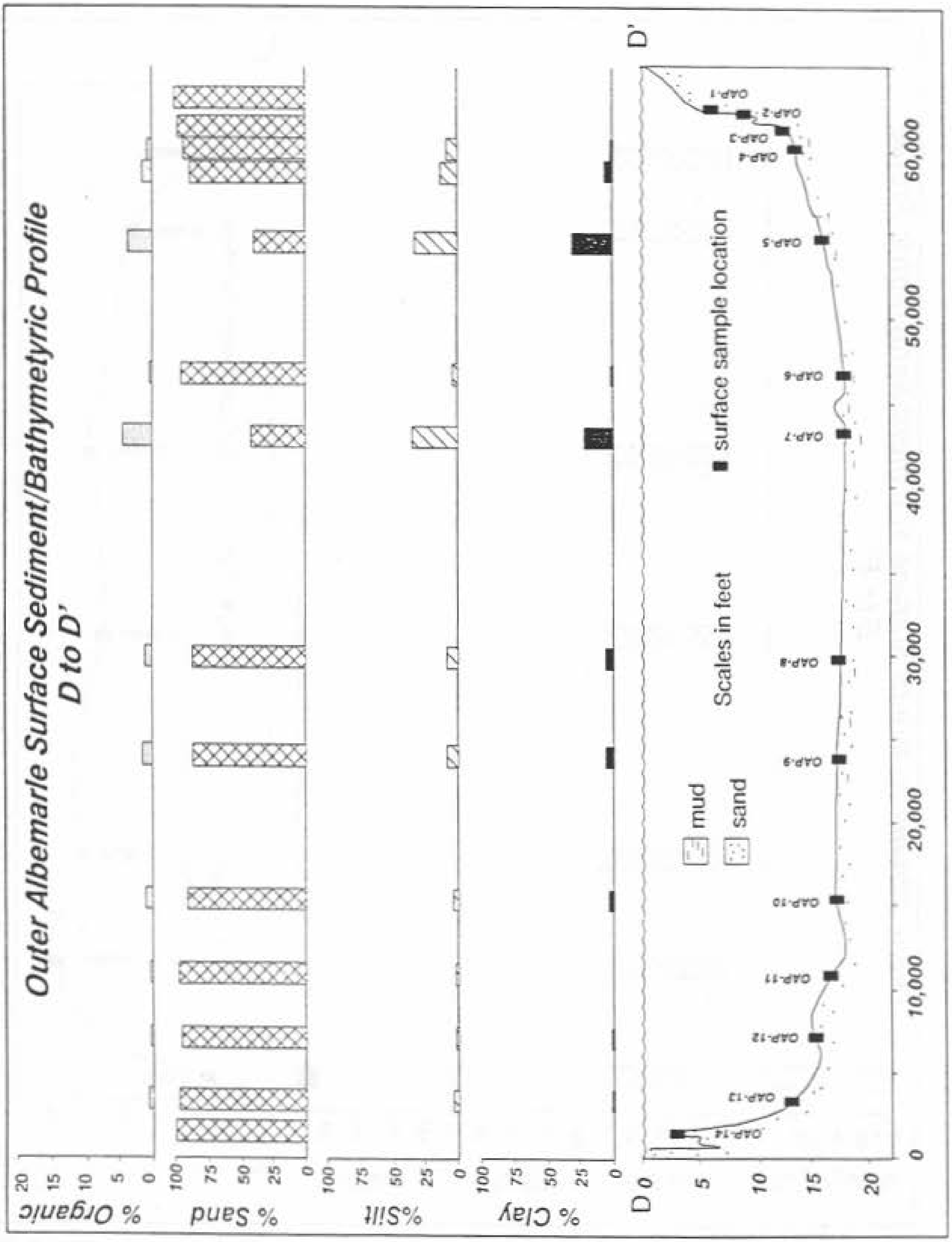


FIGURE D5. Bathymetric profile D-D' across Outer Albemarle Sound showing the distribution of four major sediment components and demonstrating their relationship to bottom morphology. Location of profile D-D' is on Figure C5.

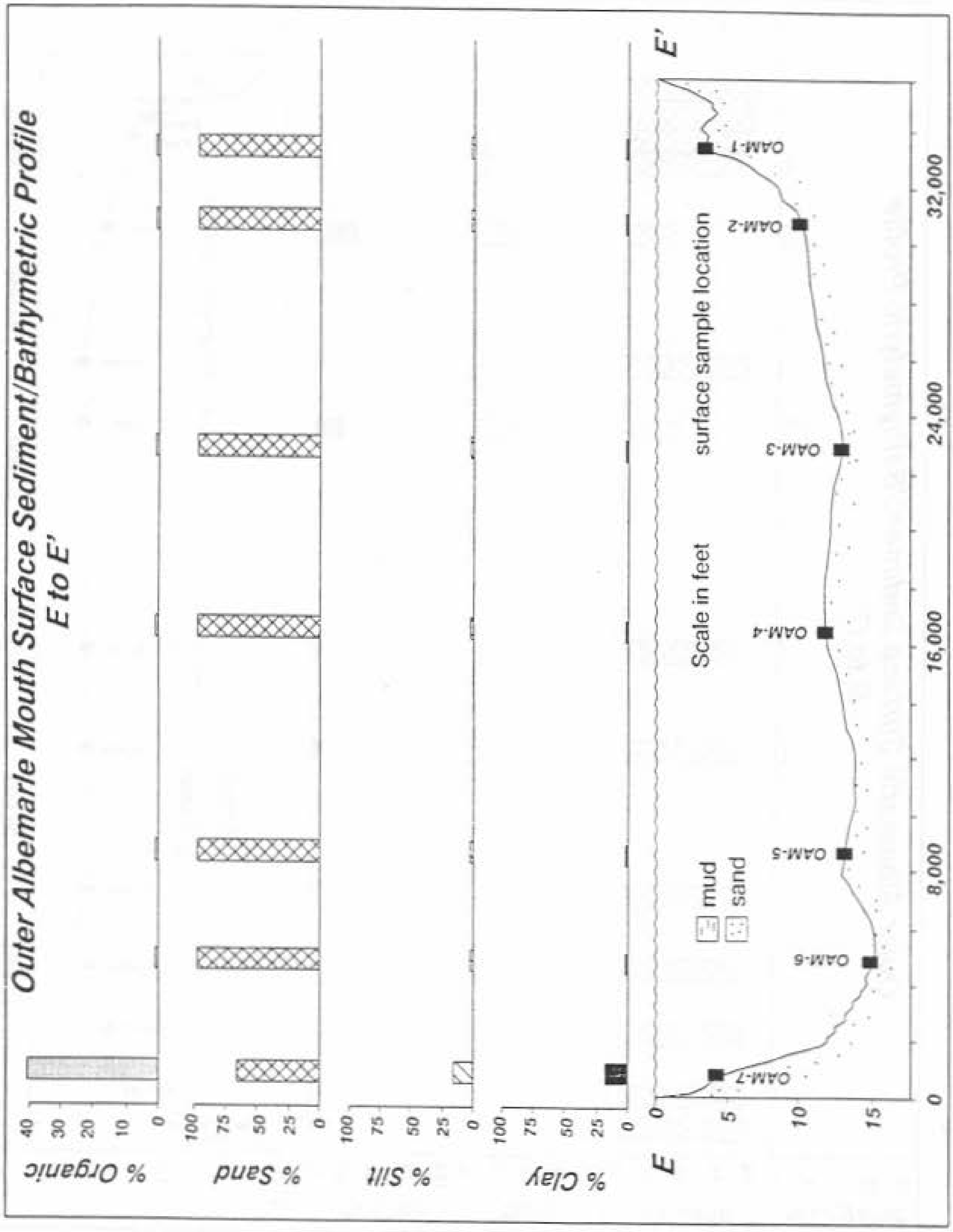


FIGURE D6. Bathymetric profile E-E' across the mouth of Outer Albemarle Sound showing the distribution of four major sediment components and demonstrating their relationship to bottom morphology. Location of profile E-E' is on Figure C5.

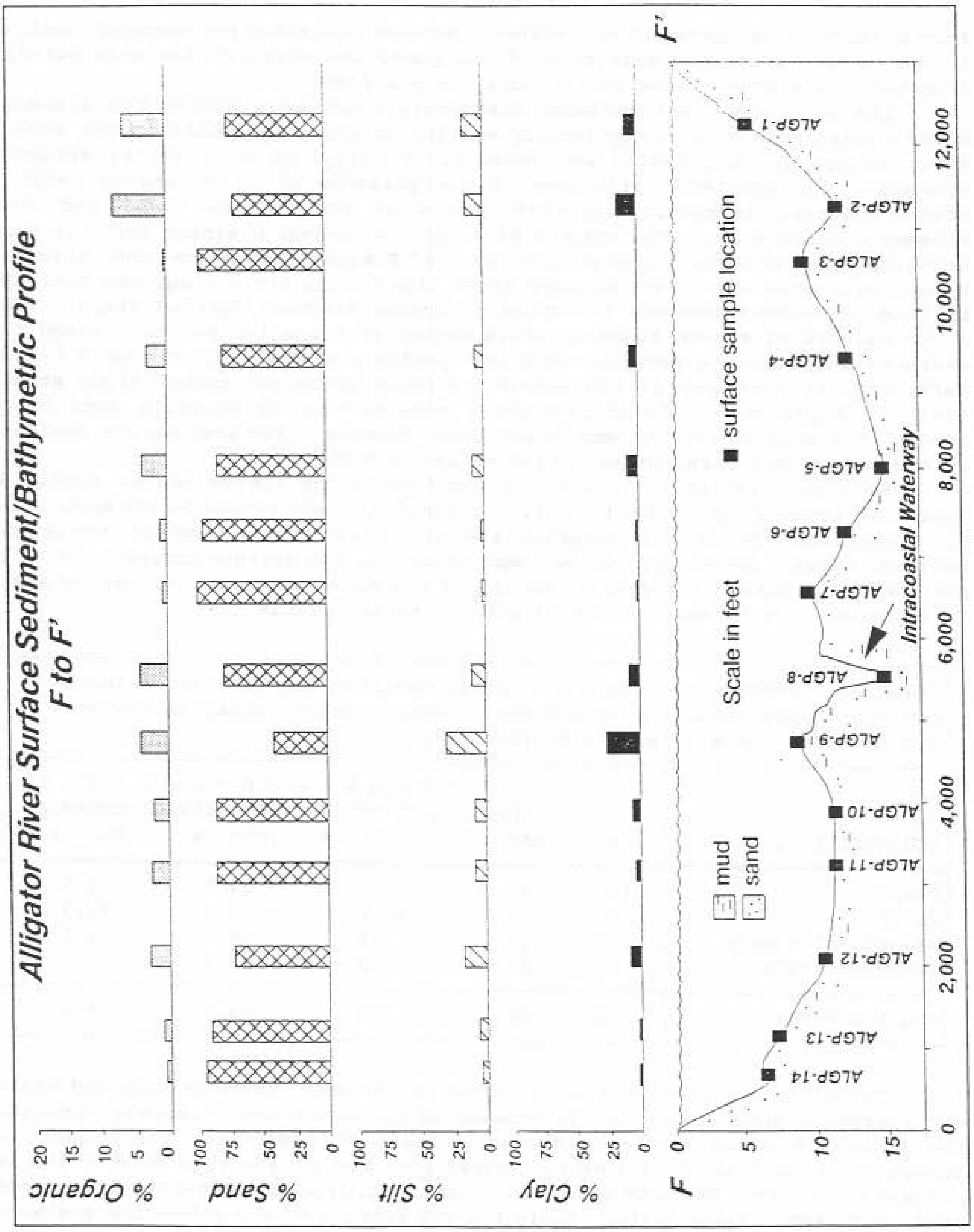


FIGURE D7. Bathymetric profile F-F' across Alligator River adjacent to the Highway 64 bridge showing the distribution of four major sediment components and demonstrating their relationship to bottom morphology. Location of profile F-F' is on Figure C5.

from erosion of the adjacent shorelines. Samples collected for chemical analysis in this study consisted primarily of inorganic and organic-rich muds obtained from below the edge of the sandy shoreline platform.

The morphology and sediment distribution patterns within the Albemarle Sound estuarine system are generally similar to those described in the Pamlico River (Riggs et al., 1989b) and Neuse River (Riggs et al., 1991c) estuarine systems. The greatest difference is the presence of an extensive wedge of orange-colored, inorganic mud that occurs in the Roanoke River and Inner Albemarle Sound areas. The Roanoke River is the largest drainage basin in North Carolina and extends through the entire Piedmont Province and into the Appalachian Mountains. The Roanoke River flow during flood stage was dominated by large suspended sediment transport of orange Piedmont derived clays. These large volumes of eroded Piedmont soils formed an extensive sediment wedge that extended into Inner Albemarle Sound and graded eastward into the more typical dark, organic-rich muds in the middle and outer estuarine zones (Riggs et al., 1991b). Riggs et al. found that after construction of multiple dams in the 1950's, the entire Inner Albemarle and Lower Roanoke River area became dominated by the ubiquitous dark, organic-rich estuarine mud.

Sediments within the Albemarle Sound estuarine system can be subdivided into four general types: sand, peat, inorganic mud, and organic-rich mud. Table D1 summarizes the average organic and inorganic composition of these main sediment types. Based upon 222 sediment analyses, the average composition of the mud sediments within the central basins of the Albemarle Sound estuarine system is 75.5% mud, 14.6% sand, and 9.9% organic matter (Table D1).

TABLE D1. Average composition of total sediment for the four major sediment types occurring within the Albemarle Sound estuarine system. Mud includes the silt plus clay fractions.

		AVERAGE		COMPOSITION	
SEDIMENT TYPE	N	INORGANIC SAND %	ORGANIC SAND %	INORGANIC MUD %	ORGANIC MUD %
SANDS	111	82.0	1.7	14.8	1.5
PEATS	30	22.7	17.5	38.5	21.3
ORGANIC-RICH MUDS	196	13.1	1.6	76.2	9.1
INORGANIC MUDS	26	25.6	0.7	70.4	3.3
ALL SEDIMENTS	363	35.9	2.9	53.8	7.4

Table D2 summarizes the distribution of sediment particle size and organic and inorganic composition of 356 subsamples by region and tributary throughout the Albemarle Sound estuarine system. Table D3 summarizes the organic and inorganic composition of 350 samples based upon organic analyses done on the sand and mud fractions. Table D4 summarizes the changing sediment patterns of percent sand, mud, and organic matter within the 350 samples of the estuarine system and based upon data in Table D3.

TABLE D2. Summary of sediment particle size and the inorganic-organic composition of the total sediment for 356 samples of the Albemarle Sound estuarine system. Sample areas are listed by regions of the Albemarle Sound trunk (from W to E) and by tributaries that drain into each region (also from W to E).

		TOTAL SEDIMENT			TOTAL SEDIMENT	
REGION	N	% SAND	% SILT	% CLAY	%ORGANIC	%INORGANIC
ALBEMARLE SOUND TRUNK SYSTEM						
Lower Roanoke River	26	22.4	47.3	30.3	8.8	91.2
Middle River	6	19.6	46.2	34.2	6.8	93.2
Cashie River	4	10.2	42.8	47.1	7.3	92.7
Inner Albemarle Sound	42	11.1	36.9	52.0	7.4	92.6
Middle Albemarle Sound	25	31.7	34.1	34.2	5.2	94.8
Outer Albemarle Sound	16	67.6	18.4	14.0	2.6	97.4
N = 119 MEANS		25.9	36.5	37.3	6.6	93.4
TRIBUTARIES--NORTH SIDE						
Lower Chowan River	20	35.6	36.0	28.4	16.4	83.6
Edenton Bay	13	23.2	42.6	34.2	23.2	76.8
Yeopim River	6	8.6	48.3	43.1	8.7	91.3
Perquimans River	16	17.4	40.2	42.4	12.6	87.4
Little River	8	17.9	36.6	45.4	10.1	89.9
Pasquotank River	50	29.1	36.9	34.0	16.6	83.4
North River	10	31.3	43.4	25.3	6.8	93.2
N = 123 MEANS		27.5	38.8	34.7	15.1	84.9
TRIBUTARIES--SOUTH SIDE						
Welch Creek	10	48.4	37.4	14.2	23.2	76.8
Deep Creek	6	30.1	34.6	35.3	24.2	75.8
Scuppernong River	20	44.0	31.4	24.6	16.0	84.0
Little Alligator River	4	51.2	24.0	24.8	6.2	93.8
Alligator River	21	54.7	28.9	16.4	7.6	92.4
N = 61 MEANS		47.5	31.4	21.1	14.4	85.6
CURRITUCK SOUND						
North Landing River	53	20.4	50.1	29.6	9.4	90.6
SUMMARY N = 356 MEANS		29.0	38.5	32.5	11.3	88.7

TABLE D3. Summary of 350 samples and their inorganic and organic composition within the Albemarle Sound estuarine system. Sample areas are listed by regions of the Albemarle Sound trunk (from W to E) and by tributaries that drain into each region (from W to E). These organic analyses were done on the sand and mud fractions and are different than total organic analyses on total sediment in Table D2.

REGION	N	INORGANIC SAND %	ORGANIC SAND %	INORGANIC MUD %	ORGANIC MUD %
ALBEMARLE SOUND TRUNK SYSTEM					
Lower Roanoke River	25	20.4	2.0	70.8	6.8
Middle River	6	18.7	0.9	74.5	5.9
Cashie River	4	9.3	0.9	83.4	6.4
Inner Albemarle Sound	42	10.4	0.7	82.2	6.7
Middle Albemarle Sound	25	31.1	0.6	63.7	4.6
Outer Albemarle Sound	16	67.0	0.6	30.4	2.0
N = 118	MEANS	25.0	1.0	68.5	5.6
TRIBUTARIES--NORTH SIDE					
Lower Chowan River	20	29.2	6.4	54.4	10.0
Edenton Bay	13	15.8	7.4	61.0	15.8
Yeopim River	6	8.1	0.5	62.3	8.7
Perquimans River	16	16.0	1.4	71.5	11.1
Little River	8	17.4	0.5	72.5	9.6
Pasquotank River	50	24.7	4.4	58.7	12.2
North River	10	29.9	1.4	63.3	5.4
N = 123	MEANS	23.5	4.0	61.4	11.2
TRIBUTARIES--SOUTH SIDE					
Welch Creek	10	36.0	12.4	40.8	10.8
Deep Creek	6	20.5	9.6	55.3	14.6
Scuppernong River	20	39.2	4.8	44.7	11.3
Little Alligator River	4	49.7	1.5	44.1	4.7
Alligator River	16	52.4	2.3	40.0	5.3
N = 56	MEANS	41.1	5.7	43.8	9.4
CURRITUCK SOUND					
North Landing River	53	18.2	2.2	72.4	7.2
SUMMARY N = 350	MEANS	26.0	3.0	62.6	8.4

TABLE D4. Changing patterns of % sand, mud, and organic matter in samples through the Albemarle Sound estuarine system. Samples are summarized by regions from upstream to downstream in the Albemarle Sound trunk and by tributaries occurring within each region of the trunk estuary. Mud includes the silt plus clay size fractions. These organic analyses were done on the sand and mud fractions and are different than organic analyses on total sediment in Table D2. Arrows point in direction of increasing concentration of that component.

REGION	N	INORGANIC SAND %	ORGANIC SAND %	INORGANIC MUD %	ORGANIC MUD %
ALBEMARLE SOUND TRUNK SYSTEM (W TO E)					
Roanoke River System*	35	18.8 ↑	1.7 ↑	72.9	6.6 ↑
Inner Albemarle Sound	42	10.4	0.7	82.2	6.7
Middle Albemarle Sound	25	31.1	0.6	63.7	4.6
Outer Albemarle Sound	16	67.0 ↓	0.6	30.4	2.0
TRIBUTARIES--NORTH SIDE	176	21.9	3.5 ↑	64.7	10.0 ↑
ALBEMARLE SOUND TRUNK	118	25.0	1.0	68.5	5.6
TRIBUTARIES--SOUTH SIDE	56	41.1 ↓	5.7 ↓	43.8	9.4 ↓

* includes the lower portions of the Roanoke, Middle, and Cashie Rivers

Within the main trunk of Albemarle Sound, the inorganic sand fraction increases dramatically downstream towards the Outer Banks (Table D4) with the inorganic mud fraction displaying the inverse pattern. Both the organic sand and organic mud fractions decrease downstream with decrease in the inorganic mud in the trunk estuary. In addition, the bathymetric profiles (Figs. D3 through D6) demonstrate a major increase in inorganic sand content onto the shoreline platforms around the perimeter of the trunk estuary. These distribution patterns reflect four primary sediment sources.

1. Inorganic mud is dominantly derived from the suspended sediment load being discharged by the Roanoke River drainage system; this includes minimal amounts of inorganic sand that are concentrated in the channel and mouth of the River.
2. Fine inorganic sand that increases in concentration eastward within the trunk estuary is related to inlets and storm processes associated with the adjacent Outer Banks.
3. Inorganic sand that occurs on the shallow perimeter platforms is totally derived from the adjacent sediment banks that are rapidly eroding.
4. The internally derived organic matter has two major sources:
   a. from extensive fresh water swamp forests in the western portion of the trunk estuary and upstream portions of tributary estuaries, or
   b. from erosion of minor fringing salt marshes in the eastern portion of the trunk estuary and outer portions of tributary estuaries.
5. Swamp forest contribution appears to be the most significant as demonstrated by the increase in concentration westward up the trunk estuary into the Roanoke River and laterally into tributary estuaries

estuary into the Roanoke River and laterally into tributary estuaries dominated by swampforests.

Considerable variability in sediment composition occurs within the tributary estuarine systems (Tables D2 and D3) depending upon two major variables: geographic location and size. The tributaries on the north side have substantially higher concentrations of mud (avenge of 75%) with less sand (average of 25%) than those on the south side of Albemarle Sound with higher concentrations of sand (average of 46%) and less mud (average of 54%) (Table D4). The northern portion of Albemarle Sound is bounded by land with generally low topography resulting in development of abundant large tributary estuaries with extensive organic-dominated shorelines. Land bounding the southern shore of Albemarle Sound is dominated by slightly higher relief resulting in generally fewer and smaller estuaries that are dominated by sediment bank shorelines. The highly variable composition of organic matter (Tables D2 and D3) within the tributaries results from several complex variables that include a) differences in size, b) relative abundance of sediment banks versus organic-dominated shorelines, and c) extent of anthropogenic activity along the shoreline.

Organic-Rich Mud (ORM) Sediment

Organic-rich mud (ORM) is the dominant sediment type within the Albemarle Sound estuarine system covering over 75% of the estuarine bottom. ORM is the major sediment type occurring within the central basin environment throughout the trunk and tributary estuaries. However, there are two exceptions to this distribution pattern. At the eastern end of Albemarle Sound, east of the Alligator and North Rivers, ORM grades eastward into the fine sands derived from barrier island processes. Extensive sand shoals extend across the central basin at the mouth of most tributary estuaries with sand concentration decreasing up the tributary and grading into ORM. The lateral distribution and thickness of organic-rich mud increases as each estuarine basin widens and deepens in the downstream direction within both the trunk estuary and tributary channels (Hartness, 1977; Duque, 1978; Riggs et al., 1989b, 1991c).

Tables D1, D2, and D3 summarize the general textural and organic composition of ORM and show the regional lateral variations in the sediment. ORM generally is dominated by inorganic mud (average = 62.6%), has less than 20% organic matter (average = 11.4%), and contains lesser amounts of inorganic sand (average = 26.0%). The content of organic matter in ORM ranges from lows of 1% to 2% in sandier sediments to highs of about 30% to 44% in muddy sediments around sewage outfalls and areas of intense agricultural development. The concentration of organic matter is generally highest in the tributaries and decreases into the trunk estuary and seaward down the trunk estuary (Table D4). Chemically inert quartz is the main mineral component within the silt and sand-size fractions of ORM.

The inorganic clays in ORM consist of four minerals: kaolinite, illite, smectite, and chlorite-intergrade. Park (1971) found the relative concentration of five clay minerals within similar ORM in the Neuse River sediments to be as follows: kaolinite (46%), illite (23%), chlorite-intergrade (17%), chlorite (8%), and smectite (5%). The clay minerals are derived primarily from river drainage off the upland portions of the drainage basin and to a lesser extent from erosion of sediment bank shorelines. Various workers have shown a downstream increase in illite and decrease in kaolinite (Brown and Ingram, 1954; Griffin and Ingram, 1955; Allen, 1964; Petree, 1974).

Benthic environments associated with ORM usually contain an oxidized zone of loose floc material that is of variable thickness. The presence or absence and degree of development of this loose floc at the sediment/water interface appears to be a direct function of the biological productivity, salt-water wedges, and storm energy levels, all of which vary greatly at scales ranging from daily to seasonal cycles. Sediments become reduced and increasingly compacted with depth below the sediment/water interface. In addition to a large population of micro-organisms, this sediment/water interface zone contains a large community of filter-feeding macrobenthos, particularly polychaetes and clams (Tenore, 1977), that are important in concentrating, pelletizing, and depositing the mud sediment.

Major differences in sediment types occur within the estuarine systems depending upon the organic concentration. Actual concentrations of organic matter within individual samples ranges from 0.3% up to 86% of the total sediment. Sediments that contain greater than 20% organic matter are generally some form of peat or muddy peat deposit. Peat deposits form in two ways. First, they can represent <u>in situ</u> growth in either swamp forests or grass marshes containing discrete plant components such as roots and stems in growth position, along with large pieces of logs, leaves, seeds, and inorganic sediments that have accumulated within the <u>in situ</u> organic framework. Second, peats can result totally from secondary accumulations of transported organic detritus eroded out of swamp forests and grass marshes. Within the Albemarle Sound estuarine system, both of these types of peats contain high concentrations of inorganic clay components. Inorganic clays settle out in the swamp forests and marshes from turbid storm waters that contain high concentrations of suspended sediments.

Swamp forest peat sediments tend to be coarser grained and are dominant in the riverine and transition zones of the Roanoke River and headwaters of associated tributary estuaries. These swamp forest peats occur on channel flanks and as coarse organic detritus mixed with coarse sand within the channel proper (Figs. D8 and D9). Within the transition zone into a flooded estuary, there is a major sediment inversion (Riggs, 1985). The swamp forest is drowned, partially eroded, and mud containing high concentrations of fine-grained organic detritus accumulates on top of the eroded swamp forest peats on the channel flanks and in the channel (Fig. D9). The peat becomes buried beneath increasingly thicker accumulations of mud within the main portions of the tributary and trunk estuaries. The shoreline platforms (Fig. D9) have been eroded into Quaternary sediment units by wave and current action and result in a thin and highly variable layer of well-sorted sand cover (Hartness, 1977; Hardaway, 1980; Riggs et al., 1989b, 1991c). Within the broad, deeper portions of Albemarle Sound, organic-rich mud sedimentation occurs. Thus, these mud-filled, depositional basins are incised into older, more indurated Quaternary sediment units.

Salt marsh peats, which generally contain much finer-grained organic matter than swamp forest peats, form around low-energy shorelines in the outer portions of the trunk and tributary estuaries. As these fringing marshes erode, abundant fine-grained organic detritus is released as suspended sediment along with associated clay minerals (Bellis et al., 1975; Copeland et al., 1983, 1984). This suspended sediment settles out of the water column by flocculation, aggregation, or via filter-feeding organisms to produce the ORM that dominates the estuarine system.

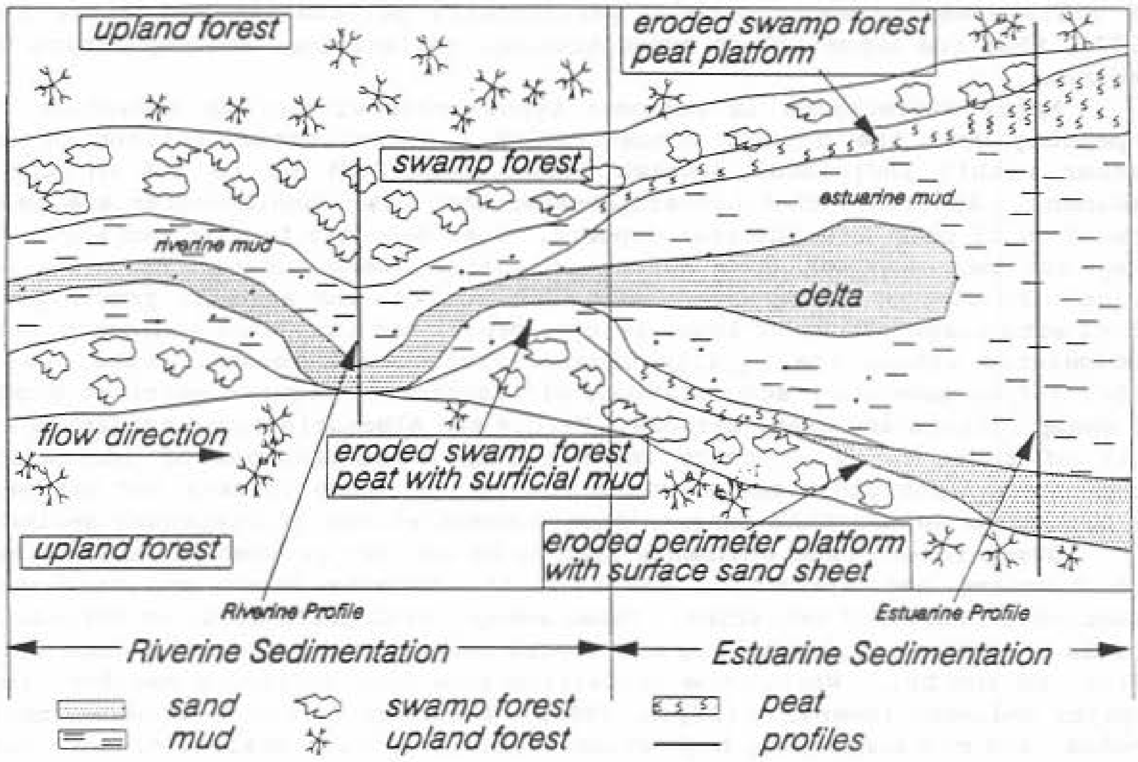


FIGURE D8. Schematic map of the upper transition zone of a drowned river estuarine system during the initial stages of flooding by rising sea level and showing the locations of two schematic cross-sections in Figure D9.

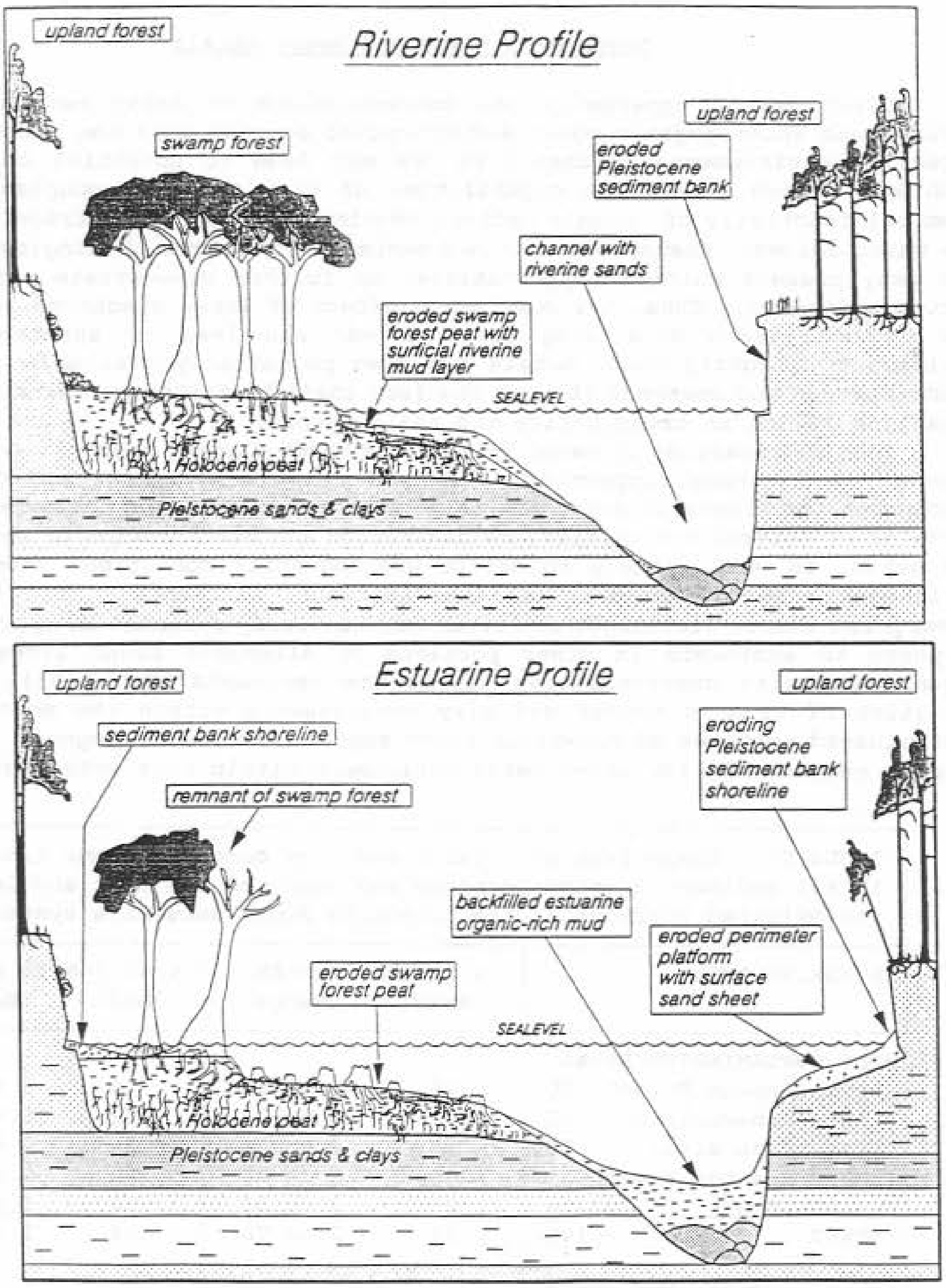


FIGURE D9. Two schematic cross-sections of the upper transition zone of a drowned river estuarine system during initial stages of flooding by rising sea level. The upper panel crosses the riverine portion prior to flooding, while the lower panel crosses the estuarine portion as flooding begins. These sections show 1) shoreline expansion into Holocene swamp-forest peats and Pleistocene sediment banks; and 2) major inversion in sedimentation as shallow organic-rich mud and channel sands within the riverine portion shift to deposition of sands on shallow perimeter platforms and orgainic-rich muds in deep central basins within the estuarine portion. Profile locations are on Figure D8.

Organic-Rich Mud and Heavy Metals

Discharge of apparently low concentrations of heavy metals from both natural and anthropogenic point and non-point sources into the Albemarle Sound estuarine environments dominated by ORM may lead to potential contamination problems. High adsorption capabilities of clay minerals coupled with high chemical reactivity of organic matter, continuously sequester trace metals from the water column. Resuspension of mud sediments by storms, biological processes and man, present multiple opportunities to further concentrate metals within bottom sediments. Thus, the cumulative effect of large discharge volumes with low concentrations over long time periods can lead to substantial metal enrichment. Lightly bound metals are then potentially available for further concentration and movement through the food chain by filter and detritus feeding organisms living in organic-rich mud environments.

Chemical analyses of major, minor, and trace element compositions have been done on the surface (uppermost 7 cm) and deep (lowermost 7 cm) ORM samples throughout the Albemarle Sound estuarine system. Analysis of these data document patterns of lateral and vertical concentration and distribution of metals within the basin, as well as help to define environmental conditions favoring metal enrichment. As discussed in previous sections, sediments in the vicinity of known point source discharges are often substantially enriched in specific metals compared to sediments in other portions of Albemarle Sound irregardless of organic and clay concentrations within the sediments (Table D5). The wide variation of organic matter and clay constituents within the most and least contaminated portions of Albemarle Sound suggest that anthropogenic sources are largely responsible for heavy metal enrichment within this estuarine system.

TABLE D5. Comparison of organic and clay concentrations (in %) in all sediment samples (surface and deep) of the most and least contaminated portions of the Albemarle Sound estuarine system.

ESTUARINE AREA	N	% ORGANIC MATTER Mean	Range	% CLAY-SIZE MATTER Mean	Range
MOST CONTAMINATED AREAS					
Lower Chowan River	20	16	3 to 51	28	5 to 59
Inner Albemarle Sd	42	7	2 to 13	52	10 to 80
Pasquotank River	50	17	2 to 78	34	2 to 66
Lower Roanoke River	26	9	5 to 24	30	7 to 66
Welch Creek	10	23	8 to 37	14	5 to 43
MEANS	148	13	2 to 78	36	2 to 80
LEAST CONTAMINATED AREAS					
Alligator River	21	8	1 to 24	16	2 to 56
Deep Creek	6	24	5 to 46	35	3 to 61
Little River	8	10	4 to 20	45	29 to 59
Outer Albemarle Sd	16	3	0 to 9	14	1 to 54
Yeopim River	6	7	4 to 11	43	26 to 65
MEANS	57	9	0 to 46	24	1 to 65

Vertical Distribution of Trace Elements

Table D6 compares mean concentrations for 15 trace elements in all deep samples with mean concentrations for all surface samples throughout the Albemarle Sound estuarine system. These data suggest that there is a general upcore increase in concentration of 5 elements (Pb, P, Cd, Zn, and Cu) while 5 elements decrease in concentration upcore (Sn, Mo, Ni, Ti, and Cr). Five elements (As, Co, Hg, Mn, and V) are either uniform upcore or show mixed relationships.

TABLE D6. Comparison of mean concentrations for 15 trace elements (in µg/g or ppm) between surface and deep sediment samples in the Albemarle Sound estuarine system. The deep samples have an average depth of 30 cm below the sediment/water interface. Bold print indicates those samples for each element with the highest mean value.

TRACE ELEMENTS	ALBEMARLE SYSTEM MEAN CONCENTRATION (in µg/g or ppm) N	SURFACE SPLS.	N	DEEP SPLS.		RATIO OF MEANS SURFACE/DEEP
ELEMENTS ENRICHED IN SURFACE SEDIMENTS						
Pb	193	**28.1**	165	16.5	**	1.7 ± 0.8
P	193	**428.**	165	261.	**	1.6 ± 0.3
Cd	193	**0.29**	165	0.20	**	1.4 ± 0.4
Zn	193	**56.3**	165	40.1	**	1.4 ± 0.3
Cu	193	**12.3**	165	10.4	**	1.2 ± 0.3
ELEMENTS WITH UNIFORM DISTRIBUTION						
As *	193	4.13	165	4.19		1.0 ± 0.2
Co	193	6.80	165	6.78		1.0 ± 0.1
Hg	156	0.22	144	0.23	**	1.0 ± 0.9
Mn	193	362.	165	350.	**	1.0 ± 0.2
V	193	24.0	165	24.7		1.0 ± 0.1
ELEMENTS ENRICHED IN DEEP SEDIMENTS						
Sn *	191	6.10	163	**6.97**		0.9 ± 0.1
Mo	193	0.32	165	**.41**	**	0.8 ± 0.1
Ni	193	4.79	165	**5.77**	**	0.8 ± 0.2
Ti	193	76.4	165	**110.**	**	0.7 ± 0.1
Cr	193	15.6	165	**27.3**		0.6 ± 0.5

* = Analyses have poor reproducibility, hence somewhat less reliability
** = Numbers are significantly different when $p < 0.05$ using the SAS Wilcoxon Signed Rank test.

This vertical distribution of elements in the Albemarle sediments is considerably less dramatic than that recorded for either the Pamlico or Neuse River estuaries (Riggs et al., 1989b, 1991c). For example, the Neuse River had 11 trace elements that displayed upcore increases in concentration, 2 elements that showed the inverse pattern and 2 elements that displayed no pattern. The general vertical distribution pattern for the Albemarle probably reflects much lower levels of sediment contamination from anthropogenic sources than either the Pamlico or Neuse Rivers.

Higher concentrations of more trace elements do occur at depth in two types of depositional areas. First, cores from the riverine environments in the Lower Roanoke River area and other tributary headwaters grade from ORM at the surface to peat deposits at depth. These peats have extremely high contents of organic matter (ranging from 20% to 86%) that increases the ability to sequester trace metals (Evans et al., 1984; Linebach, 1990). Second, areas with a long history of extensive human activity, often show high or higher concentrations of most trace elements with depth such as Welch Creek, Elizabeth City area of the Pasquotank River, etc. (see data tables and discussion of each of these areas in subsequent sections). Variation in vertical enrichment in response to human activity may result from three different scenarios:

1. discharge of metal-bearing wastes over long time periods,
2. extensive bottom disturbing and sediment mixing processes by man, and
3. changing patterns of discharges in both volume and type of trace element composition through time.

The amount of vertical enrichment of trace metals is directly related to the total elemental concentration; cores with low total concentrations (i.e., from the least contaminated areas) have small upcore changes whereas cores with high total concentrations (i.e., from the most contaminated areas) have large upcore changes. The nutrient element phosphorus shows distinct surface enrichments that average 1.6 X throughout the entire estuarine area. This phosphorus data suggest that decomposition of ORM in surface sediments represents an important source of nutrient input into the water column within the estuarine system. If this is the situation, nitrogen would also be derived from the decomposition of ORM and potentially available to the aquatic system. This corroborates the results of Matson et al. (1983) for both the Pamlico and Neuse River estuaries.

Comparison of Albemarle Sound to the Neuse and Pamlico River Systems

Table D7 compares the basic sediment composition of the Albemarle Sound estuarine system with the Neuse and Pamlico River estuaries. From this table it is clear that the sediments within the three estuarine systems are quite similar in composition, even though there are minor differences. This similarity suggests that the differences in trace element contamination are not due to sediment differences, but rather due to numbers and quantities of both point and nonpoint source, waste water discharge into each estuarine system.

Table D8 compares trimmed means of surface samples within the Albemarle Sound estuarine system with those of the Neuse and Pamlico Rivers (Riggs et al., 1989b, 1991c) and presents the relative enrichment of the Albemarle Sound estuarine system as compared to the Neuse and Pamlico River systems. Comparison of these trimmed means demonstrates several interesting points. First, Albemarle Sound has higher background levels of concentrations for only 4 of the 15 trace elements and include titanium (2.4 X NRTM), manganese (2.1 X PRTM), cobalt (1.4

X NRTM), and vanadium (1.1 X PRTM). Mercury, nickel, and chromium concentration levels are lower than those in the Neuse River, but are higher than the average levels in the Pamlico River. All other trace elements have relatively lower average concentrations than either other estuarine system, probably reflecting the generally smaller population and fewer numbers of NPDES waste water discharge permits within the associated drainage basins.

TABLE D7. Average composition of total sediment for all samples collected within the entire Pamlico, Neuse, and Albemarle estuarine systems and within the respective trunk estuaries. Pamlico River data are from Riggs et al. (1989b) and Neuse River data are from Riggs et al. (1991c).

		AVERAGE COMPOSITION			
	N	SAND %	SILT %	CLAY %	ORGANIC %
ESTUARINE SYSTEM					
Neuse River	396	42.2	29.0	28.8	14.1
Pamlico River	345	27.9	25.6	34.2	12.2
Albemarle Sound	355	25.8	34.1	28.8	11.3
TRUNK ESTUARY					
Pamlico River	158	25.5	25.5	39.4	9.8
Neuse River	175	33.1	26.4	27.6	13.0
Albemarle Sound	109	25.1	33.7	34.8	6.4

Second, background concentrations for the major elements are quite different than for the Neuse and Pamlico River estuarine systems (Table D8). The relatively low values of sodium (0.1 X NRTM) probably reflect the very low salinities throughout the Albemarle estuarine waters and associated sediment pore waters as compared to the Neuse and Pamlico Rivers. The relatively low values of calcium (0.5 X NRTM) in Albemarle Sound probably reflects lower concentrations of $CaCO_3$ shells in the sediments as compared to the Neuse and Pamlico River systems; this also would reflect the much lower salinities throughout the Albemarle Sound estuarine system. However, most of the major elements are bound within crystalline structures and reflect the basic sediment mineralogy consisting of clay minerals and quartz. Since our analytical procedure involved a partial leach technique (see Methodology section), direct comparisons should not be made for the Si, Al, Mg, and K.

TABLE D8. Comparison of trimmed mean concentrations for 22 elements (in µg/g or ppm) in surface sediments of Albemarle Sound (this study), the Neuse River (Riggs et al., 1991c), and Pamlico River (Riggs et al., 1989b) estuarine systems. For each element, the underline = system with the highest background levels, bold print = the system with intermediate background levels, and plain print = the system with the lowest background levels.

	TRIMMED MEANS			RATIO OF TRIMMED MEANS	
ELEMENT	ALBEMARLE SOUND	NEUSE RIVER	PAMLICO RIVER	ALBEMARLE / NEUSE R.	ALBEMARLE / PAMLICO R.
TRACE ELEMENTS					
Ti	75.2	31.8	**38.6**	** 2.4 ± 0.2	** 2.0 ± 0.2
Mn	329.	**288.**	154.	** 1.1 ± 0.2	** 2.1 ± 0.4
Co	6.67	4.66	**5.55**	** 1.4 ± 0.1	** 1.2 ± 0.1
V	23.4	**22.5**	21.4	1.0 ± 0.1	1.1 ± 0.1
Hg	**0.14**	0.15	0.09	0.9 ± 0.2	** 1.6 ± 0.3
Ni	**4.28**	4.64	2.66	0.9 ± 0.1	** 1.6 ± 0.2
Cr	**10.6**	16.8	10.5	** 0.6 ± 0.1	1.0 ± 0.1
Cu	10.8	19.3	**13.6**	** 0.6 ± 0.1	** 0.8 ± 0.1
Zn	50.4	95.0	**77.0**	** 0.5 ± 0.1	** 0.7 ± 0.1
Mo	0.29	0.54	**0.50**	** 0.5 ± 0.1	** 0.6 ± 0.1
P	401.	876.	**805.**	** 0.5 ± 0.1	** 0.5 ± 0.1
Cd	0.22	0.77	**0.36**	** 0.3 ± 0.1	** 0.6 ± 0.1
Sn *	5.64	21.5	NA	** 0.3 ± 0.0	---
Pb	21.7	**34.9**	35.9	** 0.6 ± 0.1	** 0.6 ± 0.1
As *	3.95	**5.98**	12.8	** 0.7 ± 0.1	** 0.3 ± 0.0
MAJOR ELEMENTS					
Si	1533.	1052.	**1174.**	** 1.5 ± 0.1	** 1.3 ± 0.1
Fe	13340.	16236.	**14692.**	** 0.8 ± 0.1	0.9 ± 0.1
Al	5088.	6912.	**6664.**	** 0.7 ± 0.1	** 0.8 ± 0.1
Ca	2340.	5039.	**3679.**	** 0.5 ± 0.0	** 0.6 ± 0.1
Mg	1713.	3220.	**2707.**	** 0.5 ± 0.0	** 0.6 ± 0.1
K	555.	1029.	**932.**	** 0.5 ± 0.0	** 0.6 ± 0.1
Na	609.	6203.	**4519.**	** 0.1 ± 0.0	** 0.1 ± 0.0

* = Analyses have poor reproducibility, hence somewhat less reliability.
NA = Not analyzed
** = Numbers are significantly different at the 95% confidence interval using the Student-t Test (Marsal, 1987).

PART E: RESULTS

AREAS OF CONCERN IN THE ALBEMARLE SOUND ESTUARINE SYSTEM

PART E: RESULTS

AREAS OF CONCERN IN THE ALBEMARLE SOUND ESTUARINE SYSTEM

Figure E1 is an index map showing the location of all area maps used in the PART E: RESULTS section of this report. Table E1 is an outline of the specific regional areas and associated maps that will be the basis for presentation and discussion of all analytical data through the remainder of this report.

Lower Roanoke River Area

One of the largest wood products facilities in the world is located on the banks of Welch Creek and the Lower Roanoke River west of Plymouth. This industrial site has been operating since 1938 and today consists of 1200 acres, which includes 750 acres of industrial waste water treatment ponds (Fig. E2). Originally, all industrial waste water from the facility was discharged directly into the Roanoke River. However, during the period between the early 1960's and 1988, all industrial waste water was discharged directly into Welch Creek (near WEL-4 in Fig. E2). Beginning in 1968 all industrial waste water, except cooling water, was processed through a secondary treatment plant before being discharged into adjacent Creek waters. Since 1988, the 55 million gallons per day of noncooling, industrial waste water has been discharged directly into the Roanoke River through a diffuser pipe across the River bottom. This discharge pipe is located downstream of the plant site and slightly upstream of the mouth of Welch Creek.

In a site inspection report for North Carolina, Durway (1986) described three on-site areas where hazardous substances occur, or in the past have been generated or disposed of. There probably have been many different sources of numerous contaminants from this large and complex industrial facility over the years. It is not known to what extent any or all of these historic sites could continue to be impacting the adjacent waterways. These sites include the following:

1. A wood treatment plant has been operating since 1979 and produces a chromate copper arsenate sludge as a by-product material. This waste material is stored in drums and removed from the site for disposal.
2. Considerable amounts of mercury were associated with various phases of the old chlorine plant that operated until 1968. Some waste mercury was volatilized, some was discharged directly into the River, and some was disposed of in the old on-site landfill.
3. An old landfill, situated on a 35 to 50 acre tract of low wetland, received much onsite chemical waste including mercury, until 1979 when it was sealed.

Welch Creek

The sediments within Welch Creek, a very small southern tributary to the Roanoke River (Fig. E2), are substantially or slightly enriched in all 15 trace elements (Table E2). Thirteen of these trace elements are substantially enriched in multiple sample sites. Four elements have extremely high enrichments with maximum enrichment factors as follows: Cr = 156 X, Hg = 73 X, Ni = 20 X, and Cu = 9.4 X the ATM, respectively). Seven of the ten samples analyzed in Welch Creek

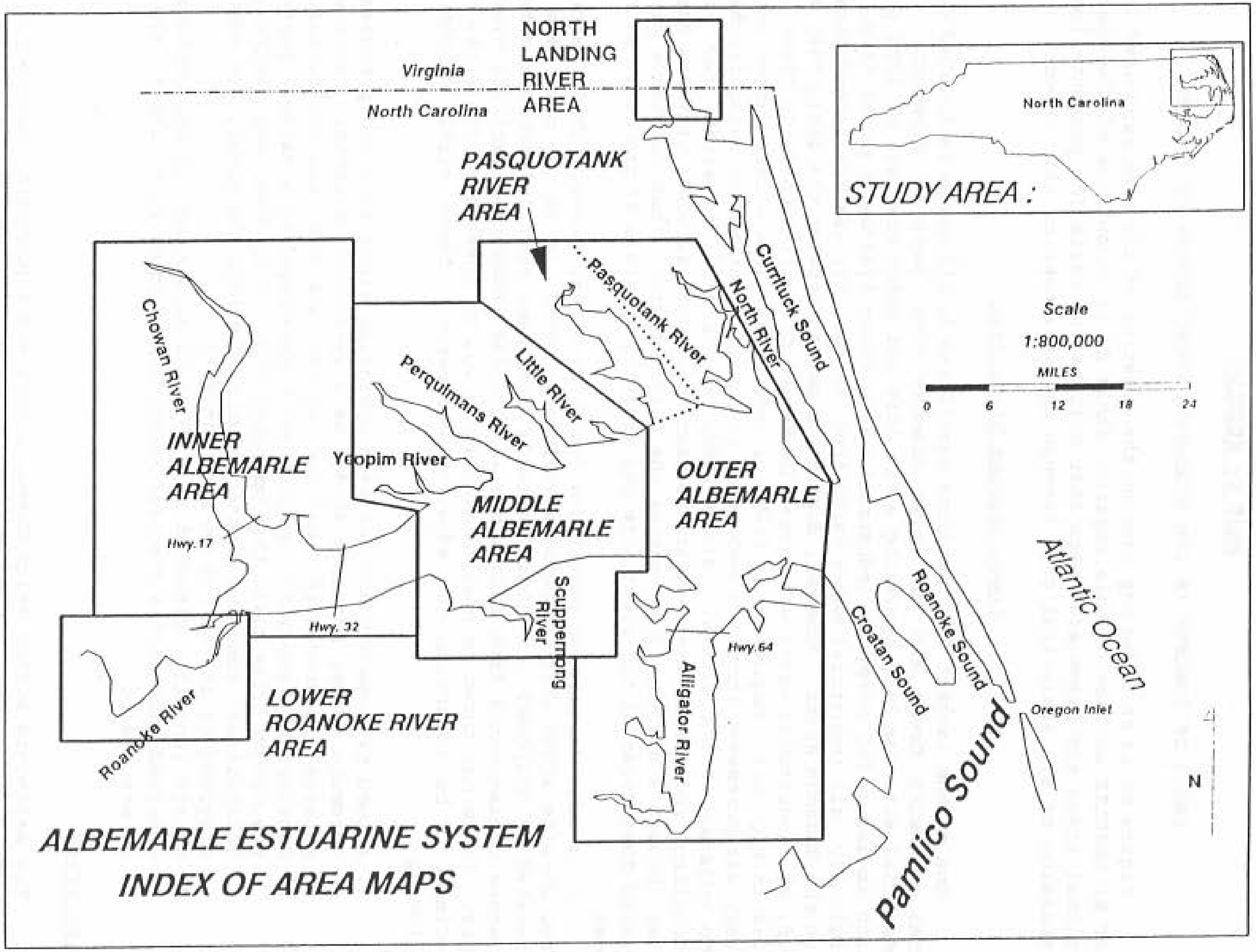


FIGURE E1. Index map of the Albemarle Sound estuarine system showing the location of specific regions with detailed sample location maps (Figures E2, E5, E6, E7, and E8) and discussed in the text.

TABLE E1. Outline of the regional areas of the Albemarle Sound estuarine system and the associated figures and tables considered in this section.

REGIONAL AREAS OF THE ALBEMARLE SOUND ESTUARINE SYSTEM	FIGURES	TABLES
Regional Index Map with Location of Area Maps	E1	
Lower Roanoke River Area: Location Map	E2	
Welch Creek: Data Summary		E2
Welch Creek: Downstream Enrichment Factors	E3	
Welch Creek: Downstream Enrichment Factors	E4	
Roanoke River: Data Summary		E3
Middle and Cashie Rivers: Data Summary		E4
Inner Albemarle Sound Area: Location Map	E5	
Lower Chowan River: Data Summary		E5
Lower Chowan River: Sediment Data		E6
Edenton Bay: Data Summary		E7
Inner Albemarle Sound: Data Summary		E8
Middle Albemarle Sound Area: Location Map	E6	
Yeopim River: Data Summary		E9
Little River: Data Summary		E9
Deep Creek: Data Summary		E9
Perquimans River: Data Summary		E10
Scuppernong River: Data Summary		E11
Middle Albemarle Sound: Data Summary		E12
Outer Albemarle Sound Area: Location Map	E7	
Pasquotank River Area: Location Map	E8	
Pasquotank River: Data Summary		E13
Newbegun Creek: Downstream Enrichment Factors	E9	
Pasquotank River: Downstream Enrichment Factors	E10	
North River: Data Summary		E14
Alligator River: Data Summary		E15
Little Alligator River: Data Summary		E15
Outer Albemarle Sound: Data Summary		E16
Albemarle Sound Synthesis		
Albemarle Sound: Data Summary		E17
Albemarle Sound: Downstream Enrichment Factors	E11	
Albemarle Sound: Downstream Enrichment Factors	E12	
Albemarle Sound: Downstream Enrichment Factors	E13	
Albemarle Sound: Downstream Enrichment Factors	E14	
Roanoke River: Maximum Enrichment Factors		E18
Albemarle Sound: Maximum Enrichment Factors		E19
Pasquotank, Chowan, and Perquimans Rivers: Maximum Enrichment Factors		E20
Albemarle Sound Region: Data Comparison		E21
North Landing River	C2	E22-E24

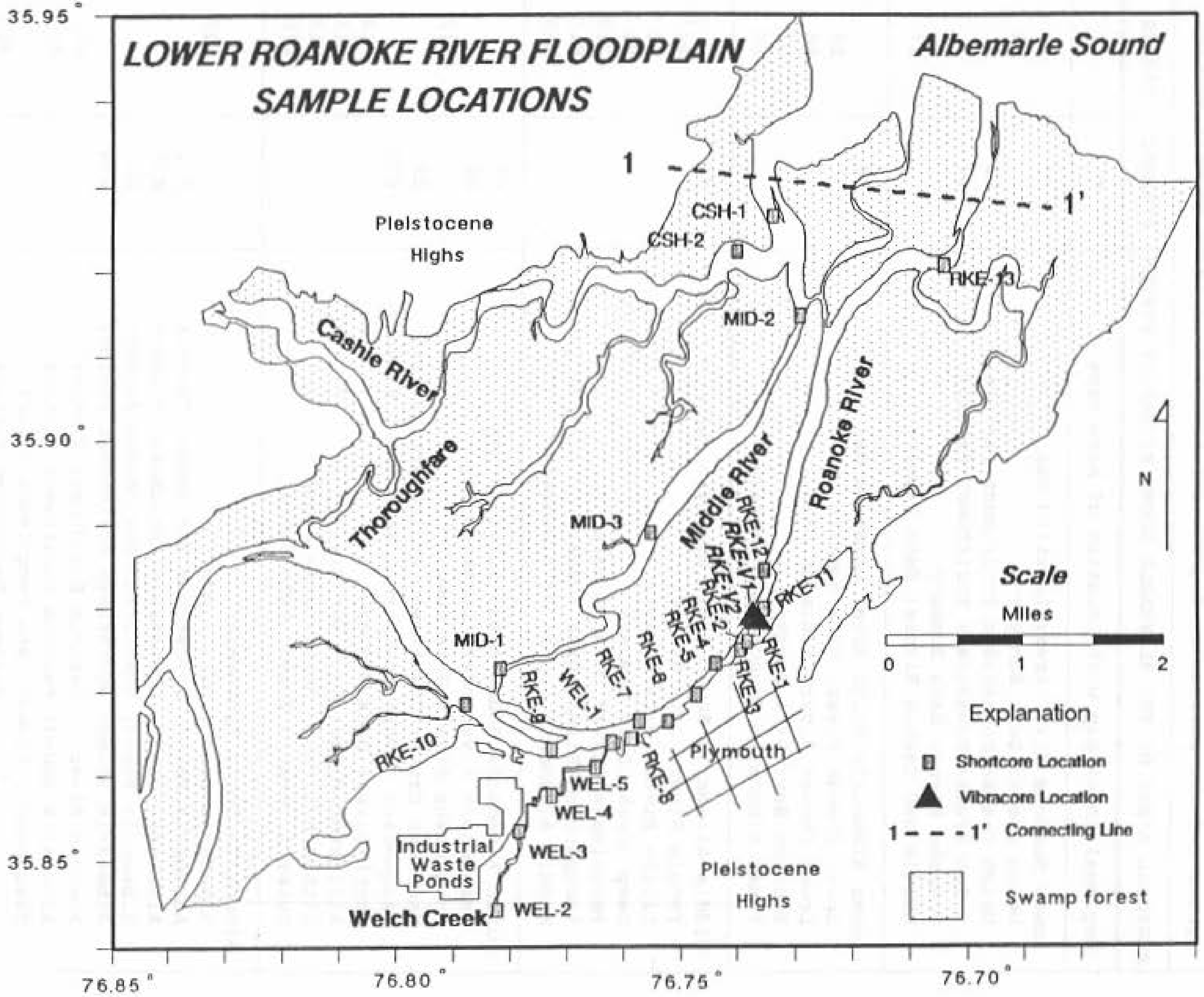


FIGURE E2. Sample location map of the Lower Roanoke River Area.

TABLE E2. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in Welch Creek. Depths of the deep samples range from 16 to 50 cm below the sediment surface for an average depth of 38 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (µg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 5		N = 5	
WELCH CREEK								
Cr	5	205.	21.8	494.	53.0	156.1	19.3	46.5
Hg	5	2.14	0.35	5.54	31.2	72.9	15.1	39.0
Ni	5	26.2	2.4	58.9	7.4	20.5	6.1	13.8
Cu	5	33.6	7.1	90.4	4.9	9.4	3.1	8.4
Zn	5	116.	18.8	244.	3.3	6.2	2.3	4.8
V	5	52.6	20.4	93.1	2.4	3.4	2.2	4.0
P	5	920.	144.	1501.	2.3	3.5	2.3	3.7
Cd	5	0.44	0.15	0.84	2.3	4.0	2.0	3.8
Sn *	5	11.4	2.8	22.0	**1.6**	2.9	2.0	3.9
Mo	5	0.46	0.25	1.29	1.3	2.0	**1.6**	4.5
Ti	5	89.1	27.3	152.	**1.5**	2.4	1.2	2.0
Mn	5	500.	85.4	945.	**1.6**	3.1	**1.5**	2.9
Co	5	6.1	1.3	13.3	0.9	1.2	0.9	2.0
Pb	5	17.1	4.3	32.4	1.0	**1.6**	0.8	**1.5**
As *	5	2.8	0.9	7.1	0.5	1.4	0.7	**1.9**
Ca	5	44339.	1586.	186079.	21.7	62.7	18.9	79.5
Al	5	15060.	2776.	29688.	3.7	8.4	3.0	5.8
Si	5	2630.	789.	5196.	2.1	4.8	**1.7**	3.4
Na	5	594.	64.8	1836.	**1.5**	3.2	1.0	3.0

* analyses have poor reproducibility, hence somewhat low reliability.

had Hg concentrations of 1 ppm or higher with samples containing very high levels of 3.3, 5.5, 9.6, and 10.3 ppm Hg. Lead and arsenic are only slightly enriched in multiple sample sites with maximum enrichment factors as follows: Pb = 1.6 X and As = 1.9 X the ATM.

Four major elements (calcium, aluminum, silica, and sodium) are also substantially enriched in the Welch Creek sediments (Table E2) with maximum enrichment factors as follows: Ca = 79 X, Al = 8.4 X, Si = 4.8 X, and Na = 3.2 X the ATM. This is the only region where all four of these elements are enriched and are unquestionably related to the industrial discharge.

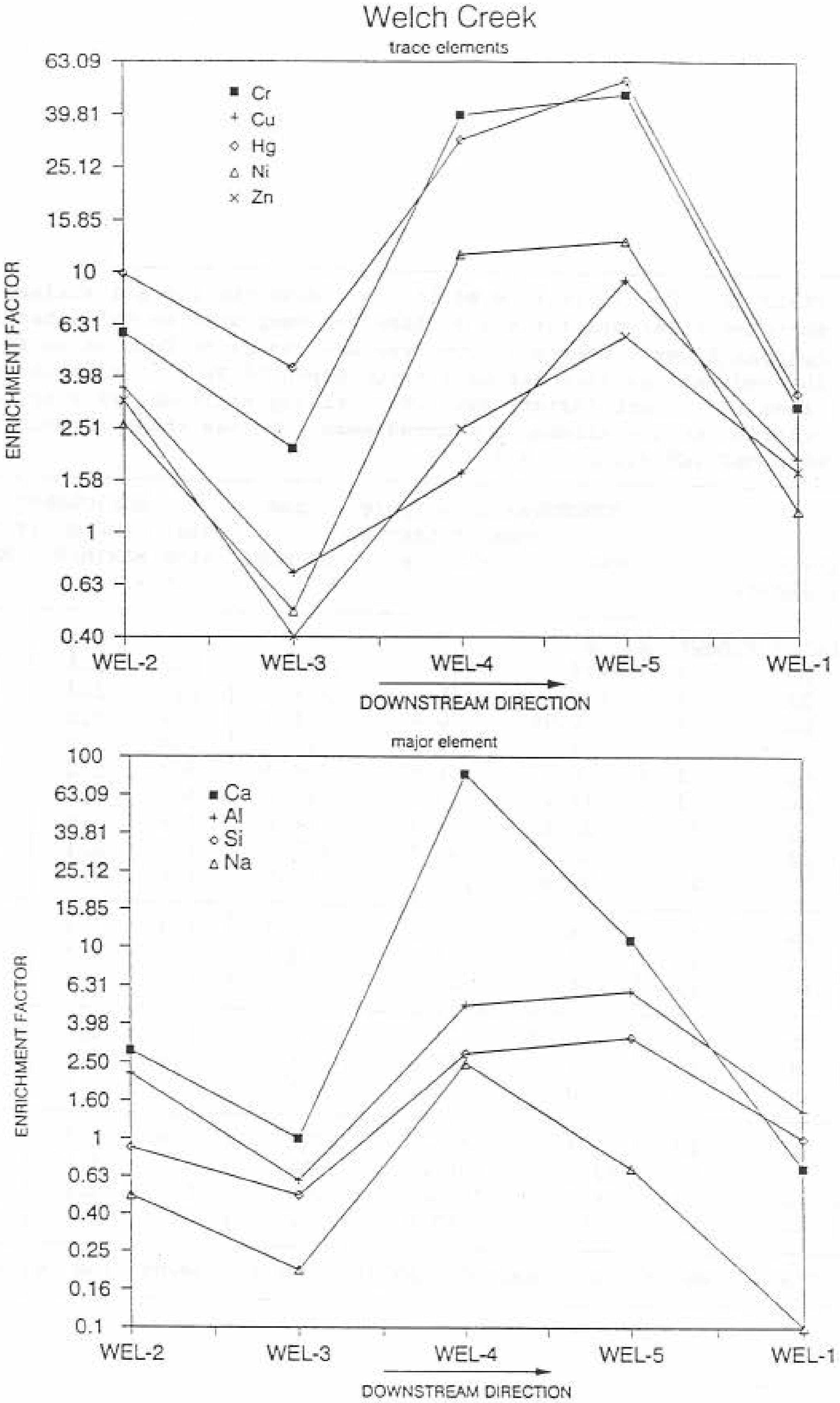
Five sites were sampled along the axis of Welch Creek (Fig. E2). Figures E3 and E4 display the lateral distribution of enriched elements in the surface sediments down the axis of Welch Creek. Two of these sites (WEL-2 and WEL-3) are above the former discharge point and have generally lower, but highly variable enrichment factors for most elements. This distribution probably reflects movement of discharged waters upstream during high-water flood conditions on the Roanoke River. The two middle sites (WEL-4 and WEL-5) are downstream of the former discharge point and have the highest levels of sediment enrichment of most elements. Concentrations generally remain high, but with a general decrease downstream to the mouth of the Creek (WEL-1). The deep sample at WEL-1 is substantially enriched in most elements; however, there is generally a major decrease in enrichment in most elements in the surface sample suggesting active deposition and dilution from the Roanoke River at this site during flood flow periods.

All elements except tin, molybdenum, manganese, and arsenic are significantly more enriched in the deeper, subsurface sediments than in the surface samples (Table E2). The four elements with increased enrichment in the surface samples are only slightly so. This vertical distribution pattern could result from several different factors. First, it may reflect the fact that the Welch Creek NPDES discharge site was abandoned in 1988 and changed to the Roanoke River. Second, it could result from ongoing discharge of groundwater through the subsurface and into the Creek on a slow and continuous basis from "leaky" on-land sites. Third, the actual distribution of each element could be a function of its chemistry and changes of bottom sediment and pore-water chemical conditions.

Lower Roanoke River

The main Roanoke River channel is the southern-most channel that flows past Plymouth (Fig. E2). This channel receives up to the 80 million gallons of waste water discharge per day (mgpd) directly from two large paper mills, up to 7 mgpd from various waste water treatment plants between Roanoke Rapids and Plymouth, and up to 3 mgpd from other small industrial dischargers. Most of this waste water is of unknown composition with respect to heavy metal concentrations.

Thirteen sites were sampled in the Lower Roanoke River (Fig. E2). Each mud-rich sample was obtained in shallow waters along the flanks of the main channel which is dominated by sand-rich sediments. In general, the Lower Roanoke River has lower levels of trace element enrichment than Welch Creek. However, nine trace elements are substantially enriched and three elements are slightly enriched in multiple sample sites (Table E3). Three elements are enriched in all samples with maximum enrichment factors as follows: Mn = 4.8 X, Co = 2.5 X, and Ti = 2.3 X the ATM. Enrichment of these three elements are probably related to the geology of the drainage district and natural weathering processes rather than from anthropogenic sources. Four other elements are enriched at multiple sample



FIGURES E3 and E4. Downstream plots of enrichment factors for Welch Creek. Upper panel plots representative trace elements, while lower panel plots major elements. The former paper mill discharge was in the approximate vicinity of WEL-4. Sample sites are located on Figure E2 and in the Appendix.

TABLE E3. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Lower Roanoke River. Depths of the deep samples range from 16 to 50 cm below the sediment surface for an average depth of 38 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (μg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 13		N = 13	
LOWER ROANOKE RIVER								
Mn	13	1088.	576.	1584.	2.5	3.2	3.3	4.8
Ti	13	144.	125.	174.	2.1	2.3	**1.9**	2.3
Hg	13	0.28	0.02	1.75	1.2	6.8	2.0	12.3
As *	13	7.6	0.9	12.9	1.4	2.5	2.0	3.4
Cr	13	16.4	11.4	39.3	**1.7**	4.0	**1.5**	3.7
Cu	13	15.9	12.3	21.9	**1.5**	2.3	**1.5**	2.0
Co	13	12.1	9.8	16.8	**1.5**	**1.7**	**1.8**	2.5
Zn	13	62.7	46.7	113.	1.0	2.1	1.2	2.2
V	13	30.6	28.7	36.0	**1.5**	2.0	1.3	**1.5**
Sn *	13	6.8	5.3	8.7	1.1	**1.5**	1.2	**1.5**
Ni	13	3.9	3.0	4.9	0.9	**1.7**	0.9	1.1
P	13	432.	147.	683.	0.7	1.0	1.1	**1.7**
Mo	13	0.25	0.25	0.25	0.9	0.9	0.9	0.9
Pb	13	15.3	13.6	19.5	0.7	1.0	0.7	0.9
Cd	13	0.16	0.15	0.31	0.7	0.7	0.7	1.4
Ca	13	2122.	1405.	5202.	1.0	4.9	0.9	2.2
Al	13	5393.	3062.	5918.	1.1	1.3	1.1	1.2
Si	13	1462.	1334.	1500.	1.0	1.0	1.0	1.0
Na	13	61.8	39.0	110.	0.1	0.4	0.1	0.2

* analyses have poor reproducibility, hence somewhat low reliability.

sites with maximum enrichment factors as follows: Hg = 12.3 X, Cr = 4.0 X, As = 3.4 X, and Cu = 2.3 X the ATM. Mercury is substantially enriched (up to 12.3 X ATM) in two samples at one site (RKE-13) off the mouth of Canaby Creek, along with arsenic, cobalt, chromium, copper, manganese, tin, titanium, and zinc. Since all other Roanoke River samples, except RKE-9 near the present industrial site, have very low concentrations of mercury, it is assumed that there could be a major source of metal contamination up Canaby Creek. This Creek should be sampled and analyzed for heavy metals.

Chromium and copper are slightly to substantially enriched (up to 4.0 X and 2.3 X ATM, respectively) in eight and 14 Lower Roanoke River samples, respectively. All copper enrichment occurs downstream of the paper mill's new NPDES discharge site. Cobalt is substantially enriched in Welch Creek and is only slightly enriched in the Roanoke River in 21 of the 26 samples. Arsenic is not enriched in Welch Creek except for the surface sample at the mouth of the Creek; however, it is slightly to substantially enriched in 17 samples in the Roanoke River downstream of the paper mill discharge.

It appears that there are significant amounts of various trace elements within the sediments of the Lower Roanoke River system. However, the general concentrations are lower than in Welch Creek and the distribution patterns of these trace elements are somewhat irregular. The Roanoke River is dominated by rapidly fluctuating flow conditions and resulting processes of sedimentation that range from low energy during low flow conditions to high energy during high flow conditions. These environmental variations would cause major changes in processes of sediment deposition and erosion within the Roanoke River channel and could explain the erratic distribution patterns.

Middle and Cashie Rivers

Middle and Cashie Rivers are distributary channels of the Lower Roanoke River that are situated north of the main channel (Fig. E2). The Cashie River has its own tributary drainage, however, it is connected to the Roanoke River by the Thoroughfare Channel.

Chemical data for surface samples at three sites in the Middle River and two sites in the outermost Cashie River are summarized in Table E4. Manganese and titanium are enriched in all samples (up to 4.2 X and 1.9 X ATM, respectively), while arsenic and cobalt are enriched in eight and seven of the ten samples (up to 2.8 X and 2.0 X ATM, respectively). Chromium and vanadium are variably enriched at both sites in the Cashie River (up to 1.7 X and 1.5 X ATM, respectively).

Inner Albemarle Sound Area

Inner Albemarle Sound extends from the mouth of the Lower Roanoke River with broad floodplain swampforests to the west to the embayed Chowan River estuary to the north, and eastward to the western sides of the Yeopim River on the north and Bull Bay on the south (Fig. E5). Inner Albemarle Sound is relatively narrow, about 5 miles wide, compared to the middle and outer portions further to the east, which are between 10 to 15 miles wide. Both the Roanoke and Chowan River Drainage Basins (Fig. B1) discharge directly into Inner Albemarle Sound, which is an irregularly flooded, fresh water, drowned-river estuarine system (Fig. D1). Three water bodies are described within this area and include the Chowan River and Edenton Bay embayed estuaries, as well as Inner Albemarle

TABLE E4. Summary of mean and maximum enrichment factors for 15 trace elements in surface sediments from Middle River and Cashie River, two tributary channels of the Lower Roanoke River. Enrichment factors in bold print are slightly enriched (EF >1.5X to <2X ATM) relative to the Albemarle Sound trimmed mean.

TRACE ELEMENTS	MIDDLE RIVER SURFACE SAMP N = 3		CASHIE RIVER SURFACE SAMP N = 2	
	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR
Mn	3.7	4.2	2.8	3.9
As *	2.3	2.8	**1.6**	2.2
Co			**1.8**	2.0
Ti	**1.8**	**1.9**	**1.8**	**1.8**
Co	**1.5**	**1.7**		
Cr			**1.5**	**1.7**
V			**1.4**	**1.5**
Cr	1.2	1.4		
V	1.2	1.4		
Cu	1.2	1.4	1.4	1.4
P	0.9	1.2	1.0	1.4
Zn	1.0	1.1	1.2	1.2
Sn *	0.8	1.4	1.0	1.1
Mo	0.9	0.9	0.9	0.9
Ni	0.8	0.9	0.9	1.0
Pb	0.6	0.7	0.8	0.9
Cd	0.7	0.7	0.7	0.7
Hg	0.4	0.6	0.7	0.8

* analyses with poor reproducibility, hence somewhat less reliability.

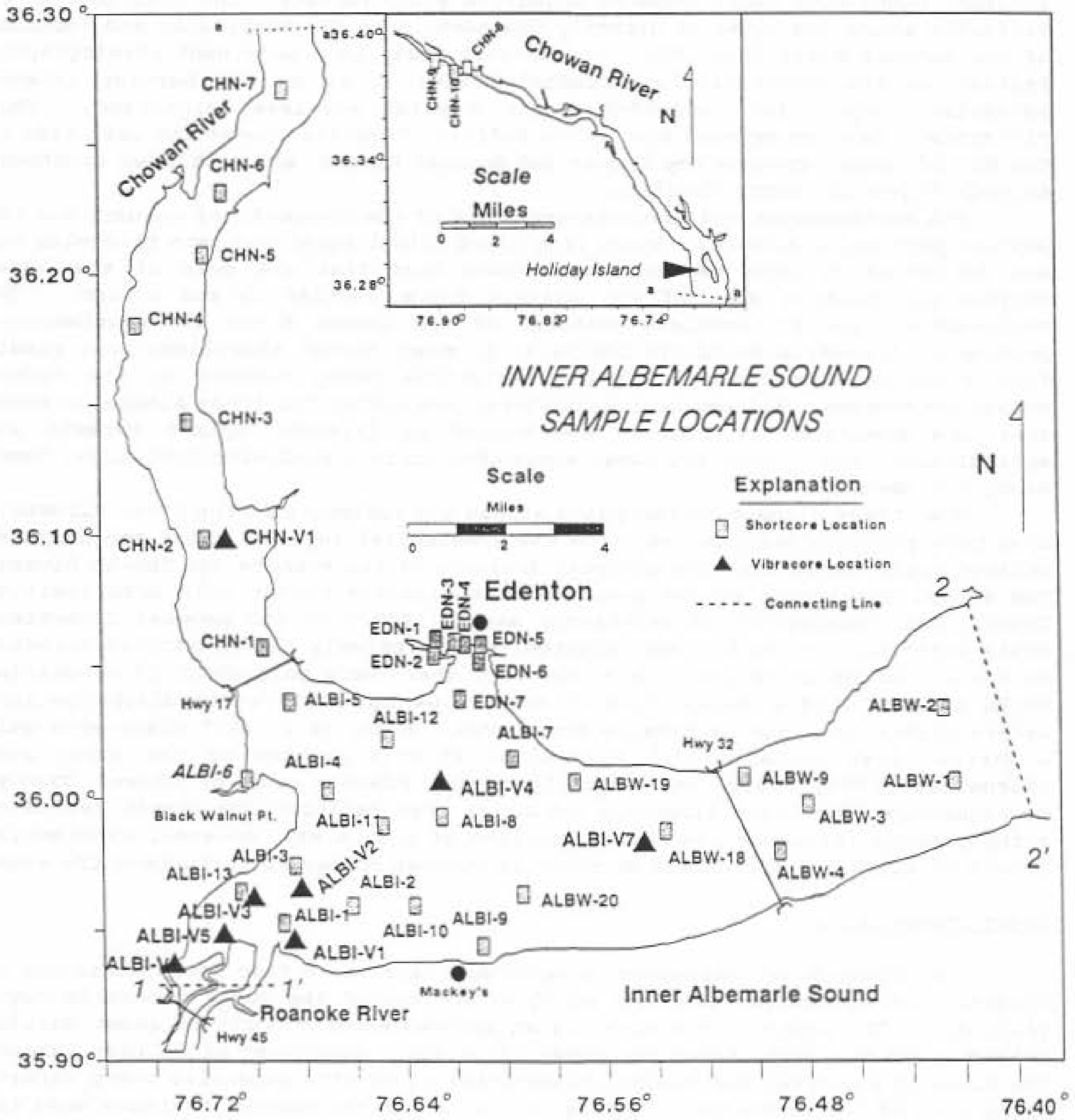


FIGURE E5. Sample location map of the Inner Albemarle Sound Area.

Sound. Figure E5 and Appendix A present the locations of all sediment samples collected within the Inner Albemarle Sound area and utilized for the following discussion.

Throughout the Inner Albemarle region, the shorelines are dominated by high sediment banks with local areas of extensive swamp forests. The distribution of different shoreline types is directly dependent upon the complexity and location of the Suffolk Scarp (Fig. B2). The Suffolk Scarp is a prominent physiographic feature on the North Carolina Coastal Plain; it is an old barrier island-estuarine complex left stranded during a prior sea-level highstand. This Pleistocene feature extends south from Suffolk, Virginia, forms the west side of the Dismal Swamp, crosses the Chowan and Roanoke Rivers, and continues southward through Plymouth, North Carolina.

The northeastern and southwestern sides of the Chowan River estuary and the western portion of Albemarle Sound from Black Walnut Point and into Batchelor Bay are dominated by high sediment bank shorelines that are part of the upper morphologic terrace west of the Suffolk Scarp barrier island system. The northwestern and southeastern portions of the Chowan River and southwestern portion of Albemarle Sound are dominated by swamp forest shorelines that result from riverine floodplains with low elevations being flooded by the modern estuarine systems. All sediment bank shorelines within the Inner Albemarle Sound area are dominated by erosion and backed by fringing upland forests and agricultural land. There are local areas that contain scattered individual homes along the shoreline.

Most trace element contaminants within the sediments in the Inner Albemarle area have probably been derived from the substantial input of point and nonpoint anthropogenic waste into the upstream drainage of the Roanoke and Chowan Rivers. The actual population of the counties that directly border this area (Bertie, Chowan, and Washington) is relatively small (1980 = 48,383 people; Tschetter, 1989) with only one small town, Edenton, and relatively few industries directly on the estuarine shoreline. As of May 1992 there were only about 27 associated NPDES permits with a design flow of about 2.04 mgd waste water discharge into waters within the Inner Albemarle Sound area. Also, as of 1987 there were only 4 marinas that contained 160 boat slips in this portion of the study area (Tschetter, 1989), which were totally in the Edenton area of Chowan County. Consequently, the Inner Albemarle estuarine area reflects low direct levels of anthropogenic influence over broad portions of this area. However, substantial levels of elemental enrichment do occur in samples collected throughout the area.

Lower Chowan River

The Chowan River represents a major drainage basin that flows south out of Virginia and discharges into the northwestern end of the Inner Albemarle Sound (Fig. B1). The Lower Chowan River is an embayed estuary north to about Holiday Island where the River turns northwest (Fig. E5). Northwest of Holiday Island, the River is a narrow, meandering, black-water river with extensive swamp forests along much of the shoreline. In this region, the River channel contains sand and is bordered by shallow perimeter platforms that consist of an eroding swamp-forest peat with scattered organic-rich mud accumulation. South of Holiday Island, the Lower Chowan River is a wide, embayed estuary with mostly eroding sediment-bank shorelines. The bottom sediments consist of sand on shallow perimeter platforms and thick accumulations of organic-rich mud in the wide and deeper, flat-bottomed central basin.

TABLE E5. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Lower Chowan River. Depths of the deep samples range from 11 to 38 cm below the sediment surface for an average depth of 25 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

TRACE ELEMENTS	N	CONCENTRATIONS (μg/g or ppm) SURFACE SAMPLES MEAN	MINIMUM	MAXIMUM	ENRICHMENT FACTORS DEEP SAMPLES MEAN N = 10	MAXIMUM	SURFACE SAMPLES MEAN N = 10	MAXIMUM
LOWER CHOWAN RIVER								
Mn	10	574.	186.	971.	**1.6**	3.0	**1.7**	2.9
Co	10	11.4	3.8	19.0	1.2	2.6	**1.7**	2.8
Pb	10	23.7	7.0	68.0	0.6	2.0	1.1	3.1
As *	10	5.4	2.2	10.1	1.3	3.1	1.4	2.4
Ni	10	5.2	1.2	8.1	**1.5**	3.8	1.2	**1.9**
V	10	28.0	8.6	38.2	1.1	2.5	1.2	**1.6**
Sn *	10	7.6	2.2	11.2	1.2	**1.6**	1.3	2.0
Cd	10	0.3	0.2	0.7	0.7	1.4	1.4	3.1
Ti	10	48.1	16.5	87.2	1.2	2.4	0.6	1.2
Mo	10	0.25	0.25	0.25	1.3	2.4	0.9	0.9
P	10	402.	225.	809.	0.6	1.1	1.0	2.0
Zn	10	56.8	26.5	92.3	0.6	**1.5**	1.1	**1.8**
Hg	10	0.11	0.02	0.21	0.3	1.1	0.8	**1.5**
Cu	10	9.4	4.5	13.8	0.8	1.3	0.9	1.3
Cr	10	7.7	2.4	11.9	0.8	1.2	0.7	1.1
Ca	10	2689.	1162.	4522.	1.3	2.4	1.1	**1.9**
Al	10	4196.	1373.	6332.	0.8	1.0	0.8	1.2
Si	10	1275.	785.	1470.	0.9	1.2	0.8	1.0
Na	10	83.4	32.8	164.	0.3	0.5	0.1	0.3

* analyses have poor reproducibility, hence somewhat low reliability.

Waste water from upstream industries, including a major paper mill located in Virginia, is probably the greatest source of trace elements in the Chowan River sediments. Several small industries in North Carolina do have permitted NPDES discharges into the Lower Chowan River with waste water discharges under two million gallons per day, including a major dye plant with a 1.5 mgpd permit. Ten sample sites were obtained along the Lower Chowan River (Fig. E5). Seven sites (CHN-1 through CHN-7) are in the estuarine portion and three sites (CHN-8 through CHN-10) are in the riverine portion.

Eleven of the 15 trace elements are substantially enriched in sediments of the Lower Chowan River and two trace elements are slightly enriched (Table E5). Even though these 13 trace elements are enriched in multiple samples within the Lower Chowan River sediments, their general concentrations are lower than in the Lower Roanoke River. Also, the distribution patterns of these trace elements are somewhat irregular. Specific samples contain substantial enrichments of a few elements, but the samples are scattered and the enriched elements change from sample to sample.

Some of this irregularity may be due to the variability in concentration of chemically inert sands and silts relative to the chemically reactive clay and organic contents. The relative proportions of these sediment components vary considerably from sample to sample. For example, CHN-5 has no enriched elements in either of the samples, whereas the samples on either side of CHN-5, CHN-4 and CHN-6 (Fig. E5), are relatively enriched in 12 and 11 trace elements, respectively. Table E6 suggests a relationship between trace element enrichment and clay and organic content for these three samples. CHN-5 is adjacent to the flank of the estuarine basin and directly off an industrial discharge with sediments that are dominantly silty sand with little clay or organic matter, and consequently no enriched elements. In contrast, the two sites further into the estuarine basin have considerably higher concentrations of clay and organic matter and are substantially enriched in eight trace elements (As, Cd, Co, Mn, Ni, P, Sn, and Ti) and slightly enriched in three others (Hg, V, and Zn).

TABLE E6. Relationship between trace element enrichment and sediment composition for selected samples in the Lower Chowan River estuary. See Figure E5 for sample location.

SAMPLE NO	ELEMENTS ENRICHED	SEDIMENT COMPOSITION % COARSE	%ORGANIC	%CLAY	RATIO OF SAND + SILT / CLAY + ORGANIC
CHN-5	0	91	5	9	6.7
CHN-4	7	57	8	43	1.1
CHN-6	10	53	22	47	0.8

Eleven elements are irregularly enriched in six samples collected around Tunis (CHN-8, CHN-9, and CHN-10) (Fig. E5). Six elements are substantially enriched in five of the samples with maximum enrichment factors as follows: Pb = 3.1 X, Cd = 3.0 X, Co = 2.8 X, Mn = 2.5 X, Mo = 2.4 X, and As = 2.0 X the ATM. The other three elements are only slightly enriched in three of the samples with maximum enrichment factors as follows: Zn = 1.8 X, V = 1.6 X, and Ni = 1.6 X the ATM. The Tunis area has in the recent past had several major industries discharging into the Chowan River and including a fertilizer and aluminum plants; neither of which operate any longer. No substantial phosphorus enrichment was found in these samples.

Edenton Bay

Edenton is a small urban area located at the northern end of Edenton Bay and is the only major town directly on the water within the Inner Albemarle area (Fig. B2). It was an important coastal seaport town in colonial North Carolina during the 18th and 19th centuries. Historic industrialization is evidenced by abundant ruined docks, pilings, and shipwrecks. Many portions of the shoreline and harbor region have been modified by dredging, filling, and bulkheading. Today, the waterfront of the small town is dominated by residential areas and parks, all with manicured lawns and gardens. The paved streets and parking lots have gutters and storm sewers that discharge storm runoff into the estuary.

The Edenton WWTP is the largest discharger of point source waste water with an NPDES permit to discharge up to one mgpd. Several other small industries have NPDES permits to discharge small and irregular amounts of waste water into the surrounding creeks and Edenton Bay. As of 1987, there were three marinas along the Edenton waterfront with 156 slips (Tschetter, 1989).

Seven sites were sampled in Edenton Bay with six being along the Edenton waterfront and adjacent creeks (Fig. E5). The resulting chemical data for the 14 samples are summarized in Table E7. Multiple samples from the Edenton waterfront contain both substantially and slightly enriched concentrations of ten trace elements with maximum enrichment factors as follows: Cu = 7.1 X, Cd = 3.3 X, Ni = 3.3 X, Pb = 2.6 X, P = 2.6 X, Sn = 3.0 X, Mn = 2.8 X, As = 2.5 X, Zn = 2.3 X, and Hg= 2.2 X the ATM. Two other trace elements are slightly enriched in only one sample each (Ti = 1.8 X, and Co = 1.5 X the ATM).

Two sites (EDN-1 and EDN-2) are associated with marinas in Pembroke Creek. All three of the samples are enriched in 4 elements (maximum enrichment factors: Cd = 3.3 X, Pb = 2.1 X, Sn = 2.8 X, and Zn = 2.3 X the ATM) while two of the samples are also enriched in 4 other elements (maximum enrichment factors: Cu = 7.1 X, P = 2.6 X, Co = 1.5 X, and Ni = 1.5 X the ATM). Copper, lead, and zinc are three elements that are ubiquitously concentrated in sediments in marinas, whereas cadmium, copper, mercury, phosphorus, and zinc are commonly enriched off waste water treatment plants throughout the Albemarle-Pamlico estuarine system (Riggs et al., 1991c).

Four sites (EDN-3, EDN-4, EDN-5, and EDN-6) are along the Edenton Bay waterfront. These eight samples are irregularly enriched in nine elements with maximum enrichment factors as follows: Mn = 2.8 X, Pb = 2.6 X, As = 2.5 X, Cd = 2.4 X, Hg = 2.2 X, Sn = 2.1 X, Cu = 2.0 X, P = 2.0 X, and Zn = 2.0 X the ATM. The one site that is well out into Edenton Bay (EDN-7) is only enriched in five elements (As, Mn, Ni, Sn, and Ti) and then either only slightly enriched or only substantially enriched in one of the two samples.

TABLE E7. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in Edenton Bay. Depths of the deep samples range from 16 to 50 cm below the sediment surface for an average depth of 38 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (μg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 6		N = 7	
EDENTON BAY								
Sn *	7	10.6	4.60	15.7	2.0	3.0	**1.9**	2.8
Cd	7	0.46	0.15	0.72	1.3	2.3	2.1	3.3
Cu	7	26.0	3.80	76.2	1.1	**1.5**	2.4	7.1
Pb	7	36.1	7.96	57.5	1.3	2.1	**1.7**	2.6
P	7	643.	152.	1040.	1.2	2.0	**1.6**	2.6
As *	7	3.97	0.90	8.80	**1.5**	2.5	1.1	2.3
Mn	7	429.	210.	907.	1.3	2.8	1.3	2.8
Zn	7	81.3	23.1	114.	1.2	**1.7**	**1.6**	2.3
Ni	7	5.06	1.99	6.54	1.4	3.3	1.2	**1.5**
Hg	7	0.13	0.02	0.18	1.1	2.2	1.0	1.3
Co	7	7.33	3.50	10.3	1.1	**1.4**	1.1	**1.5**
Ti	7	32.6	27.6	38.8	1.0	**1.8**	0.4	0.5
V	7	18.0	11.0	22.4	1.0	1.2	0.8	1.0
Cr	7	7.97	3.29	11.1	0.9	1.1	0.7	1.0
Mo	7	0.25	0.25	0.25	0.9	0.9	0.9	0.9

* analyses have poor reproducibility, hence somewhat low reliability.

Inner Albemarle Sound

Twenty one sites were sampled within the Inner Albemarle Sound area producing 42 sediment samples (Fig. E5). Chemical data for these samples are summarized in Table E8. Nine of the 15 trace elements are substantially enriched in multiple samples with maximum enrichment factors as follows: Hg = 6.5 X, Mn = 5.6 X, As = 5.1 X, Cr = 3.2 X, Co = 2.6 X, V = 2.5 X, Ti = 2.5 X, P = 2.1 X, and Ni = 2.0 X the ATM. Four trace elements are slightly enriched within the mud sediments in this area with only 12 samples being slightly enriched in zinc (up to 1.8 X the ATM), six samples in copper (up to 1.7 X the ATM), three samples in cadmium (up to 1.9 X the ATM), and two samples in lead (up to 1.6 X the ATM). No samples are enriched in molybdenum or tin.

Most sample sites directly off the mouth of the Roanoke River have generally low concentrations of the enriched elements. This is probably due to higher contents of chemically inert sand and silt from the Roanoke River in these samples. On the other hand, higher concentrations of trace elements occur in the richer mud sediments off the mouth of the Chowan River and extend southeast into the central and southern portion of Inner Albemarle Sound. Concentrations of all elements decrease significantly toward the east and generally approach mean concentrations east of the Highway 32, Albemarle Sound bridge (Fig. E5).

Middle Albemarle Sound Area

This portion of the estuarine system is bounded primarily by Perquimans and Tyrell Counties. Land use is dominated by forests and large-scale agriculture. These two counties have very small populations. The 1980 population of this region was 13,461 (Tschetter, 1989). The two largest towns are Hertford on the banks of the Perquimans River and Columbia on the banks of the Scuppernong River. In 1987, Tschetter (1989) reported two marinas with 44 boat slips in Tyrell County; one of these marinas is on the Scuppernong River in Columbia and the other is at the Alligator River bridge. A second small marina has since been built on the Columbia waterfront. The NPDES permits for this area include two small waste water treatment plants with no specified design flow into the Perquimans River at Hertford and three facilities that discharge into the Scuppernong River at Columbia. The Columbia WWTP is the largest discharger with a design flow of 150,000 gpd.

Figure E6 presents the distribution of samples within Middle Albemarle Sound and adjacent tributary estuaries. The trunk estuary becomes considerably wider at this point with one intermediate- and two large-size tributary estuaries on the north and one small- and one intermediate-size estuary on the south side. All of these estuaries are dominated by fresh water and irregular wind tides (Fig. D1).

Yeopim River

Yeopim River is a small tributary estuary on the north side of Albemarle Sound (Fig. E6). The shoreline is dominated by woodlands fronting extensive agricultural fields throughout the upland areas. Low density residential areas with septic systems are scattered along the River bank and there are no known NPDES discharge sites within this estuary.

These dominantly organic-rich (9%) mud (83%) samples generally contain low amounts of sand (average = 8%). This, in combination with the low levels of

TABLE E8. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Inner Albemarle Sound. Depths of the deep samples range from 13 to 51 cm below the sediment surface for an average depth of 38 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (μg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 21		N = 21	
INNER ALBEMARLE SOUND								
Mn	21	919.	175.	1271.	2.1	5.6	2.8	3.9
Hg	21	0.30	0.07	0.68	0.9	6.5	2.1	4.8
As *	21	8.6	2.8	13.0	**1.6**	5.1	2.3	3.5
Co	21	11.3	5.9	17.2	1.4	2.1	**1.7**	2.6
Cr	21	16.9	8.0	25.8	1.3	3.2	**1.6**	2.4
V	21	41.1	15.8	51.9	**1.7**	2.5	**1.7**	2.2
Ti	21	95.5	35.6	163.	**1.7**	2.5	1.3	2.2
Ni	21	5.1	2.3	8.4	1.0	**1.6**	1.2	2.0
P	21	466.	248.	828.	0.6	1.3	1.2	2.1
Zn	21	70.4	41.5	87.6	0.7	**1.8**	1.4	**1.7**
Cu	21	13.2	7.7	17.0	1.2	**1.7**	1.2	**1.6**
Pb	21	23.3	7.9	35.0	0.7	1.4	1.1	**1.6**
Cd	21	0.19	0.15	0.42	0.7	0.7	0.9	**1.9**
Mo	21	0.25	0.25	0.25	0.9	0.9	0.9	0.9
Sn *	21	3.9	1.1	7.5	0.8	1.4	0.7	1.3
Ca	21	2173.	1312.	3333.	0.6	1.2	0.9	1.4
Al	21	6226.	3057.	7576.	1.2	**1.5**	1.2	**1.5**
Si	21	1478.	1229.	1699.	1.0	1.0	1.0	1.1
Na	21	474.	44.6	1633.	0.9	2.3	0.8	2.7

* analyses have poor reproducibility, hence somewhat low reliability.

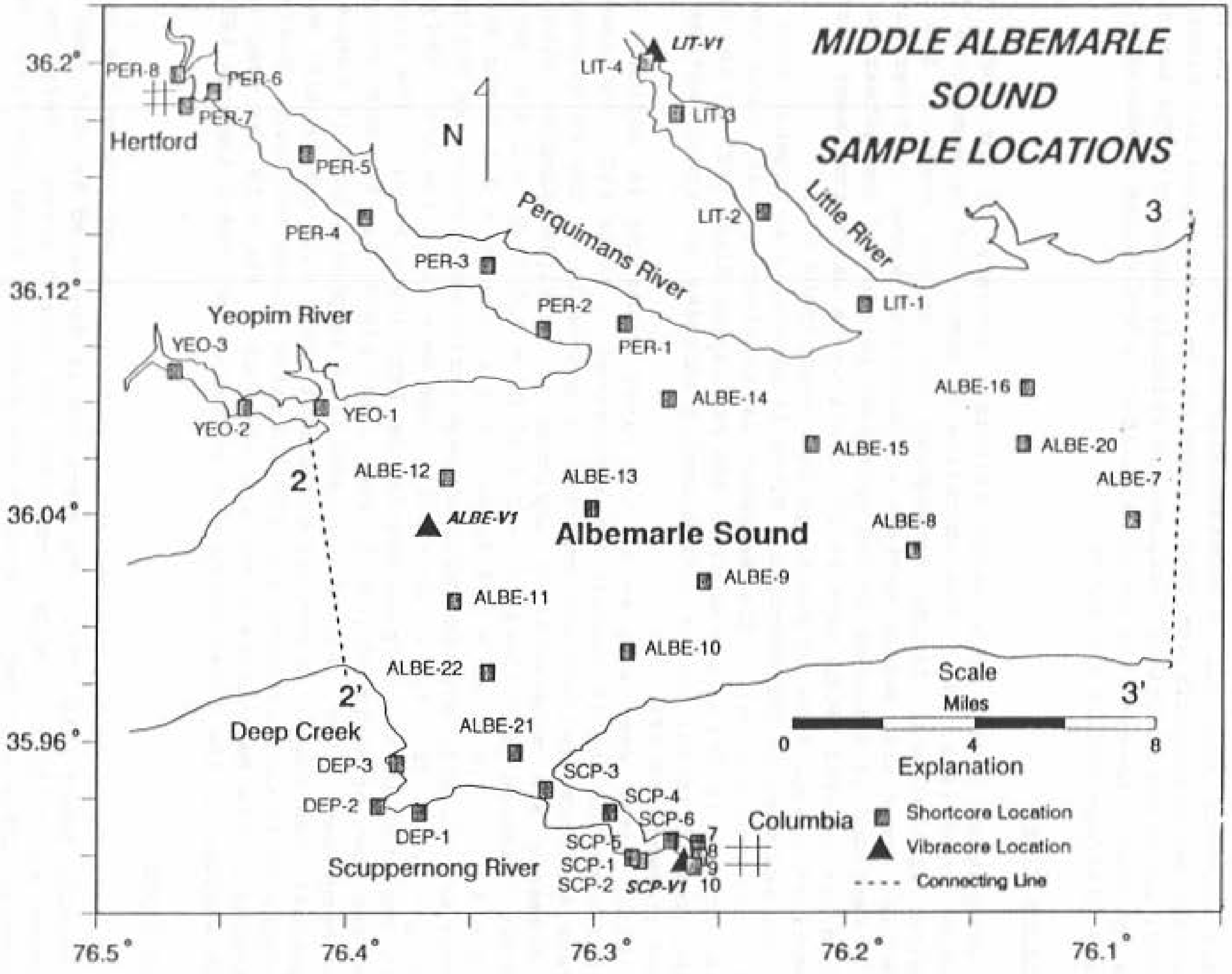


FIGURE E6. Sample location map of the Middle Albemarle Sound Area.

trace element enrichment, suggests that there is a minimal supply of trace elements entering this estuarine system.

Three sites were sampled in the River producing six total sediment samples. Chemical data for the three surface samples are summarized in Table E9. Of the 15 trace elements, only tin is substantially enriched (Sn = 2.4 X the ATM) with no elements being slightly enriched. Three of the six samples are substantially enriched, while two additional samples are slightly enriched. The source of the tin is not clear, however, it could be related to activities associated with the military platform within the River.

Perquimans River

Perquimans River is a large tributary estuary on the north side of Albemarle Sound (Fig. E6). The shoreline is dominated by woodlands fronting extensive agricultural fields throughout the upland areas. Low density residential areas with septic systems are scattered along the River bank. The town of Hertford is situated in the uppermost portion of the estuarine system. Hertford has several NPDES permits for small waste water treatment plants with no specified design flow to discharge into Perquimans River.

The sediment in the Perquimans River is generally an organic-rich (12.6%), sandy (16%) mud (71.4%). The sediment is sandiest (12.4%) with the lowest organic content (5.7%) at the mouth of the Perquimans River (PER-1) and decreases in sand content (6.0%) with a corresponding increase in organic matter (28.4%) upriver to Hertford (PER-6).

Eight sites were sampled in the River producing 16 sediment samples. Chemical data for the 16 samples are summarized in Table E10. Fourteen of the 15 trace elements analyzed are enriched in sediments in the Perquimans River. Nine elements are substantially enriched in multiple samples with maximum enrichment factors as follows: Ni = 3.3 X, Cd = 3.0 X, Ti = 2.9 X, Sn = 2.8 X, Mo = 2.8 X, P = 2.6 X, Mn = 2.4 X, As = 2.3 X, and Pb = 2.1 X the ATM. Five elements are slightly enriched with maximum enrichment factors as follows: Zn = 1.8 X, V = 1.7 X, Cr = 1.6 X, Cu = 1.5 X, and Co = 1.5 X the ATM. Only mercury is not enriched in any samples within the Perquimans River. The three sites around the town of Hertford (PER-6, PER-7, and PER-8) are the most contaminated in the Perquimans River. All of the cadmium (4 samples), lead (4 samples), zinc (2 samples), and copper (1 sample) enrichment along with substantial enrichment of phosphorus (3 samples) occurs at these 3 sites around Hertford. Twelve of the 16 samples in the Perquimans River are enriched in tin with the samples in the middle section of the River being most contaminated (PER-3 through PER-6).

Little River

Little River is an intermediate size tributary estuary on the north side of Albemarle Sound (Fig. E6). The shoreline is dominated by woodlands fronting extensive agricultural fields throughout the upland areas. Very low density residential areas with septic systems are scattered along the River bank. No known NPDES discharge sites exist along this River.

The sediment at the entrance to Little River (LIT-1) is very sandy (45% sand) while the sediments within the Little River are dominantly organic-rich (12%) mud (79%) with low amounts of sand (average = 9%). This, in combination with the low levels of trace element enrichment, suggests that there is a minimal supply of trace elements entering this estuarine system.

TABLE E9. Summary of mean and maximum enrichment factors for 15 trace elements in surface sediments from Yeopim and Little Rivers, two tributary estuaries on the north side of Albemarle Sound and Deep Creek, a tributary estuary on the south side of Albemarle Sound. Enrichment factors in bold print are slightly enriched (EF >1.5X to <2X ATM) relative to the Albemarle Sound trimmed mean.

	YEOPIM RIVER SURFACE SAMP N = 3		LITTLE RIVER SURFACE SAMP N = 4		DEEP CREEK SURFACE SAMP N = 3	
TRACE ELEMENTS	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR
As *	0.8	1.1	0.6	1.3	0.4	0.9
Cd	0.7	0.7	0.7	0.7	1.0	**1.6**
Co	0.7	0.8	0.7	0.8	0.8	1.0
Cr	1.0	1.2	1.2	1.4	0.7	1.1
Cu	1.0	1.1	1.0	1.0	0.7	1.0
Hg	1.0	1.1	0.9	1.0	0.5	0.8
Mn	0.6	0.9	0.6	0.8	0.3	0.4
Mo	0.9	0.9	0.9	0.9	0.9	0.9
Ni	0.8	0.9	0.7	0.8	0.6	1.0
P	0.9	1.2	1.2	**1.5**	0.5	0.9
Pb	1.0	1.2	1.3	1.4	0.6	1.1
Sn *	2.0	2.4	**1.6**	**1.7**	**1.7**	2.3
Ti	0.5	0.7	0.6	1.0	1.0	**1.7**
V	1.1	1.4	1.3	**1.6**	1.0	**1.9**
Zn	0.8	1.0	0.7	0.8	0.5	0.9

* analyses with poor reproducibility, hence somewhat less reliability.

TABLE E10. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Perquimans River. Depths of the deep samples range from 29 to 57 cm below the sediment surface for an average depth of 38 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (μg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 8		N = 8	
PERQUIMANS RIVER								
Sn *	8	10.9	9.38	13.7	**1.9**	2.8	**1.9**	2.4
Cd	8	0.27	0.15	0.66	0.8	2.0	1.2	3.0
Mn	8	334.	219.	780.	0.7	**1.5**	1.0	2.4
As *	8	3.44	0.90	8.68	0.8	**1.7**	0.9	2.3
Pb	8	30.4	18.3	45.3	0.5	**1.5**	1.4	2.1
P	8	581.	280.	1062.	0.5	1.0	1.4	2.6
Ni	8	4.83	3.96	5.49	**1.5**	3.3	1.1	1.2
Mo	8	0.25	0.25	0.25	1.4	2.8	0.9	0.9
Ti	8	55.0	29.6	80.5	1.4	2.9	0.7	1.1
Zn	8	55.4	40.5	93.1	0.7	**1.6**	1.1	**1.8**
V	8	26.7	10.7	38.8	1.0	**1.6**	1.1	**1.7**
Cu	8	10.1	7.81	15.8	0.7	0.9	0.9	**1.5**
Cr	8	11.0	6.52	13.2	0.9	**1.6**	1.0	1.2
Co	8	6.62	5.58	8.21	1.1	**1.5**	1.0	1.2
Hg	8	0.11	0.05	0.15	0.4	1.2	0.8	1.1

* analyses have poor reproducibility, hence somewhat low reliability.

Four sites were sampled in Little River producing eight sediment samples. Chemical data for the surface samples at these four sites are summarized in Table E9. Of the 15 trace elements, no elements are substantially enriched and three elements are slightly enriched with maximum enrichment factors as follows: Sn = 1.7 X, P = 1.5 X, and V = 1.6 X the ATM within the mud sediments in this region. Six of the eight total samples are enriched in tin, which is most enriched at the mouth of Little River with concentrations decreasing up stream; this suggests a source from Albemarle Sound. Only two samples are enriched in phosphorus and vanadium.

Deep Creek

Deep Creek is a very small tributary estuary on the southwest side of Bull Bay in southern Albemarle Sound (Fig. E6). The riverine portion of Deep Creek is ditched and drains extensive agricultural land throughout the upland reaches. However, within the estuarine portion, the shoreline is dominated by extensive swamp forest with no residential development. No known NPDES permits discharge into this Creek.

The sediments have relatively high sand contents (23%) with high concentrations of organic matter (24%). This, in combination with the low levels of trace element enrichment, suggests that there is a minimal supply of trace elements entering this estuarine system.

Three sites were sampled in Deep Creek producing 6 sediment samples. Chemical data for the three surface samples are summarized in Table E9. Of the 15 trace elements, only tin is substantially enriched (Sn = 2.3 X the ATM) and 3 elements are slightly enriched with maximum enrichment factors as follows: V = 1.9 X, Ti = 1.7 X, and Cd = 1.6 X the ATM within the mud sediments in this region. Five of the six total sediment samples are enriched in tin, whereas only two are enriched in vanadium, titanium, and cadmium. Phosphorus concentrations are surprisingly low considering the amount of agricultural activity occurring within the Deep Creek area.

Scuppernong River

Scuppernong River is an intermediate-size tributary estuary on the south side of Albemarle Sound (Fig. E6). The shoreline is dominated by extensive swampforests and associated adjacent wooded upland areas. Low density residential areas with septic systems occur locally along the River bank. The town of Columbia is situated in the transition zone from an embayed estuary to the black water riverine portion of the Scuppernong River. Three NPDES waste water discharge permits exist for the Scuppernong River. Two of the permits have no specified design flow while the largest permit is for the Columbia WWTP to discharge 150,000 gpd into a ditch north of Columbia. Two marinas are located on the Scuppernong, the largest occurs about one mile downstream from Columbia and a small marina is now located along the Columbia waterfront.

The sediment in the Scuppernong River is generally an organic-rich (16.0%), very sandy (39.2%), mud (44.7%). Sediment at the mouth of the Scuppernong River (SCP-3) is generally a sand (73.3%) with very low organic content (3.8%); the sand content decreases (13.2%) with a corresponding increase in organic matter (10.8%) within the estuarine portion of the Scuppernong River (SCP-4). The organic matter continues to increase upstream to 32.4%. Samples from the Columbia waterfront (SCP-7 and SCP-10) have extremely variable sand contents that range from 5.6% up to 82.0% and organic contents that vary from 5.7% up to 86.4%.

Ten sites were sampled in the Scuppernong River producing 20 sediment samples. Chemical data for all the samples are summarized in Table E11. Eight of the 15 trace elements analyzed are substantially enriched with maximum enrichment factors as follows: Pb = 10.4 X, Cu = 5.4 X, P = 4.5 X, Sn= 2.9 X, Cd = 2.6 X, Zn = 2.4 X, Ni = 2.1 X, and Ti = 2.0 X the ATM in sediments in the Scuppernong River. Cobalt is the only element that is slightly enriched (Co = 1.6 X the ATM) within the mud sediments in this region. Six elements (As, Cr, Hg, Mn, Mo, and V) are not enriched in the Scuppernong River.

One site (SCP-7) was located in the ditch receiving the discharge from the Columbia WWTP and one site (SCP-8) was located in the River off the ditch (SCP-8). These sites were substantially enriched in two elements (Zn = 2.4 X and P = 2.3 X the ATM) and slightly enriched in five elements in one sample each (Cd = 1.8 X, Sn = 1.7 X, Zn = 1.7 X, Cu = 1.5 X, and Pb = 1.5 X the ATM). Two sites (SCP-1 and SCP-2) were located in the excavated area of the marina downstream of Columbia. The surface samples in the marina were substantially enriched in copper (5.4 X and 2.6 X the ATM); copper concentration decreased with depth; one sample at -6 cm was slightly enriched (1.5 X the ATM) whereas the sample at -16 cm was not significantly enriched (1.3 X the ATM). No other elements were enriched in the marina.

Two sites were located along the Columbia waterfront (SCP-9 and SCP-10). These four samples are the most contaminated of all samples from the Scuppernong River. Four elements are substantially enriched with maximum enrichment factors as follows: Pb = 10.4 X, P = 4.5 X, Cd = 2.6 X, and Sn = 2.2 X the ATM. An additional four elements are slightly enriched with maximum enrichment factors as follows: Zn = 1.9 X, Cu = 1.7 X, Co = 1.5 X, and Ni = 1.6 X the ATM. The enrichment of these trace elements generally decreases downstream (Fig. E6): site SCP-6 has ten enriched elements, site SCP-5 has seven enriched elements, site SCP-4 has five enriched elements, and site SCP-3 at the mouth of the Scuppernong River has no enriched elements.

Middle Albemarle Sound

Thirteen sites were sampled within the Middle Albemarle Sound area, producing 25 sediment samples (Fig. E6). Chemical data for these samples are summarized in Table E12. Six of the 15 trace elements are substantially enriched with maximum enrichment factors as follow: Mo = 4.9 X, As = 2.4 X, Ti = 2.3 X, V = 2.1 X, Sn = 2.2 X, and Ni = 2.1 X the ATM. Three trace elements are slightly enriched with maximum enrichment factors as follow: Hg = 1.8 X, Mn = 1.6 X, and Co = 1.6 X the ATM within the mud sediments in this region. No samples are enriched in chromium, copper, lead, zinc, phosphorus, or cadmium.

Only seven sites (ALBE-9, ALBE-11, ALBE-12, ALBE-13, ALBE-15, ALBE-16, and ALBE-20) contain substantially enriched elements. These seven sites occur down the central axis of Albemarle Sound and are dominantly clays (average = 48%). Three sites (ALBE-8, ALBE-21, and ALBE-22) have no samples enriched in any of the 15 trace elements. The other three sites (ALBE-7, ALBE-10, and ALBE-14) are only slightly enriched in As, Mn, Sn, and V in a few of the samples. All six of the latter sites are on the outer edge of the central basin along the south shore of Albemarle Sound with 21 and 22 occurring within Bull Bay. The samples along the outer edges of the central basin contain decreasing concentrations of clays (average = 19%) and are composed dominantly of sands and silts derived from the shallow perimeter platforms. The two sites at the mouth of the Scuppernong River

TABLE E11. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Scuppernong River. Depths of the deep samples range from 6 to 40 cm below the sediment surface for an average depth of 23 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (μg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM N = 10	MEAN	MAXIMUM N = 10
SCUPPERNONG RIVER								
Pb	10	41.9	8.65	227.	1.0	3.5	**1.9**	10.4
P	10	611.	99.0	1820.	0.6	2.3	**1.5**	4.5
Sn *	10	7.13	2.33	13.8	**1.6**	2.9	1.3	2.5
Cu	10	16.5	3.30	58.6	0.9	**1.7**	**1.5**	5.4
Cd	10	0.28	0.15	0.57	1.0	**1.8**	1.2	2.6
Zn	10	58.9	20.2	122.	0.8	**1.7**	1.2	2.4
Ni	10	3.59	1.11	7.90	0.9	2.1	0.8	**1.8**
Ti	10	32.3	11.9	61.6	0.8	2.0	0.4	0.8
Co	10	5.83	1.78	10.8	0.7	**1.6**	0.9	**1.6**
As *	10	1.86	0.90	4.86	0.4	0.8	0.5	1.3
Hg	10	0.10	0.02	0.17	0.6	1.2	0.7	1.2
Cr	10	6.22	2.06	11.9	0.6	1.2	0.6	1.1
V	10	12.7	2.79	22.2	0.6	1.1	0.5	0.9
Mo	10	0.25	0.25	0.25	0.9	0.9	0.9	0.9
Mn	10	99.9	22.4	291.	0.2	0.5	0.3	0.9

* analyses have poor reproducibility, hence somewhat low reliability.

TABLE E12. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Middle Albemarle Sound. Depths of the deep samples range from 32 to 37 cm below the sediment surface for an average depth of 35 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (µg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 12		N = 13	
MIDDLE ALBEMARLE SOUND								
Sn *	13	7.48	1.10	12.5	1.4	2.0	1.3	2.2
V	13	35.4	7.91	48.3	1.0	**1.6**	**1.5**	2.1
As *	13	2.22	0.90	5.89	1.1	2.4	0.6	**1.6**
Mo	13	0.25	0.25	0.25	**1.9**	4.9	0.9	0.9
Ti	13	66.4	29.5	79.6	**1.5**	2.3	0.9	1.1
Ni	13	3.83	0.30	4.92	1.3	2.1	0.9	1.1
Hg	13	0.11	0.02	0.24	0.2	0.2	0.8	**1.8**
Mn	13	305.	35.1	528.	0.9	1.3	1.0	**1.6**
Co	13	6.07	1.11	7.76	1.0	**1.6**	0.9	1.2
Cr	13	10.6	2.23	14.9	0.9	1.3	1.0	1.4
Cu	13	9.81	2.03	13.6	0.6	1.0	1.0	1.3
Pb	13	17.4	2.52	26.8	0.3	0.5	0.9	1.2
Zn	13	34.2	9.40	51.5	0.5	0.8	0.7	1.0
P	13	253.	15.2	347.	0.5	0.8	0.6	0.9
Cd	13	0.15	0.15	0.15	0.7	0.7	0.7	0.7

* analyses have poor reproducibility, hence somewhat low reliability.

in Bull Bay, contain more sand (average = 83%) than any other site in Middle Albemarle Sound and consequently these samples have extremely low enrichment factors.

Outer Albemarle Sound Area

This portion of the estuarine system is characterized by fresh to low-brackish water, irregular wind tides, and high wave energy due to the large fetch. The area includes Pasquotank, Camden, and Currituck Counties on the north and Tyrell and Dare Counties on the south. The population for the southern portion of this area is essentially nil with no towns; the land areas of Dare and Tyrell Counties are dominantly forest with some large-scale agricultural operations. There is a significant population on the north side of Albemarle Sound, with 34,291 people in Pasquotank and Camden Counties in 1980 and an additional 11,089 people in Currituck County (Tschetter, 1989). Most of this population is located in the area of Elizabeth City, a major urban region at the northern end of the Pasquotank River estuary.

Figure E7 presents the distribution of samples within Outer Albemarle Sound and adjacent tributary estuaries. The trunk estuary is very wide in this region with two large tributary estuaries on the north and one very large tributary estuary on the south side. The tributary estuaries are dominated by fresh water and irregular wind tides (Fig. D1), whereas salinities within the trunk estuary vary from fresh to low brackish depending upon the season and storm patterns.

Pasquotank River

Pasquotank River is a large tributary estuary on the north side of Albemarle Sound (Fig. E7). The shoreline is dominated by woodlands fronting extensive agricultural fields throughout the upland areas. Low density residential areas with septic systems are scattered along the River bank. Elizabeth City, a major urban region is situated in the uppermost portion of the estuarine system. It was an important coastal seaport town in colonial North Carolina during the 18th and 19th centuries. Historic industrialization is evidenced by abundant ruined docks, pilings, and shipwrecks. Today, the waterfront is dominated by ruins of the historic industrial sites and wharfs. Some portions of the shoreline and harbor region have been modified by dredging, filling, and bulkheading. The paved streets and parking lots have gutters and storm sewers that discharge storm runoff into the estuary.

In 1987, Tschetter (1989) reported two marinas with 74 boat slips in Pasquotank County and two marinas with 38 boat slips in Camden County. There are at least four NPDES permits in this area, all of which discharge either into tributaries to the Pasquotank River or the River directly. The largest discharger is the Elizabeth City WWTP which has a design flow up to 2.5 mgpd of waste water. There are two permits that discharge up to 20,000 gpd into Newbegun Creek and one permit to discharge a limited amount of waste water on an irregular basis into Knobbs Creek. In addition the U.S. Coast Guard has a large airport facility on Newbegun Creek and the west shore of the Pasquotank River.

The sediment in the Pasquotank River is generally an organic-rich (15%), sandy (24.7%), mud (58.7%). The sediment is generally the sandiest (71%) with the lowest organic content (3%) at the mouth of the Pasquotank River (PAS-1) and decreases in sand content (5%) with a corresponding increase in organic matter (18%) and mud (95%) upriver to Elizabeth City (PAS-12).

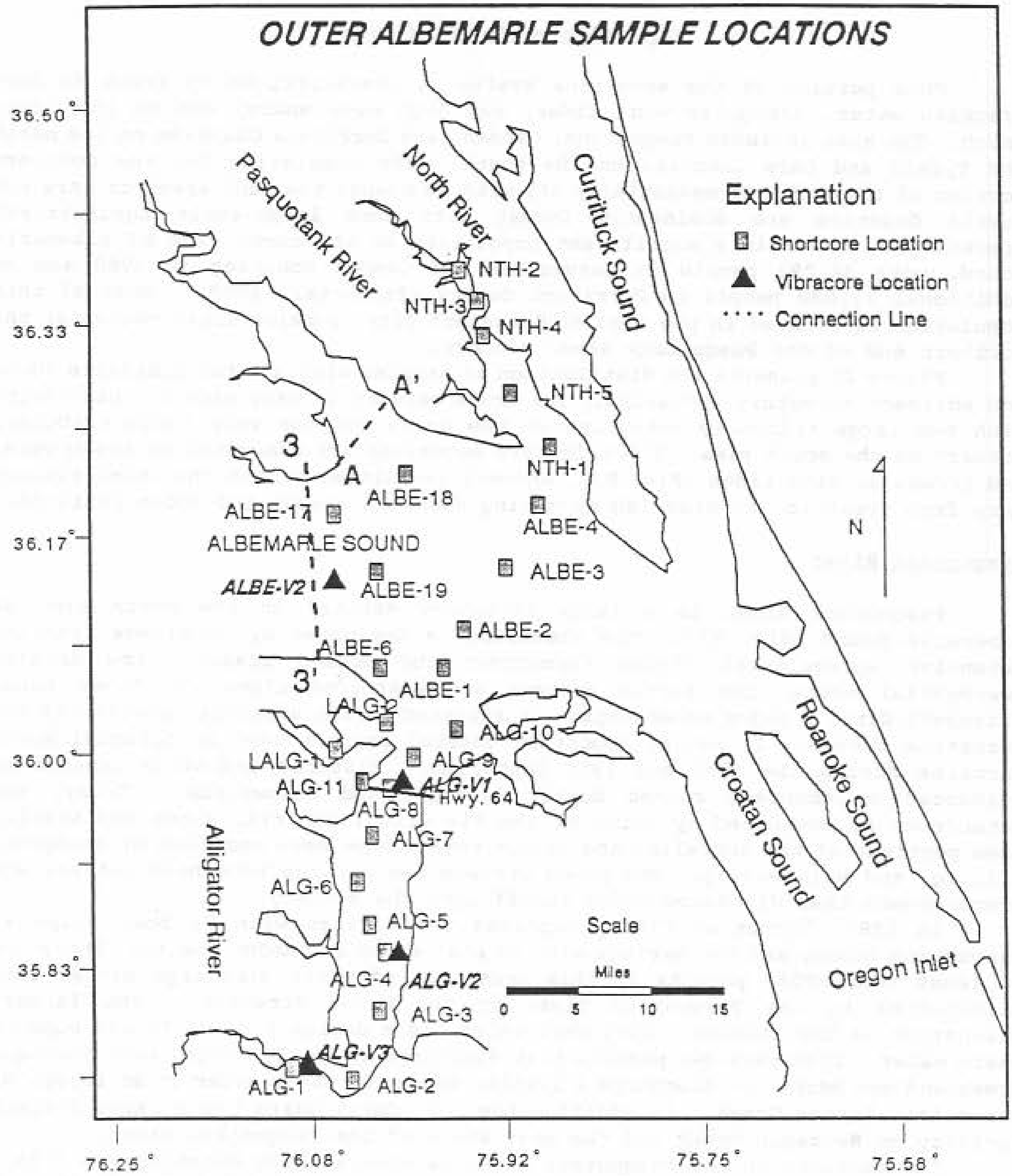


FIGURE E7. Sample location map of the Outer Albemarle Sound Area.

Twenty eight sites were sampled in the River (Fig. E8) producing 50 sediment samples. Chemical data for these 50 samples are summarized in Table E13. All 15 of the trace elements analyzed are enriched in sediments in the Pasquotank River. Twelve elements are substantially enriched with maximum enrichment factors as follow: Pb = 30.3 X, Zn = 13.3 X, Cd = 12.9 X, Cu = 7.3 X, Mo = 5.6 X, Hg = 4.7 X, P = 3.5 X, Ti = 3.4 X, Sn = 3.2 X, Ni = 2.7 X, As = 2.4 X, and Cr = 2.0 X the ATM. Three elements are slightly enriched with maximum enrichment factors as follow: Co = 1.7 X, Mn = 1.7 X, and V = 1.6 X the ATM within the mud sediments in this region.

No sample sites in the entire Pasquotank River are free of enriched trace elements. Only two sites (PAS-3 and PAS-7), which are located at the mouth of Newbegun Creek (Fig. E8), are not substantially enriched in any trace elements; however, these sites are slightly enriched in cadmium, tin, and titanium. The three sites in Newbegun Creek (PAS-4, PAS-5, and PAS-6) are enriched in multiple elements (10 of the 15) that increase in concentration and numbers of elements systematically into the Creek. Figure E9 demonstrates the changes in downstream pattern of elemental enrichment within the sediments of Newbegun Creek. Enrichment increases from PAS-7 (Ti = 1.5 X the ATM) to PAS-3 (Sn = 1.8 X, Cd = 1.7 X, and Ti = 1.5 X the ATM), to PAS-6 (Cd = 2.9 X, Sn = 2.3 X, P = 2.1 X, Ti = 1.8 X, Pb = 1.5 X, and Cr = 1.5 X the ATM), to maximums at PAS-5 (Cd = 12.9 X, Zn = 6.0 X, Hg = 4.0 X, Cu = 3.0 X, Pb = 2.7 X, P = 2.1 X, Cr = 2.0 X, and Sn = 1.5 X the ATM). Concentrations decrease further up the Creek to PAS-4 (Cd = 3.1 X, Zn = 2.3 X, Pb = 1.6 X, Cu = 1.6 X, As = 1.6 X, Sn = 1.6 X, and P = 1.5 X the ATM).

The site at the mouth of the Pasquotank River (PAS-1) and off the U.S. Coast Guard airport facility (PAS-8) are substantially enriched only in Ti in all samples; maximum enrichment factors range from 2.0 to 2.5 X the ATM. Figure E10 demonstrates that the sites within the main axis of the Pasquotank River are enriched in multiple elements that generally increase in both number of elements enriched and elemental concentrations upstream towards Elizabeth City waterfront. The sample at the mouth of the Pasquotank River (PAS-1) is enriched in one element (Ti), PAS-2 is enriched in six elements, PAS-9 is enriched in seven elements, and all samples in the Elizabeth City area (from PAS-10 to PAS-25) are enriched in nine elements. Six sites (PAS-19, PAS-20, PAS-21, PAS-22, PAS-25, and PAS-28) are located in front of historic and active dock facilities. These sites are substantially contaminated with eight elements with very high maximum enrichment factors as follows: Pb = 30.3 X, Zn = 13.3 X, Cd = 8.8 X, Cu = 7.3 X, Hg = 4.4 X, P = 3.3 X, Sn = 2.3 X, and Cr = 2.0 the ATM). Three other elements are only slightly enriched with maximum enrichment factors as follows: As = 1.7 X, Co = 1.7 X, and Ni = 1.7 X the ATM.

Two sites are adjacent to the Elizabeth City WWTP discharge (PAS-26 and PAS-27). These samples are substantially enriched in seven elements with maximum enrichment factors as follows: Cd = 12.4 X, P = 3.5 X, Pb = 3.4 X, Hg = 3.3 X, Sn = 2.7 X, Zn = 2.3 X, and Cu = 2.2 X the ATM. These samples are slightly enriched in two additional elements with maximum enrichment factors as follows: Ni = 1.8 X and Cr = 1.6 X the ATM. Three sites (PAS-14, PAS-23, and PAS-24) occur adjacent to marinas of various sizes and ages. These sites are enriched in 9, 6, and 5 elements, respectively; however, all sediments surrounding these sites are so contaminated with the same elements that it is highly probable that this enrichment is not due solely to the marinas alone. Rather, contamination throughout the entire Elizabeth City waterfront region is probably in part due to generally high levels of industrial activity within the harbor region over the

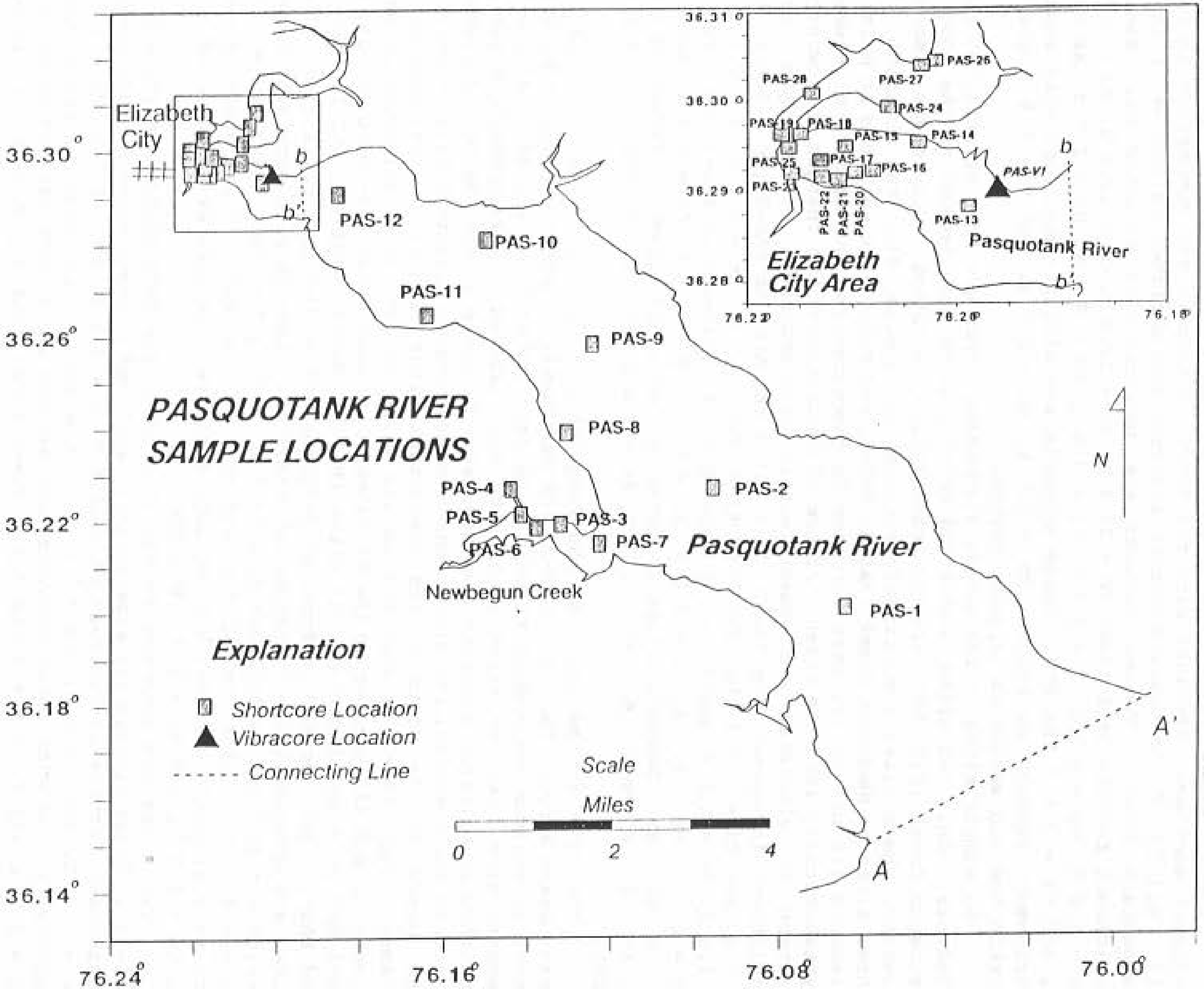


FIGURE E8. Sample location map of the Pasquotank River.

TABLE E13. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Pasquotank River. Depths of the deep samples range from 17 to 55 cm below the sediment surface for an average depth of 33 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (µg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 21		N = 29	
PASQUOTANK RIVER								
Pb	29	75.6	3.97	659.	1.7	22.7	3.5	30.3
Cd	29	0.78	0.15	2.77	1.4	12.9	3.5	12.5
Zn	29	102.	13.4	668.	0.9	6.0	2.0	13.3
Cu	29	20.0	3.34	50.7	1.1	7.3	**1.9**	4.7
Hg	29	0.22	0.02	0.66	0.7	4.0	**1.6**	4.7
P	29	606.	55.0	1420.	0.7	2.8	**1.5**	3.5
Sn *	29	9.21	1.10	15.2	**1.9**	3.2	**1.6**	2.7
Mo	29	0.27	0.25	0.89	**1.5**	5.6	1.0	3.1
As *	29	3.14	0.90	8.74	0.8	2.4	0.8	2.3
Ti	29	76.5	14.5	171.	1.7	3.4	1.0	2.3
Cr	29	11.12	2.56	21.6	1.0	**1.7**	1.0	2.0
Ni	29	4.26	0.30	7.50	1.3	2.7	1.0	**1.8**
Co	29	5.73	1.46	11.2	0.8	**1.6**	0.9	**1.7**
V	29	16.7	1.45	35.7	0.9	**1.6**	0.7	**1.5**
Mn	29	121.	11.7	231.	0.5	**1.7**	0.4	0.7

* analyses have poor reproducibility, hence somewhat low reliability.

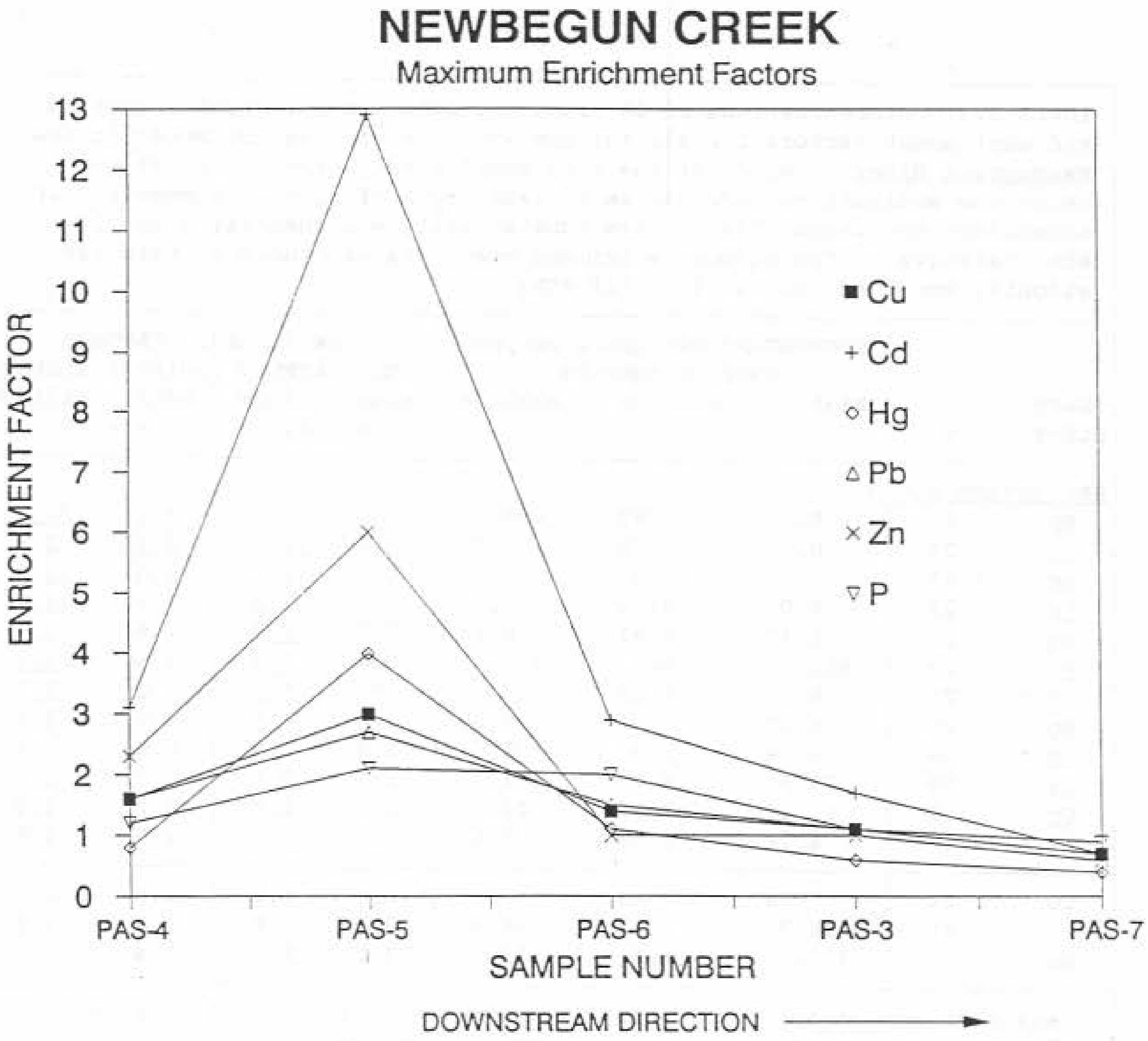


FIGURE E9. Downstream plot of maximum enrichment factors for Newbegun Creek. Sample sites are located on Figure E2 and in the Appendix.

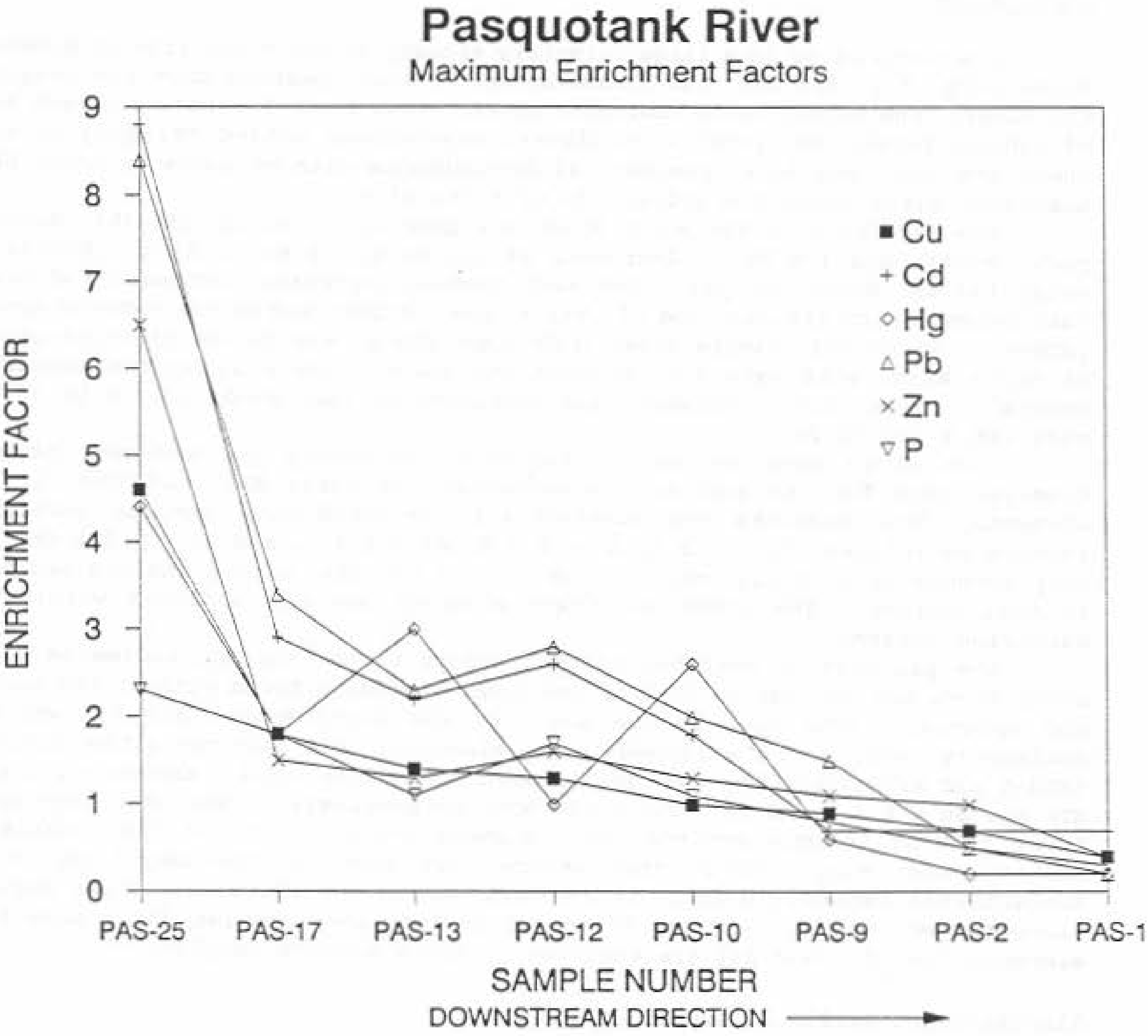


FIGURE E10. Downstream plot of maximum enrichment factors for Pasquotank River. Sample sites are located on Figure E2 and in the Appendix.

past several hundred years; this would be in addition to what is being contributed today.

North River

The North River is a large tributary estuary on the north side of Albemarle Sound (Fig. E7) with the U.S. Intracoastal Waterway passing down the length of the River. The shoreline is dominated by extensive swamp forests with vast areas of upland forest and local agricultural development behind fringing forests. There are only very local residential developments with no towns or known NPDES discharge sites along the shorelines of North River.

The sediments in the North River are generally a sandy (18.7%), organic-rich (6.8%), mud (74.5%). Sediments at the mouth of North River (NTH-1) are muddy (31.8%) sands (65.3%). The sand content decreases northward and grades into organic-rich (15.2%), mud (79.5%) at the northern end of the embayed estuary (NTH-4). Northward, sample sites (NTH-3 and NTH-2) are in the riverine portion of North River with extensive marshes and swamp forests along the meandering channel. These latter sediments are dominated by very sandy (31.7% to 37.7%), muds (55.5% to 63.3%).

Five sites were sampled in the River producing ten sediment samples. Chemical data for the samples are summarized in Table E14. Of the 15 trace elements, four elements are substantially enriched with maximum enrichment factors as follows: Mo = 3.3 X, Sn = 2.1 X, Ni = 2.3 X, and Ti = 2.3 X the ATM. Only arsenic is slightly enriched (As = 1.7 X the ATM) within the mud sediments in this region. The other ten trace elements are not enriched within this estuarine system.

The patterns of enriched trace elements in the surface sediments of the North River are similar to that of the Outer Albemarle Sound without the mercury and vanadium. The site at the mouth of the North River (NTH-1), which is dominantly sand, is not enriched in any elements. The next two sites northward (NTH-5 and NTH-4) are enriched in 2 elements each (Mo = 2.8 X and Sn = 1.5 X the ATM and Sn = 2.1 X and As = 1.5 X the ATM, respectively). The next site up the River (NTH-3) is only enriched in 1 element (Sn = 1.6 X the ATM), while the northern-most site (NTH-2) that occurs just south of the beginning of the Intracoastal Waterway ditch, is not enriched in any elements. Five enriched elements (Mo, Ni, Sn, As, and Ti) occur in four deep samples while only three elements (Mo, Sn, and As) are enriched in three surface samples.

Alligator and Little Alligator Rivers

Alligator River is a very large, embayed, black-water tributary estuary on the south side of Albemarle Sound (Fig. D1). The shoreline is dominated by extensive swampforests and associated woodlands in the adjacent upland areas. This broad estuary is connected to the Pamlico River estuarine system by a canal for the U.S. Intracoastal Waterway, which passes down the length of the River. The canal comes into the Alligator River within the transition zone where the estuary narrows down and grades into the riverine zone of the River. The Little Alligator River is a small lateral tributary to the Alligator River which drains agricultural land in Tyrell County.

There are no towns, residential areas, industries, agricultural areas adjacent to the Alligator River and no NPDES discharges into the River. One marina is cut into the mainland at the western end of the U.S. Highway 64 bridge.

TABLE E14. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the North River. Depths of the deep samples range from 32 to 37 cm below the sediment surface for an average depth of 35 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (μg/g or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM N = 5	MEAN	MAXIMUM N = 5
NORTH RIVER								
Mo	5	0.36	0.25	0.80	**1.7**	3.3	1.2	2.8
Sn *	5	7.83	3.50	12.0	1.4	**1.9**	1.4	2.1
Ti	5	82.4	70.7	104.	1.4	2.3	1.1	1.4
Ni	5	3.11	2.05	4.87	1.3	2.3	0.7	1.1
As *	5	3.41	0.90	5.67	0.9	**1.7**	0.9	**1.5**
V	5	17.1	11.9	29.3	0.9	1.2	0.7	1.3
Cr	5	7.38	5.89	11.2	0.9	1.4	0.7	1.1
Pb	5	11.9	4.83	23.7	0.6	1.2	0.5	1.1
Cu	5	5.50	3.74	9.89	0.6	0.9	0.5	0.9
Co	5	3.88	2.79	5.04	0.9	1.4	0.6	0.8
Zn	5	22.7	17.2	38.5	0.6	0.8	0.5	0.8
Mn	5	123.	51.8	232.	0.5	1.1	0.4	0.7
Cd	5	0.15	0.15	0.15	0.7	0.7	0.7	0.7
P	5	166.	92.1	241.	0.5	0.7	0.4	0.6
Hg	5	0.04	0.02	0.09	0.4	0.8	0.3	0.6

* analyses have poor reproducibility, hence somewhat low reliability.

After many decades of logging and attempts at large-scale farming and peat mining, most of the adjacent land area has now been incorporated into the Alligator National Wildlife Refuge.

Sediment in the Alligator River is generally an organic-rich (7.6%), very muddy (40.0%), sand (52.4%). The sediments are actually quite variable ranging from relatively pure muds to almost pure sands with no apparent pattern either with depth or laterally through the estuary. The organic content also varies from 1% to 24%. There appears to be a general relationship between number of enriched elements and the relative % sand and % mud in each sample. With the exception of one sample, a sediment with more than 40% sand or less than 20% clay has no enriched elements.

Eleven sites were sampled in the Alligator River and two sites in the Little Alligator River (Fig. E7) producing 25 sediment samples. Chemical data for the 13 surface samples are summarized in Table E15. The surface samples are substantially enriched in only 1 trace element (As = 3.1 X the ATM) in the Alligator River and slightly enriched in two other elements (Cr = 1.6 X and Sn = 1.5 X the ATM). In the deep samples, 4 elements are substantially enriched in 1 to 4 samples (Ni = 3.1 X, As = 2.7 X, Ti = 2.6 X, and Mo = 2.9 X the ATM) and 3 elements are slightly enriched in 1 sample each (Cr = 1.6 X, Mn = 1.6 X, and Sn = 1.5 X the ATM) in the Alligator River. Twelve elements are not enriched in the surface sediments and eight elements are not enriched in any of the deep sediments in the Alligator River.

In the Little Alligator River (Fig. E7), 1 site (LALG-2) contains no enriched trace elements. One site (LALG-1) is substantially enriched in five elements with maximum enrichment factors as follows: Mo = 3.9 X, Sn = 2.9 X, Ni = 2.8 X, As = 2.6 X, and Ti = 2.5 X the ATM. This site is also slightly enriched in three other elements as follows: Cr = 1.5 X, Co = 1.5 X, and V = 1.5 X the ATM, however, these are all in the deep sample. At this site tin is the only element (Sn = 2.1 X the ATM) that is substantially enriched in the surface sample.

Outer Albemarle Sound

Eight sites were sampled within Outer Albemarle Sound resulting in 16 sediment samples (Fig. E7). Chemical data for these samples are summarized in Table E16. Five of the 15 trace elements are substantially enriched with maximum enrichment factors as follows: Mo = 3.0 X, Ni = 3.1 X, Co = 2.0 X, Sn = 2.0 X, Va = 2.0 X the ATM. Molybdenum is enriched in four deep samples and slightly enriched in two other deep samples. Ni and Co are substantially enriched in one and the same deep sample. Two other trace elements are slightly enriched in deep samples with maximum enrichment factors as follows: As = 1.7 X and Ti = 1.5 X the ATM. Sn is enriched in both surface and deep samples at 4 sites. No samples are enriched in Cr, Cu, Pb, Hg, Zn, Mn, P, and Cd.

The sediments in the Outer Albemarle Sound are generally muddy (30.4%), sands (67.0%) with 2.6% organic matter. This high sand and low mud and organic content may in part explain the seaward decrease in concentration of all 15 trace elements. Three sites (ALBE-2, ALBE-3, and ALBE-4) are the easternmost sites sampled while two other sites (sites ALBE-1 and ALBE-6) are located at the mouth of the Alligator River. All of these samples are dominantly sands which range in composition from 69% up to 97.8% and which contain from 27.0% down to 1.9% mud, respectively. Two of the latter sites (ALBE-4 and ALBE-6) are not enriched in any trace elements; the other three sites are enriched only in the deep samples and only in molybdenum with one sample being enriched in tin.

TABLE E15. Summary of mean and maximum enrichment factors for 15 trace elements in surface sediments from the Alligator and Little Alligator Rivers, two tributary estuaries on the south side of Albemarle Sound. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarl Sound trimmed mean, whereas those in bold print are slightly enriched (EF >1.5X to <2X ATM).

	ALLIGATOR RIVER N = 11		LITTLE ALLIGATOR RIVER N = 2	
TRACE ELEMENTS	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR	MEAN ENRICH FACTOR	MAXIMUM ENRICH FACTOR
As *	1.1	3.1	0.8	1.1
Cd	0.7	0.7	0.7	0.7
Co	0.4	0.7	0.5	0.8
Cr	0.5	**1.5**	0.5	0.7
Cu	0.4	1.2	0.4	0.5
Hg	0.2	0.6	0.3	0.5
Mn	0.3	0.6	0.3	0.5
Mo	0.9	1.3	0.9	0.9
Ni	0.4	1.0	0.5	0.7
P	0.4	1.0	0.3	0.4
Pb	0.5	1.4	0.5	0.7
Sn * #	0.6	**1.5**	1.1	2.1
Ti	0.7	1.1	0.8	0.9
V	0.4	0.9	0.7	1.0
Zn	0.4	1.2	0.4	0.5

* analyses with poor reproducibility, hence somewhat less reliability.

\# n = 9

TABLE E16. Concentrations of 15 trace elements for all surface samples and enrichment factors for all surface and deep samples collected in the Outer Albemarle Sound. Depths of the deep samples range from 7 to 35 cm below the sediment surface for an average depth of 26 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

TRACE ELEMENTS	N	CONCENTRATIONS ($\mu g/g$ or ppm)			ENRICHMENT FACTORS			
		SURFACE SAMPLES			DEEP SAMPLES N = 7		SURFACE SAMPLES N = 9	
		MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
OUTER ALBEMARLE SOUND								
Sn *	9	5.68	1.10	11.1	1.4	2.0	1.0	2.0
V	9	19.1	1.19	45.8	0.5	0.6	0.8	2.0
Mo	9	0.25	0.25	0.25	2.1	3.0	0.9	0.9
Ni	9	2.45	0.30	5.08	1.0	3.1	0.6	1.2
Co	9	3.80	0.20	7.05	0.8	2.0	0.6	1.1
As *	9	1.68	0.90	4.32	0.8	**1.7**	0.4	1.1
Ti	9	46.7	4.25	78.2	1.0	**1.5**	0.6	1.0
Cr	9	6.83	0.20	14.2	0.5	0.8	0.6	1.3
Cu	9	4.79	0.20	12.6	0.3	0.5	0.4	1.2
Pb	9	10.3	0.35	24.8	0.2	0.2	0.5	1.1
Hg	9	0.06	0.02	0.16	0.2	0.2	0.4	1.1
Zn	9	22.6	2.65	46.0	0.3	0.6	0.4	0.9
Mn	9	127.	4.75	292.	0.5	1.0	0.4	0.9
P	9	195.	5.45	289.	0.4	0.7	0.5	0.7
Cd	9	0.15	0.15	0.15	0.7	0.7	0.7	0.7

* analyses have poor reproducibility, hence somewhat low reliability.

Three sites (ALBE-17, ALBE-18, and ALBE-19) all occur in the northwestern portion of Outer Albemarle Sound. These sites are characterized by organic-rich (4.1 to 9.0%), mud (83.9 to 87.5%) samples at the surface which grade downward into muddy (18.6% to 34.9%), sands (63.3% to 80.1%) in the deep samples. The three surface samples are enriched in tin and vanadium. The deep samples are enriched in molybdenum and arsenic with one sample enriched in nickel and cobalt.

Areas of Concern Summary: Albemarle Sound Estuarine System

Regional Patterns within the Albemarle Sound Estuarine System

Table E17 compares mean concentrations of 15 trace elements in the surface sediments as they change from the lower Roanoke River systematically down the trunk of Albemarle Sound. Figure E11 presents a plot for four enriched trace elements (Mn, Ti, Co, and Cu) with maximum concentrations in the Lower Roanoke River and a regular eastward decrease to minor concentrations down the Albemarle. The abundance and distribution patterns for manganese, titanium, and cobalt are thought to be related to the geology of the drainage district and natural weathering processes rather than anthropogenic sources and the decreasing concentration downstream is interpreted to be related to changing sediment composition and associated water column chemistry.

Figures E12 and E13 present the plots for nine trace elements (As, Cd, Cr, Hg, Ni, P, Pb, V, and Zn) that increase to maximum concentrations in Inner Albemarle Sound and then decrease rapidly to minor concentrations eastward down the Albemarle. Most of the latter elements plus copper represent, at least in part, anthropogenic input from point and nonpoint sources in the upstream reaches of the Roanoke and Chowan River drainage basins. Maximum concentrations of these trace elements correspond to the turbidity maxima within most estuarine bodies. Within the turbidity maxima, estuarine mixing is an important process, the water column chemistry begins to change and there are maximum rates of accumulation of suspended mud sediments. This general pattern also mimics the distribution pattern of changing sediment types as depicted in Table D4. The location of maximum mud is in the Inner Albemarle Sound area and decreases dramatically seaward as the sand concentration increases to a maximum in Outer Albemarle Sound. The content of organic matter is highest in the Lower Roanoke River area and decreases regularly downstream.

Figure E14 displays an irregular distribution pattern for tin throughout the estuarine system. Molybdenum, which occurs in low concentrations everywhere, has no regional change in its distribution (Fig. E14).

Tables E18, E19, and E20 summarize the maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas within the Albemarle estuarine system. Table E18 shows a general decrease in sediment contamination from the highest levels in Welch Creek and decreasing into the Lower Roanoke River and to the lowest levels in the Middle-Cashie Rivers. Table E19 displays the pattern of decreasing enrichment from Inner Albemarle Sound, eastward through the Middle and into Outer Albemarle Sound, which is one of the least contaminated estuarine areas. Table E20 compares the enrichment between two urban areas of significantly different sizes (Elizabeth City and Hertford) and between each of the urban areas within the upper estuary to the less contaminated downstream portion of that tributary estuary (Pasquotank and Perquimans Rivers, respectively). All three of these tables also demonstrate that there are no consistent patterns of enrichment between the surface and deep samples within these areas.

TABLE E17. Summary of mean concentrations of 15 trace elements and composition of associated sediments of surface samples as they change from the Lower Roanoke River systematically down the trunk of the Albemarle Sound estuarine system. The highest mean concentration of each element is underlined and the lowest mean concentration is in bold print.

TRACE ELEMENTS	MEAN ENRICHMENT FACTORS OF SURFACE SEDIMENT (μg/g or ppm)			
	LOWER ROANOKE RIVER n = 13	INNER ALBEMARLE SOUND n = 21	MIDDLE ALBEMARLE SOUND n = 13	OUTER ALBEMARLE SOUND n = 9
ELEMENTS THAT DECREASE IN CONCENTRATION DOWNSTREAM				
Mn	3.3	2.8	0.9	**0.4**
Ti	1.9	1.3	0.9	**0.6**
Co	1.8	1.7	0.9	**0.6**
Cu	1.5	1.2	0.9	**0.4**
ELEMENTS THAT DECREASE IN CONCENTRATION DOWNSTREAM WITH MAXIMUM VALUES IN THE INNER ALBEMARLE				
As *	2.0	2.3	0.6	**0.4**
Hg	2.0	2.1	0.8	**0.4**
Cd	0.7	1.9	0.7	**0.7**
V	1.3	1.7	1.5	**0.8**
Cr	1.5	1.6	1.0	**0.6**
Zn	1.2	1.4	0.7	**0.4**
Ni	0.9	1.2	0.9	**0.6**
P	1.1	1.2	0.6	**0.5**
Pb	0.7	1.1	0.8	**0.5**
ELEMENTS WITH NO DOWNSTREAM CHANGE				
Mo	0.9	0.9	0.9	0.9
ELEMENTS WITH AN IRREGULAR DISTRIBUTION PATTERN				
Sn *	1.2	**0.7**	1.3	1.0
SEDIMENT	MEAN COMPOSITION OF SURFACE SEDIMENTS			
% Sand	15.9	**12.0**	36.7	78.0
% Mud	76.0	81.6	59.4	**20.5**
% Organic	8.1	6.4	4.0	**1.6**

* analyses have poor reproducibility, hence somewhat less reliability.

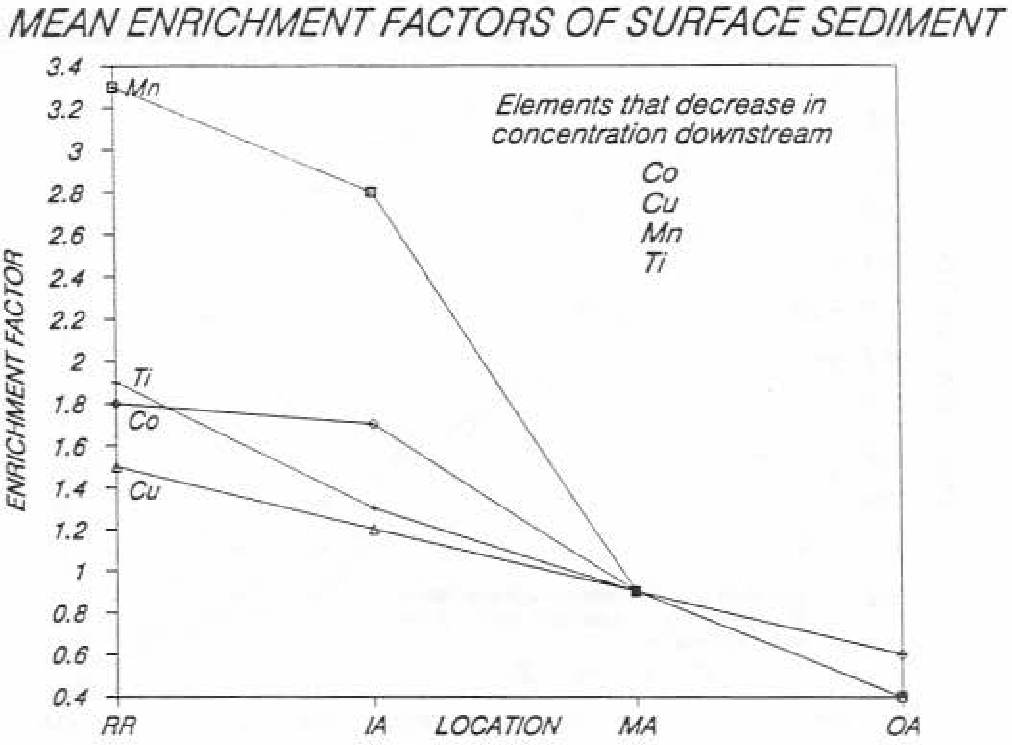


FIGURE E11. Downstream plot of mean enrichment factors for Albemarle Sound (Cu, Co, Mn, and Ti). Sample sites are located on Figure E2 and in the Appendix.

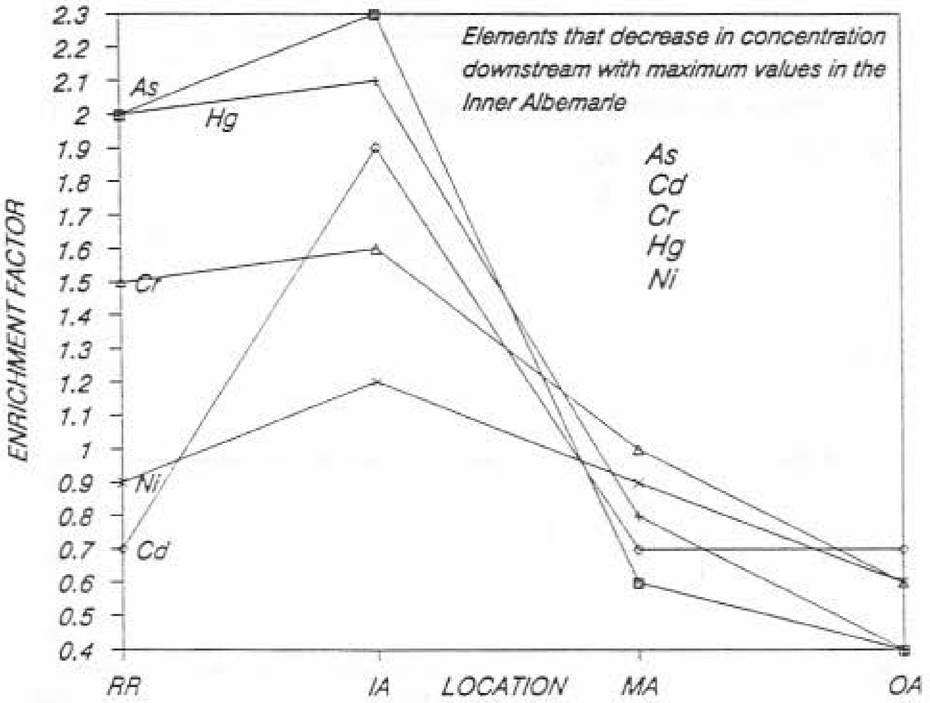


FIGURE E12. Downstream plot of mean enrichment factors for Albemarle Sound (As, Cd, Cr, Hg, Ni). Sample sites are located on Figure E2 and in the Appendix.

MEAN ENRICHMENT FACTORS OF SURFACE SEDIMENT

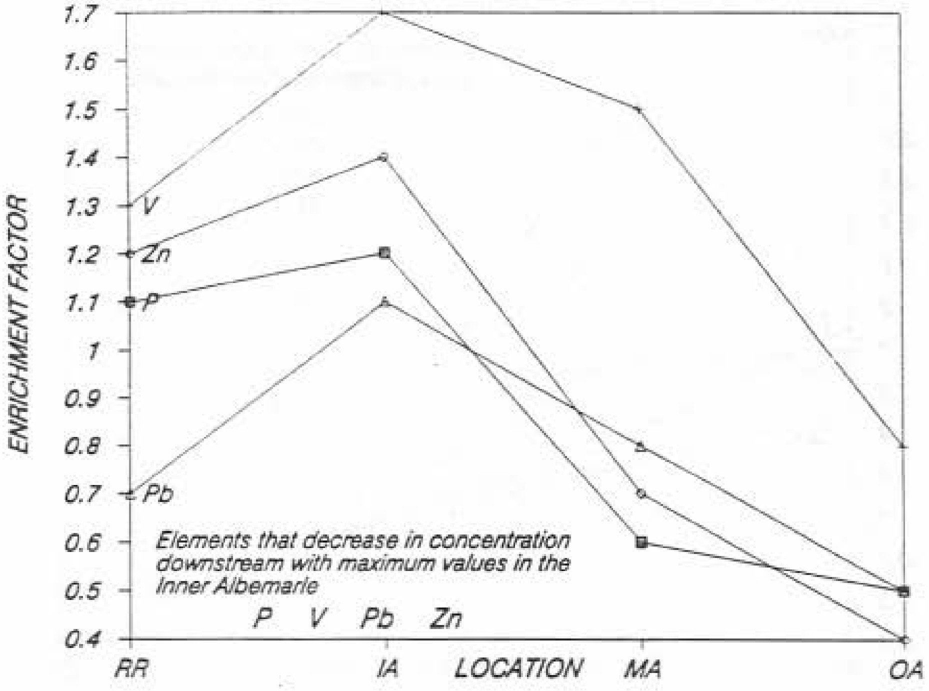


FIGURE E13. Downstream plot of mean enrichment factors for Albemarle Sound (P, Pb, V, Zn). Sample sites are located on Figure E2 and in the Appendix.

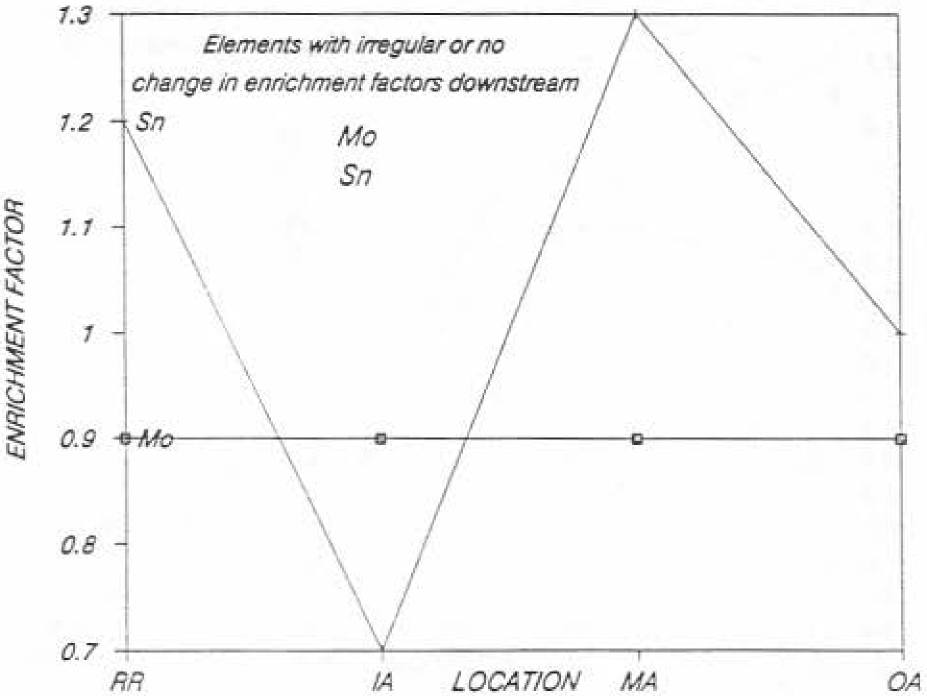


FIGURE E14. Downstream plot of mean enrichment factors for Albemarle Sound (Mo, Sn). Sample sites are located on Figure E2 and in the Appendix.

TABLE E18. Maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas of concern in the Lower Roanoke River area. MEF values of 1 are equal to the Albemarle trimmed mean; therefore, values = or >1.5 are slightly enriched (in bold print), values = or > 2 are substantially enriched (underlined), and values < 1 are deficient relative to the Albemarle trimmed mean.

	MAXIMUM ENRICHMENT FACTORS (X ALBEMARLE TRIMMED MEAN)					
	LOWER ROANOKE RIVER AREA					
	Welch Creek		**Roanoke River**		**Middle-Cashie Riv**	
TRACE ELEMENTS (15)	Surf	Deep	Surf	Deep	Surf	Deep
Arsenic (As)	**1.9**	1.4	3.4	2.5	2.7	2.8
Cadmium (Cd)	3.8	4.0	1.4	0.7	0.7	0.7
Chromium (Cr)	46.5	156.1	3.7	4.0	**1.7**	2.0
Cobalt (Co)	2.0	1.2	2.5	**1.7**	**2.0**	**1.7**
Copper (Cu)	8.4	9.4	2.0	2.3	1.4	**1.7**
Lead (Pb)	**1.5**	**1.6**	0.9	1.0	0.9	0.8
Manganese (Mn)	2.9	3.1	4.8	3.2	4.2	3.9
Mercury (Hg)	39.0	72.9	12.3	6.8	0.8	0.8
Molybdenum (Mo)	4.5	2.0	0.9	0.9	0.9	0.9
Nickel (Ni)	13.8	20.5	1.1	**1.7**	1.0	0.9
Phosphorus (P)	3.7	3.5	**1.7**	1.0	1.4	1.1
Tin (Sn)	3.9	2.9	**1.5**	**1.5**	1.4	1.2
Titanium (Ti)	2.0	2.4	2.3	2.3	**1.9**	2.3
Vanadium (V)	4.0	3.4	**1.5**	2.0	**1.5**	**1.7**
Zinc (Zn)	4.8	6.2	2.2	2.1	1.2	**1.5**
NUMBER ENRICHED	**15**	**13**	**11**	**11**	**6**	**8**

TABLE E19. Maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas of concern in the Albemarle Sound area. MEF values of 1 are equal to the Albemarle trimmed mean; therefore, values = or >1.5 are slightly enriched (in bold print), values = or > 2 are substantially enriched (underlined), and values < 1 are deficient relative to the Albemarle trimmed mean.

TRACE ELEMENTS (15)	**MAXIMUM ENRICHMENT FACTORS (X ALBEMARLE TRIMMED MEAN)**					
	ALBEMARLE SOUND AREA					
	Inner Albemarle Sound		**Middle Albemarle Sound**		**Outer Albemarle Sound**	
	Surf	Deep	Surf	Deep	Surf	Deep
Arsenic (As)	3.5	5.1	**1.6**	2.4	1.2	**1.7**
Cadmium (Cd)	**1.9**	0.7	0.7	0.7	0.7	0.7
Chromium (Cr)	2.4	3.2	1.4	1.3	1.3	0.8
Cobalt (Co)	2.6	2.1	1.2	**1.6**	1.1	2.0
Copper (Cu)	**1.6**	**1.7**	1.3	0.9	1.2	0.5
Lead (Pb)	**1.6**	1.4	1.2	0.5	1.1	0.2
Manganese (Mn)	3.9	5.6	**1.6**	1.3	0.9	1.0
Mercury (Hg)	4.8	6.5	**1.7**	0.2	1.1	0.2
Molybdenum (Mo)	0.9	0.9	0.9	4.9	0.9	3.0
Nickel (Ni)	2.0	**1.6**	1.2	2.2	1.2	3.1
Phosphorus (P)	2.0	1.3	0.9	0.8	0.7	0.7
Tin (Sn)	1.3	1.4	2.2	2.0	2.0	2.0
Titanium (Ti)	2.2	2.5	1.0	2.3	1.0	**1.5**
Vanadium (V)	2.2	2.5	2.1	**1.6**	2.0	0.6
Zinc (Zn)	**1.7**	**1.8**	1.0	0.8	0.9	0.6
NUMBER ENRICHED	**13**	**10**	**5**	**7**	**2**	**6**

TABLE E20. Maximum enrichment factors (MEF) for 15 trace elements in both surface and deep sediments of the major contaminated areas of concern in the Pasquotank, Lower Chowan, and Perquimans River areas, including the urban areas of Elizabeth City and Hertford. MEF values of 1 are equal to the Albemarle trimmed mean; therefore, values = or >1.5 are slightly enriched (in bold print), values = or > 2 are substantially enriched (underlined), and values < 1 are deficient relative to the Albemarle trimmed mean.

		MAXIMUM ENRICHMENT FACTORS (X ALBEMARLE TRIMMED MEAN)					
TRACE ELEMENTS (15)		**PASQUOTANK RIVER AREA**				**LOWER CHOWAN RIVER**	
		Elizabeth City		**Pasquotank River**			
		Surf	Deep	Surf	Deep	Surf	Deep
Arsenic	(As)	2.3	**1.9**	**1.8**	2.4	2.7	3.1
Cadmium	(Cd)	12.4	3.7	12.5	12.9	3.1	1.4
Chromium	(Cr)	2.0	1.4	2.0	**1.7**	1.1	1.2
Cobalt	(Co)	**1.7**	1.4	1.2	**1.6**	2.8	2.6
Copper	(Cu)	4.7	7.3	3.0	2.3	1.3	1.3
Lead	(Pb)	30.3	22.7	2.8	2.7	3.1	2.0
Manganese	(Mn)	0.7	**1.7**	0.7	1.3	3.0	3.0
Mercury	(Hg)	4.7	2.8	1.3	4.0	**1.5**	1.1
Molybdenum	(Mo)	0.9	5.6	3.1	5.2	0.9	2.4
Nickel	(Ni)	**1.8**	2.0	1.1	2.7	**1.9**	3.8
Phosphorus	(P)	3.5	2.8	2.1	**1.5**	2.0	1.1
Tin	(Sn)	2.7	3.2	2.3	3.0	2.0	**1.6**
Titanium	(Ti)	**1.6**	2.4	2.3	3.4	1.2	2.4
Vanadium	(V)	1.0	1.4	**1.5**	**1.6**	**1.6**	2.5
Zinc	(Zn)	13.3	**1.7**	2.9	6.0	**1.8**	**1.5**
NUMBER ENRICHED		**12**	**12**	**11**	**14**	**11**	**10**

		PERQUIMANS RIVER AREA				
TRACE		**Hertford**		**Perquimans River**		
ELEMENTS (15)		Surf	Deep	Surf	Deep	
Arsenic	(As)	0.8	0.8	2.1	**1.7**	
Cadmium	(Cd)	3.0	2.0	0.7	0.7	
Chromium	(Cr)	0.9	0.6	1.2	**1.6**	
Cobalt	(Co)	1.0	1.0	1.2	**1.5**	
Copper	(Cu)	**1.5**	0.8	0.9	0.9	
Lead	(Pb)	2.1	**1.6**	1.4	0.9	
Manganese	(Mn)	0.5	0.7	2.4	**1.5**	
Mercury	(Hg)	0.8	1.2	1.1	0.9	
Molybdenum	(Mo)	0.9	**1.9**	0.9	2.8	
Nickel	(Ni)	1.3	**1.9**	1.2	3.3	
Phosphorus	(P)	2.6	1.0	**1.5**	0.9	
Tin	(Sn)	**1.9**	2.6	2.4	2.8	
Titanium	(Ti)	0.5	**1.5**	1.1	2.9	
Vanadium	(V)	0.8	0.8	**1.7**	**1.6**	
Zinc	(Zn)	**1.8**	**1.6**	1.1	1.0	
NUMBER ENRICHED		**6**	**7**	**5**	**9**	

Comparison with Benkert Trace Metal Data

The U.S. Fish and Wildlife Service (Benkert, 1992) made a contaminant assessment for eight trace metals within bottom sediments from several portions of the Albemarle Sound estuarine system. Analyses were for total metals as compared to the partial extraction procedure utilized in the present report. Also, the Benkert data consists of only a few samples in a limited number of sites within the Albemarle system; however, the results do reflect similar levels of contamination for problem areas delineated by the present study (Table E21). Benkert interprets all elements presented in Table E21 as occurring in concentrations that represent "polluted sediments". Benkert also concluded that cadmium (maximum value = 0.40 ppm) and nickel (maximum value = 13.0 ppm) residues were low throughout the regions analyzed. Our data suggest that in general the Cd (n = 358; mean = 0.25 with maximum values up to 2.88 ppm) and Ni (n = 358; mean = 5.24 ppm with maximum values up to 87.8 ppm) are low but can be significantly enriched in the vicinity of specific point sources. Table E21 corroborates the conclusions within the present report.

TABLE E21. Comparison of sediment analyses for metals that occur in concentrations considered to represent "polluted" sediments by the U.S. Fish and Wildlife Service (Benkert, 1992). Benkert had only a few samples from scattered areas and the analyses represent total metal concentration. The Riggs et al. data (this report) represent many samples, however the data were derived from a partial extraction procedure of the total amounts present.

ELEMENT	BENKERT, 1992			RIGGS ET AL, THIS REPORT		
	N	MEAN VALUE ppm	MAX VALUE ppm	N	MEAN VALUE ppm	MAX VALUE ppm
WELCH CREEK						
Cr	1		376.	10	384.	1660.
Cu	1		56.5	10	43.6	102.
Hg	1		4.00	10	3.28	10.34
Zn	1		161.	10	141.	311.
LOWER ROANOKE RIVER						
Cr	4	44.5	60.0	26	17.4	42.5
Cu	4	28.8	31.0	26	16.0	24.8
Hg	4	0.70	1.20	26	0.23	1.75
Zn	4	116.	133.	26	57.5	113.
PERQUIMANS RIVER NEAR HERTFORD						
Pb	2	73.0	78.0	6	20.5	38.3
SCUPPERNONG RIVER						
Pb	6	22.6	46.0	20	31.6	227.

Analyses of the Rangia clam demonstrated that those from the Pasquotank, Alligator, and Scuppernong Rivers had the highest mercury levels with individuals having concentrations up to 0.66 ppm Hg. Chromium values were relatively greater in clams from the Chowan, Middle, and Roanoke Rivers with values up to 6.57 ppm in the Middle River. Cadmium, lead, copper, nickel, and zinc levels in the clams were considered to be generally low. The highest values for cadmium in clams was in the Chowan River (Cd = 2.2 ppm), for lead in clams was from the Alligator River (Pb = 1 ppm), for copper in clams from the Middle River (Cu = 20 ppm), for nickel in clams from the Scuppernong River (Ni = 3 ppm), and for zinc from clams in the Chowan River (Zn = 92 ppm).

North Landing River Area

Chemical data for 55 surface and shallow subsurface samples (Fig. C2) from the North Landing River in Currituck Sound are summarized in Table E22. Table E22 demonstrates that only 5 of the 15 trace elements are substantially enriched with maximum enrichment factors as follows: Mo = 10.1 X, Pb = 6.6 X, As = 2.7 X, Ni = 2.4 X, and Ti = 2.4 X the ATM. Two additional elements are slightly enriched with maximum enrichment factors as follows: Zn = 1.7 X and Cr = 1.5 X the ATM.

Table E23 demonstrates that 3 of these 7 elements (Pb, Zn, and Cr) are only enriched in 1 of 55 samples each with all 54 of the other samples having very low mean enrichment factors (Pb = 0.7 X, Zn = 0.7 X, and Cr = 0.9 X the ATM). This suggests that these individual samples represent anomalies and reflect a single, localized contaminant that occurs in that particular sample only. For example, the sample substantially enriched in lead probably contains a piece of lead shot, fishing sinker, or was in the proximity of a discarded battery, etc. Consequently, the general sediment system within the North Landing River is not considered to be contaminated with Pb, Zn, or Cr. No samples are enriched in the following 6 trace elements: Cd, Co, Cu, Mn, P, Sn and V.

On the other hand, Table E23 demonstrates that trace elements Mo, Ni, Ti, and As are enriched in significant portions of the 55 samples (85%, 35%, 27%, and 25% of the samples, respectively). The mean enrichment factor for all samples for each of these elements is as follows: Mo = 2.3 X, Ti = 1.4 X, Ni = 1.3 X, and As = 1.1 X the ATM. This data suggest that Mo is a major contaminant throughout most of the North Landing River area, whereas Ti, Ni, and As are not everywhere enriched. Molybdenum is substantially enriched (up to 10.1 X the ATM) in 25 of the 55 total samples and slightly enriched in another 22 samples. Ti enrichment is generally in the sediment subsurface with 14 of the 15 enriched samples occurring in the shallow subsurface. Eighteen of the 19 samples enriched in Ni are only slightly enriched with enrichment factors between 1.5 and <2.0 X the ATM; the one substantially enriched sample is 2.4 X the ATM. Arsenic is substantially enriched in 4 samples (up to 2.7 X the ATM) and slightly enriched in an additional 10 samples.

Consequently, the elements that are enriched and represent the most pervasive contaminants in the North Landing River area are Mo, Ni, Ti, and As. Actual concentrations of arsenic, even though it is relatively enriched in 25% of the samples, are not that high when compared with the trimmed mean concentrations of all samples for the Albemarle, Pamlico and Neuse estuarine systems (Table E24). Mo, Ni, and Ti mean concentration values for the North Landing River are significantly higher than the trimmed mean values for the

Albemarle, Neuse, and Pamlico estuarine systems (Table E24). Of these four substantially enriched elements, only As and Ni are included on the U.S. EPA list of "priority pollutants". Also, the As and Mo data have large analytical variances and uncertainties (see Methodology section).

TABLE E22. Concentrations of 15 trace elements and enrichment factors for all surface and shallow subsurface samples collected in the North Landing River in Currituck Sound. Depths of the shallow subsurface samples range from 13 to 63 cm below the sediment surface for an average depth of 40 cm. Elements with underlined enrichment factors are substantially enriched (EF = or >2X ATM) relative to the Albemarle trimmed mean, whereas those in bold are slightly enriched (EF >1.5X to <2X ATM).

		CONCENTRATIONS (µg/g or ppm) ALL SAMPLES			ENRICHMENT FACTORS			
					SUBSURF SPLS		SURFACE SAMPLES	
TRACE ELEMENTS	N	MEAN	MINIMUM	MAXIMUM	MEAN	MAXIMUM	MEAN	MAXIMUM
					N = 20		N = 35	
NORTH LANDING RIVER--CURRITUCK SOUND								
Mo	55	0.66	0.21	2.90	2.7	8.4	2.0	10.1
As *	55	3.94	0.75	10.3	1.4	2.7	0.8	2.5
Ti	55	103.	57.3	180.	1.7	2.3	1.2	2.4
Ni	55	5.51	1.52	10.3	1.3	**1.9**	1.3	2.4
Pb	55	14.8	3.46	143.	0.7	6.6	0.7	1.0
Cr	55	9.78	3.89	15.6	0.9	1.2	0.9	**1.5**
Zn	55	34.7	3.20	83.2	0.7	**1.7**	0.7	1.0
V	55	17.5	7.93	33.1	0.8	1.4	0.7	1.4
P	55	317.	38.1	523.	0.6	0.9	0.9	1.3
Co	55	4.91	2.25	6.16	0.7	0.9	0.7	0.9
Cd	55	0.15	0.15	0.15	0.7	0.7	0.7	0.7
Cu	55	5.53	1.71	7.97	0.4	0.6	0.5	0.7
Mn	55	123.	27.0	257.	0.4	0.8	0.3	0.4
Sn *	55	0.21	0.20	0.56	0.0	0.0	0.0	0.1
Hg	0	na	na	na	na	na	na	na

* analyses have poor reproducibility, hence somewhat low reliability.
na = not analyzed.

TABLE E23. Number and percent of samples in the North Landing River that are substantially and slightly enriched in 7 trace elements above the trimmed mean for Albemarle Sound estuarine system.

ENRICHED ELEMENT	TOTAL NO. SAMPLES SURF/SUBS	SUBSTANT. SURFACE NO. / %	ENRICHED SUBSURF. NO. / %	SLIGHTLY SURFACE NO. / %	ENRICHED SUBSURF. NO. / %	TOTAL EN-RICHED SPLS NO. / %
Mo	35/20	12/34%	13/65%	18/51%	4/20%	47/85%
Ni	35/20	1/ 3%	0/ 0%	11/31%	7/35%	19/35%
Ti	35/20	1/ 3%	5/25%	0/ 0%	9/45%	15/27%
As	35/20	1/ 3%	3/15%	5/14%	5/25%	14/25%
Pb	35/20	1/ 3%	0/ 0%	0/ 0%	0/ 0%	1/ 1.8%
Zn	35/20	0/ 0%	0/ 0%	0/ 0%	1/ 5%	1/ 1.8%
Cr	35/20	0/ 0%	0/ 0%	1/ 3%	0/ 0%	1/ 1.8%

TABLE E24. Comparison of mean concentrations of enriched elements in the North Landing River with trimmed means for the Albemarle, Neuse, and Pamlico estuarine systems (in µg/g or ppm). Highest mean concentration for each element is underlined, whereas lowest mean concentration is in bold print. Trimmed mean data are from Riggs et al., this report, 1991, and 1989, respectively.

ENRICHED ELEMENT	MEAN CONCENTRATION NORTH LANDING RIVER	TRIMMED ALBEMARLE SOUND	MEAN CONCENTRATIONS NEUSE RIVER	PAMLICO RIVER
Mo	0.66	**0.29**	0.54	0.50
Ni	5.51	4.28	4.64	**2.66**
Ti	103.	75.2	**31.8**	38.6
As	**3.94**	**3.75**	5.98	12.8
Pb	**14.8**	21.8	34.9	35.9
Zn	**34.7**	50.5	95.0	77.0
Cr	**9.78**	10.7	16.8	10.5

The 4 substantially enriched elements (Mo, Ni, Ti, and As) have no apparent pattern to their distributions. They are all enriched in both surface and deep samples, in dredged and nondredged areas, in dredge spoil and undisturbed sediments, on the shallow platforms and in the channel, and appear to be independent of the composition of sand, clay, and organic matter. Lack of any obvious pattern or apparent factor controlling the distribution and concentration of any of these 4 elements and lack of enrichment in more common anthropogenic metals (i.e., lead, zinc, copper, chromium, and mercury) suggest that elemental enrichment in the North Landing River 1) is not the result of anthropogenic point sources and 2) that there is not a movement of metals into Currituck Sound from the Elizabeth River and the Norfolk harbor area.

PART F. REFERENCES CITED

REFERENCES CITED

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PART G: APPENDIX

SUMMARY OF SAMPLE LOCATION MAPS FOR ESTUARINE AREAS

ABBREVIATION	ESTUARINE AREA	REGIONAL LOCATION MAPS	
		FIGURE NO.	PAGE NO.
INDEX MAP	Albemarle System: Regional Map Areas	Figure E1	Page 90
INDEX MAP	Albemarle System: Regional Map Areas with Abbreviations	Figure G1	Page 145
ALG	Alligator River (estuarine portions)	Figure E7	Page 115
CSH	Cashie River (from the Thoroughfare channel, east to the Inner Albemarle Sound)	Figure E2	Page 91
CHN	Lower Chowan River (from the mouth at Inner Albemarle Sound, north to the US Highway 13 bridge at Winton)	Figure E5	Page 98
CTK	North Landing River in Currituck Sound (from the highway 726 bridge at Pungo Ferry, VA, south to Gibbs Pt. and Faraby Island, NC)	Figure C2	Page 37
DEP	Deep Creek (estuarine portions)	Figure E6	Page 106
EDN	Edenton Bay	Figure E5	Page 98
ALBI/ALBW	Inner Albemarle Sound (from the Lower Roanoke and Lower Chowan Rivers, east to the western side of Bull Bay and Yeopim River)	Figure E5	Page 98
LALG	Little Alligator River (estuarine portions)	Figure E7	Page 115
LIT	Little River (estuarine portions)	Figure E6	Page 106
ALBW	Middle Albemarle Sound (from western side of Bull Bay and Yeopim River, east to western side of Alligator and Pasquotank Rivers)	Figure E6	Page 106
MID	Middle River (entire channel)	Figure E2	Page 91
NTH	North River (estuarine portions)	Figure E7	Page 115
ALBE	Outer Albemarle Sound (from western side of Alligator and Pasquotank Rivers, east to Mashoes and Point Harbor)	Figure E7	Page 115
PAS	Pasquotank River (estuarine portions)	Figure E8	Page 117
PER	Perquimans River (estuarine portions)	Figure E6	Page 106
RKE	Lower Roanoke River (from west end of Great Island, east to the Inner Albemarle Sound)	Figure E2	Page 91
SCP	Scuppernong River (estuarine portions)	Figure E6	Page 106
WEL	Welch Creek (from the southern RR bridge, north to the Roanoke River)	Figure E2	Page 91
YEO	Yeopim River (estuarine portion)	Figure E6	Page 106

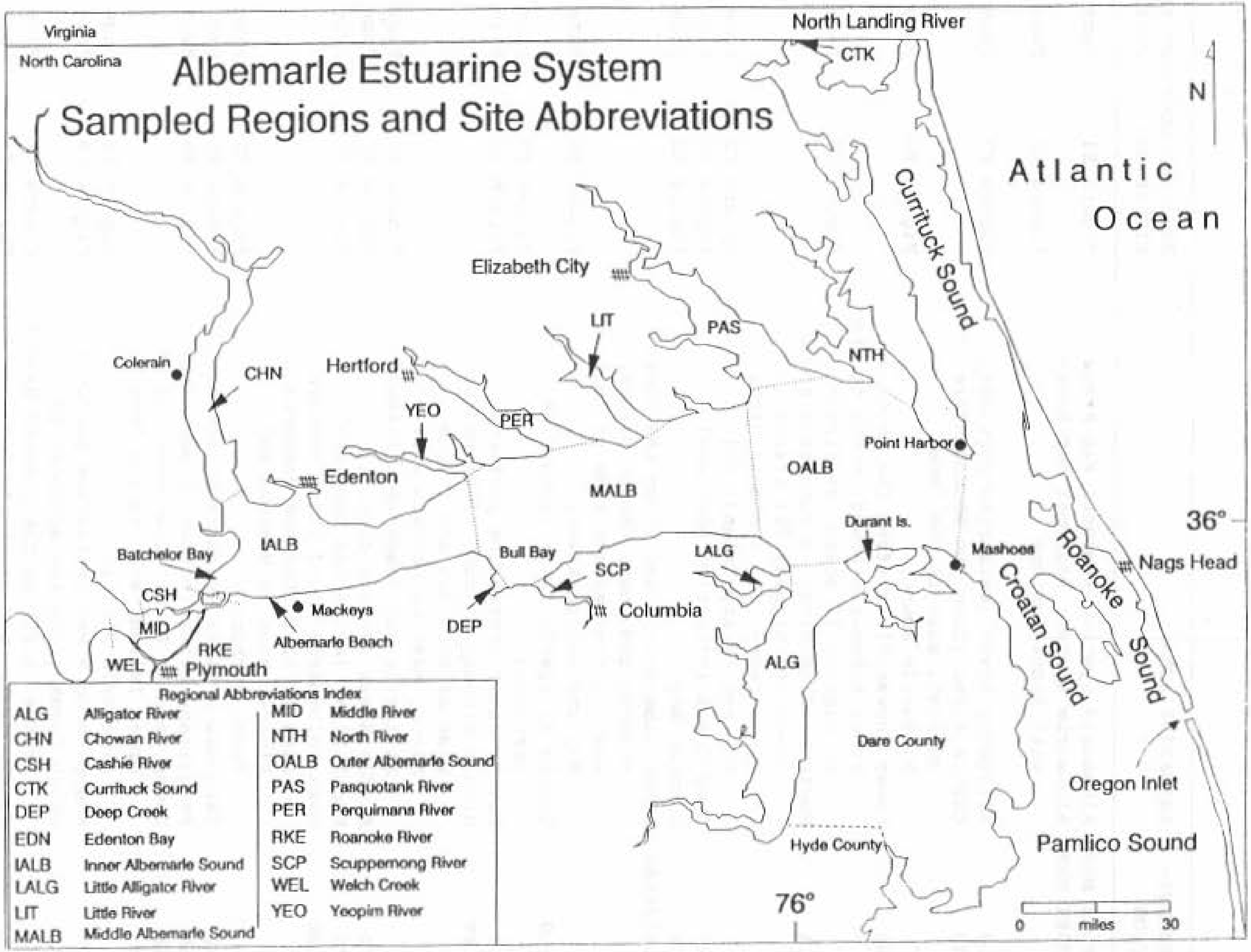

FIGURE G1. Map of the Albemarle Sound estuarine system showing the location of sampled regions and site abbreviations used for samples.

SAMPLE LOCATION DATA FOR THE ALBEMARLE SOUND ESTUARINE SYSTEM

Column 1: Core hole number with location prefix and core number; these designations have been used for all sediment, chemical, and statistical analyses, designations on maps and in the text, and summarized on Figure G1.
Column 2: Latitude in degrees with minutes and seconds converted to decimals.
Column 3: Longitude in degrees with minutes and seconds converted to decimals.
Column 4: Water depth in meters.
Column 5: Location description.

CORE NO	LATITUDE	LONGITUDE	H2O DEPTH M	LOCATION DESCRIPTION
ALLIGATOR RIVER				
ALG-1	35.6664	76.0299	2.44	0.75 nmi ESE of Newport News Pt
ALG-2	36.6696	76.0872	2.44	Winn Bay; 3000 ft S of Tuckahoe Pt
ALG-3	35.7058	76.0115	3.05	50 ft S of ICWW MKR 31; E & adjacent to channel
ALG-4	35.7570	76.0039	3.96	1000 ft E of ICWW MKR 26
ALG-5	35.7821	76.0197	3.66	400 ft N of ICWW MKR 24
ALG-6	35.8115	76.0429	3.66	midway between MKRS 22 & 20; W of channel
ALG-7	35.8516	76.0225	3.05	300 ft E of ICWW MKR 18
ALG-8	35.8856	76.0282	3.05	200 ft E of ICWW MKR 14; S of Alligator River bridge
ALG-9	35.9155	76.0052	3.05	middle of ICWW navigational channel at MKR 10
ALG-10	35.9270	75.9658	3.96	2 nmi SW of Sound Pt on Durants Island
ALG-11	35.9056	76.0296	3.05	Alligator River Marina; 10 ft N of fuel dock
CASHIE RIVER				
CSH-1	35.9300	76.7348	5.49	mid-channel; 0.75 nmi N of hwy 45 bridge; W side of islands
CSH-2	35.9241	76.7389	4.27	mid-channel; 0.5 nmi W of hwy 45 bridge
CHOWAN RIVER				
CHN-1	36.0536	76.6989	6.40	mid-channel; 0.5 nmi N of hwy 17 bridge
CHN-2	36.0971	76.7212	6.10	700 ft E of MKR 3 & 0.5 nmi from W shore
CHN-3	36.1401	76.7256	5.40	off mid-channel Chowan River; 1 nmi W of Harris Landing
CHN-4	36.1823	76.7456	5.18	1 nmi N of MKR 5; W side of Chowan River
CHN-5	36.2081	76.7181	6.10	0.5 nmi E of MKR 7; 200 yds from E shore
CHN-6	36.2288	76.7156	4.88	150 ft S MKR 9
CHN-7	36.2703	76.6915	5.18	150 ft NW of MKR 12; near Holiday Island
CHN-8	36.3818	76.8750	2.44	Upper Chowan River; 300 ft W of MKR 29; 150 ft off S shore in lily pads

CHN-9	36.3893	76.8992	2.44	Upper Chowan River; 450 ft W of MKR 31; 150 ft off S shore
CHN-10	36.3835	76.8858	1.83	Upper Chowan River at Tunis; 100 ft N of mouth of Catherine Crk
CURRITUCK SOUND: NORTH LANDING RIVER				
CTK-1	36.5570	76.0329	1.47	90 yds N of Green Pt
CTK-2	36.5608	76.0370	0.76	60 yds E of W shore on P2
CTK-3	NO SAMPLE			
CTK-4	36.5671	76.0411	1.34	200 yds E of W bank on P3
CTK-5	NO SAMPLE			
CTK-6	36.5862	76.0495	1.37	177 yds E of W bank on P4; N5E to MKR 49
CTK-7	36.5818	76.0484	1.14	195 yds E of W bank on P5; N20E to MKR 51
CTK-8	36.5789	76.0473	1.52	207 yds E of W bank on P6; N55E to MKR 53
CTK-9	36.5721	76.0434	0.00	120 yds E of W bank on P7; N60W to MKR 57
CTK-10	36.5599	76.0352	1.22	S of Walnut Island Crk on P1; N45E to MKR 59
CTK-11	36.5542	76.0321	1.07	200 yds S of Green Pt on P8; N20W to Green Pt.
CTK-12	36.5397	76.0298	1.22	50 ft E of W bank at Gibbs Pt on P9
CTK-13	36.6210	76.0501	0.00	mid-channel between MKR 40 & 41
CTK-14	36.6028	76.0605	0.00	mid-channel between MKR 44 & 45
CTK-15	36.5927	76.0517	1.52	150 ft N of MKR 49 on NE platform
CTK-16	36.5920	76.0516	0.00	mid-channel at MKR 49 on P9
CTK-17	36.5410	76.0251	0.00	100 ft W of channel on P9
CTK-18	36.5404	76.0274	0.00	midway between channel and W bank on P9
CTK-19	36.5413	76.0242	3.96	mid-channel on P9
CTK-20	36.5493	76.0296	2.29	E side of channel on P10
CTK-21	36.5498	76.0274	3.96	mid-channel on P10
CTK-22	36.5485	76.0326	0.00	600 ft E of W bank on P10

CTK-23	36.5543	76.0307	0.00	midway between W bank and channel on P8
CTK-24	36.5541	76.0330	1.22	390 ft E of W bank on P8
CTK-25	36.5545	76.0292	4.88	mid-channel on P8
CTK-26	36.5632	76.0318	2.13	150 ft E of channel on P1
CTK-27				W side of spoil pile on P1
CTK-27A				top of spoil pile on P1
CTK-28	36.5715	76.0320	1.83	middle of platform E of channel on P3
CTKC-1	36.5819	76.0493	0.61	195 yds E of W bank; 33 yds N of CTK-7
CTKC-2	36.5784	76.0479	1.46	65 yds E of W bank on P6
CTKC-3	36.5780	76.0485	0.61	20 ft E of W bank on P6
CTKC-4	36.5795	76.0477	1.46	200 yds E of W bank on P6
CTKC-5	36.5794	76.0469	1.07	320 yds E of W bank on P6
CTKC-6	36.5797	76.0464	0.98	350 yds E of W bank on P6
CTKC-7	36.5801	76.0460	1.04	400 yds E of W bank on P6
CTKC-8	36.5803	76.0456	1.65	200 yds E of W bank on P6
CTKC-9	36.5806	76.0452	1.98	550 yds E of W bank (E edge of channel) on P6
CTKC-10	36.5812	76.0446	4.88	52 yds W of MKR 53 in channel on P6
CTKC-11	36.5819	76.0436	1.98	70 yds E of MKR 53 on P6
CTKC-12	36.5823	76.0432	1.68	350 yds W of E bank on P6
CTKC-13 CTKC-14	36.5830	76.0422	1.22	100 yds W of E bank on P6 300 yds W of E bank on P6
DEEP CREEK				
DEP-1	35.9312	76.3672	1.83	Bull Bay; mid-channel where Bunton Crk narrows
DEP-2	35.9350	76.3866	2.44	Bull Bay; mid-channel where Deep Crk narrows
DEP-3	35.9498	76.3788	2.44	Bull Bay; 100 yds E of mouth of Bull Crk

EDENTON BAY				
EDN-1	36.0574	76.6251	2.13	Pembroke Crk; mid-channel in Edenton marina
EDN-2	36.0559	76.6264	2.74	Pembroke Crk; mid-channel outside Edenton marina; 400 ft. SE of hwy 17 bridge
EDN-3	36.0558	76.6202	2.74	Pembroke Crk; 150 ft E of MKR 6 and S of old sunken barges
EDN-4	36.0579	76.6153	2.74	Edenton Bay; 100 ft N of MKR 1; 200 ft S of permanent tug
EDN-5	36.0554	76.6105	3.96	Edenton Bay; S end of paved city dock
EDN-6	36.0531	76.6107	1.83	100 ft N of MKR 8 at entrance to Edenton Harbor
EDN-7	36.0336	76.6156	4.57	100 ft N of MKR 2 at entrance to Edenton Bay
INNER ALBEMARLE				
ALBI-1	35.9500	76.6833	3.96	0.5 nmi N of S shore at mouth of Roanoke River; 500 ft NE of MKR 3
ALBI-2	35.9586	76.6559	3.96	1.5 nmi N of S shore; 50 ft N of MKR 1
ALBI-3	35.9723	76.6814	3.66	1.0 nmi S of Black Walnut Pt
ALBI-4	36.0032	76.6697	4.27	1.0 nmi E of Black Walnut Pt
ALBI-5	36.0339	76.6848	5.49	midway between MKR 2 & Edenhouse Pt; 2 nmi NE of mouth of Salmon Crk
ALBI-6	36.0053	76.7053	2.13	Salmon Crk near Avoca; 0.5 nmi E of tank & 300 ft N of S shore
ALBI-7	36.0100	76.5950	5.18	W of N end of RR bridge
ALBI-8	35.9858	76.6231	5.49	1 nmi S of MKR CR in mid-bay
ALBI-9	35.9378	76.6066	3.66	200 yds downstream of old RR bridge at mouth of Kendrick Crk
ALBI-10	35.9507	76.6359	4.57	midway between Mackeys & MKR 3 to Roanoke River
ALBI-11	35.9849	76.6460	5.18	mid-inner Albemarle; midway between Black Walnut Pt & RR bridge
ALBI-12	36.0165	76.6461	5.18	midway between Edenton Bay & Chowan River mouth
ALBI-13	35.9639	76.7102	2.13	0.75 nmi E of W bank of Batchelor Bay
ALBW-1	35.9996	76.4218	6.40	1.5 nmi W of MKR 3
ALBW-2	36.0291	76.4244	5.79	midway between Drummond Pt and Bluff Pt
ALBW-3	35.9952	76.4696	7.01	mid-sound; due E of main span of hwy 32 bridge

ALBW-4	35.9717	76.4898	4.88	0.25 nmi E of S end of hwy 32 bridge
ALBW-5	hwy 32 bridge profile		1.52	N end of bridge profile; 100 ft S of beach
ALBW-6	hwy 32 bridge profile		2.74	N end; piling 82
ALBW-7	hwy 32 bridge profile		3.35	N end; piling 79
ALBW-8	hwy 32 bridge profile		4.88	N end; piling 76
ALBW-9	hwy 32 bridge profile		6.10	N end; piling 73
ALBW-10	hwy 32 bridge profile		6.40	N end; piling 64
ALBW-11	hwy 32 bridge profile		6.40	high span in mid-bridge
ALBW-12	hwy 32 bridge profile		6.10	S end; piling 20
ALBW-13	hwy 32 bridge profile		5.79	S end; piling 21
ALBW-14	hwy 32 bridge profile		3.05	S end; piling 13
ALBW-15	hwy 32 bridge profile		1.83	S end; piling 9; S of 2nd sand bar
ALBW-16	hwy 32 bridge profile		1.22	S end; piling 5
ALBW-17	hwy 32 bridge profile		1.52	S end; 200 ft offshore & at 2nd pier to E
ALBW-18	35.9760	76.5436	6.10	mid-sound between the 2 bridges
ALBW-19	35.9981	76.5707	5.49	1 nmi ESE of Horniblow Pt
ALBW-20	35.9528	76.5938	4.57	250 ft W of power lines & RR; 1 nmi N of S shore; 5th power tower
LITTLE ALLIGATOR				
LALG-1	35.9275	76.0534	2.44	200 yds SE of Rock Pt
LALG-2	35.9378	76.0142	2.74	just outside mouth of Little Aligator River
LITTLE RIVER				
LIT-1	36.1187	76.1853	3.35	mid-channel; midway between mouth & Mills Pt
LIT-2	36.1516	76.2290	2.74	mid-channel; 3 nmi upriver
LIT-3	36.1837	76.2670	2.74	mid-channel; between Trueblood Pt and Deep Creek Pt

LIT-4	36.2043	76.2828	2.13	W of Nixonton; 100yds E of W shore
MIDDLE ALBEMARLE				
ALBE-7	36.0435	76.0755	6.10	100 ft SW of MKR 1; NE corner of Tyrell County bombing range
ALBE-8	36.0285	76.1640	5.79	mid-bombing range; N of radio tower on S shore
ALBE-9	36.0200	76.2500	6.10	N of bombing range; N of Soundside
ALBE-10	35.9925	76.2829	6.40	W end of bombing range; NE entrance to Bull Bay
ALBE-11	36.0089	76.3561	6.10	1.5 nmi E of MKR 3 near Laurel Pt
ALBE-12	36.0543	76.3604	6.40	1 nmi SE of MKR 2 near Drummond Pt
ALBE-13	36.0440	76.3010	5.79	0.5 nmi S of 'CIA' platforms
ALBE-14	36.0850	76.2680	4.88	due S of mid-mouth of Perquimans River
ALBE-15	36.0651	76.2094	6.10	1 nmi S of MKR 2 near Reed Pt
ALBE-16	36.0904	76.1204	5.79	1 nmi SE of MKR 1 near Stevenson Pt
ALBE-20	36.0674	76.1189	6.40	2.5 nmi NW of MKR 1 on NE corner of bombing range
ALBE-21	35.9532	76.3307	3.96	300 yds NW MKR 1 in Bull Bay near entrance to SCP
ALBE-22	35.9821	76.3418	5.79	mid-Bull Bay
MIDDLE RIVER				
MID-1	35.8720	76.7831	5.49	0.5 nmi from mouth; 100 ft SE of NW bank
MID-2	35.9163	76.7281	6.10	1500 yds SW of hwy 45 bridge; mid-channel
MID-3	35.8931	76.7516	4.27	2 nmi SW of hwy 45 bridge; mid-channel
NORTH RIVER				
NTH-1	36.1753	75.8905	2.74	100 ft NW of ICWW MKR 167 at mouth of North River
NTH-2	36.3073	75.9714	1.52	100 ft NW of ICCWW MKR 132; just W of channel
NTH-3	36.2816	75.9482	2.44	100 ft W of ICWW MKR 143; along edge of channel
NTH-4	36.2518	75.9540	4.27	100 ft SW of ICWW MKR 157; mid-channel
NTH-5	36.2088	75.9252	3.96	midway between ICWW MKRs 164 & 163; mid-channel

OUTER ALBEMARLE				
ALBE-1	36.0024	75.9659	5.49	1 nmi SW of ICWW MKR SOUTH PA
ALBE-2	36.0181	75.9591	5.18	100 ft E of ICWW MKR SOUTH PA
ALBE-3	36.0612	75.9315	5.18	200 ft NE of ICWW MKR "AS" PA
ALBE-4	36.0997	75.9097	4.57	200 ft NE of ICWW MKR NORTH
ALBE-6	35.9987	76.0236	5.49	NW of the mouth to Alligator River
ALBE-17	36.0983	76.0441	5.79	3 nmi S of Frog Island
ALBE-18	36.1326	75.9755	5.18	1 nmi S of MKR 1 to Pasquotank River entrance
ALBE-19	36.0730	76.0052	6.10	midway between ICWW MKR AS & MKR 1 on NE corner of Tryell County bombing range
PASQUOTANK RIVER				
PAS-1	36.2015	76.0664	3.35	50 ft E of MKR 3 in Pasquotank River
PAS-2	36.2280	76.0963	3.96	W of Miller Pt; mid-river
PAS-3	36.2219	76.1322	0.91	N side of Newbegun Crk; off 1st ditch W of Pool Pt
PAS-4	36.2294	76.1433	0.91	in tributary crk on N bank & W of Pool Pt; between RR & hwy bridges
PAS-5	36.2233	76.1404	0.91	in tributary crk on N bank & W of Pool Pt; 300 ft inside mouth of crk
PAS-6	36.2196	76.1379	1.52	mid-channel Newbegun Crk; 1200 ft E of Jordan Is
PAS-7	36.2153	76.1232	1.52	mid-channel at mouth of Newbegun Crk; S of Pool Pt
PAS-8	36.2394	76.1310	2.44	300 ft off Coast Guard Station boat ramp along W bank
PAS-9	36.2588	76.1235	3.96	mid-channel; 2000 ft E of MKR 5
PAS-10	36.2813	76.1521	3.96	3000 ft S of shoreline between Anson & Treasure Pts
PAS-11	36.2640	76.1606	2.74	300 ft N of shoreline off Coast Guard Air Base fuel dock
PAS-12	36.2917	76.1830	3.35	mid-channel; 2000 ft NE of MKR 7
PAS-13	36.2940	76.2003	4.27	mid-channel between Hospital and Cottage Pts
PAS-14	36.2996	76.2053	2.74	150 ft S of ramp at Causeway Marina; N shore
PAS-15	36.3000	76.2119	2.74	10 ft S of dock at Pelican Marina; N shore

PAS-16	36.2974	76.2093	5.49	in channel 100 ft N of S shore; between Pelican and Causeway Marinas
PAS-17	36.2981	76.2142	3.66	mid-river & 660 ft E of MKR 8
PAS-18	36.3002	76.2166	2.13	mid-river & S of bridge; 660 ft N of MKR 8
PAS-19	36.3010	76.2176	3.35	Elizabeth City dock next to BP station; S of hwy 158 bridge
PAS-20	36.2966	76.2112	7.01	150 ft N of S shore; near RR complex at E end of docks
PAS-21	36.2968	76.2130	7.62	150 ft N of S shore; between 2 old docks
PAS-22	36.2968	76.2144	2.74	100 ft N of S shore; W side of dock complex
PAS-23	36.2971	76.2174	2.44	100 ft N of S shore; entrance to Little Crk
PAS-24	36.3019	76.2051	1.83	20 ft N of outer sailboat slip; Causeway Marina NE of main hwy bridge
PAS-25	36.2990	76.2177	5.49	middle of Municipal Marina; off outer end of slips; NE of main hwy bridge
PAS-26	36.3086	76.2024	2.44	30 ft E of old bulkhead off Elizabeth City WWTP; NE of main hwy bridge
PAS-27	36.3061	76.2038	3.66	120 ft W of MKR 9 near WWTP; NE of main hwy bridge
PAS-28	36.3037	76.2150	8.53	200 ft S of dock next to grain elevator; NE of main hwy bridge
PERQUIMANS RIVER				
PER-1	36.1069	76.2872	4.27	mouth of Perquimans River
PER-2	36.1052	76.3177	4.57	500 ft N of CIA dock along SW shoreline
PER-3	36.1309	76.3410	3.66	mid-river; NE of MKR 7
PER-4	36.1467	76.3911	3.66	mid-river off White Hat Landing
PER-5	36.1665	76.4171	3.96	mid-river; 2 nmi downstream hwy 17 bridge
PER-6	36.1893	76.4547	3.35	mid-channel; 450 ft E of hwy 17 channel bridge span
PER-7	36.1845	76.4650	2.13	mid-channel; 210 ft E of Racoon Crk Bridge
PER-8	36.1944	76.4657	7.32	mid-channel; 300 ft E of Perquimans River bridge; N side of Hertford
ROANOKE RIVER				
RKE-1	35.8766	76.7400	1.22	140 ft off south bank; 200 ft E of wreck
RKE-2	35.8751	76.7414	3.05	500 ft SW of MKR 17; 100 ft off S bank; beside old pier

RKE-3	35.8747	76.7417	4.88	800 ft downstream & NE of stacks; 50 ft from S bank
RKE-4	35.8716	76.7469	2.13	halfway between stacks and Plymouth waterfront; 35 ft off S bank
RKE-5	35.8687	76.7496	3.05	1500 ft from WaterFront Church in Plymouth; 40 ft off S bank
RKE-6	35.8665	76.7545	4.57	W end of Plymouth waterfront; E of apartment complex; 50 ft off S bank at pier
RKE-7	35.8660	76.7597	2.44	E of Welch Crk eastern most meander; 25 ft off N bank
RKE-8	35.8647	76.7608	4.88	E of the mouth of Welch Crk; beside old dock pilings; 50 ft off S bank
RKE-9	35.8625	76.7748	3.66	adjacent to Weyerhaeuser Plant; 75 ft off S bank
RKE-10	35.8686	76.7894	3.05	500 ft SE of Highland Prong; 100 ft off SW bank
RKE-11	35.8945	76.7300	2.44	Plymouth WWTP outfall; halfway between hwy 45 bridge & MKR 17; 50 ft from SE bank
RKE-12	35.9049	76.7278	2.74	1500 yds S of MKR 12 on SE bank
RKE-13	35.9234	76.7037	2.44	80 yds W of MKR 13 on S bank
SCUPPERNONG RIVER				
SCP-1	35.9167	76.2750	1.83	middle of boat docks; Sawyers marina
SCP-2	35.9150	76.2750	1.52	canal entrance to Sawyers marina
SCP-3	35.9400	76.3126	3.66	1000 ft SE of MKR 3; mid-river
SCP-4	35.9317	76.2894	3.35	1000 ft NW of MKR 4; mid-river
SCP-5	35.9200	76.2787	3.96	midway between MKR 7 & 1; entrance to Sawyers marina
SCP-6	35.9243	76.2633	3.66	275 ft E of MKR 10; mid-channel
SCP-7	35.9217	76.2500	0.91	in ditch on downstream corner of Columbia WWTP
SCP-8	35.9217	76.2567	2.44	100 ft off end of ditch discharge point
SCP-9	35.9167	76.2567	3.05	100 ft N of old hwy 64 bridge; Columbia waterfront marina
SCP-10	35.9133	76.2567	6.10	in channel between new & old hwy 64 bridges
WELCHES CREEK				
WEL-1	35.8639	76.7632	1.52	W mouth of Welch Crk; 50 ft off island to E
WEL-2	35.8446	76.7846	4.57	250 ft upstream from second RR bridge; 30 off NW bank

WEL-3	35.8537	76.7805	1.83	E of large building; 50 ft off N bank
WEL-4	35.8578	76.7739	2.13	1000 yds NE of hwy 1341 bridge; center of crk
WEL-5	35.8611	76.7671	2.74	at first RR bridge in downstream area; center of crk
YEOPIM RIVER				
YEO-1	36.0761	76.4113	2.74	mouth of Yeopim River
YEO-2	36.0772	76.4422	2.44	700 ft NW of platform
YEO-3	36.0902	76.4723	1.83	0.5 nmi SSE mouth of Bethel Crk near head of river