DEEPWATER PORTS MAINTENANCE DREDGING AND DISPOSAL MANUAL

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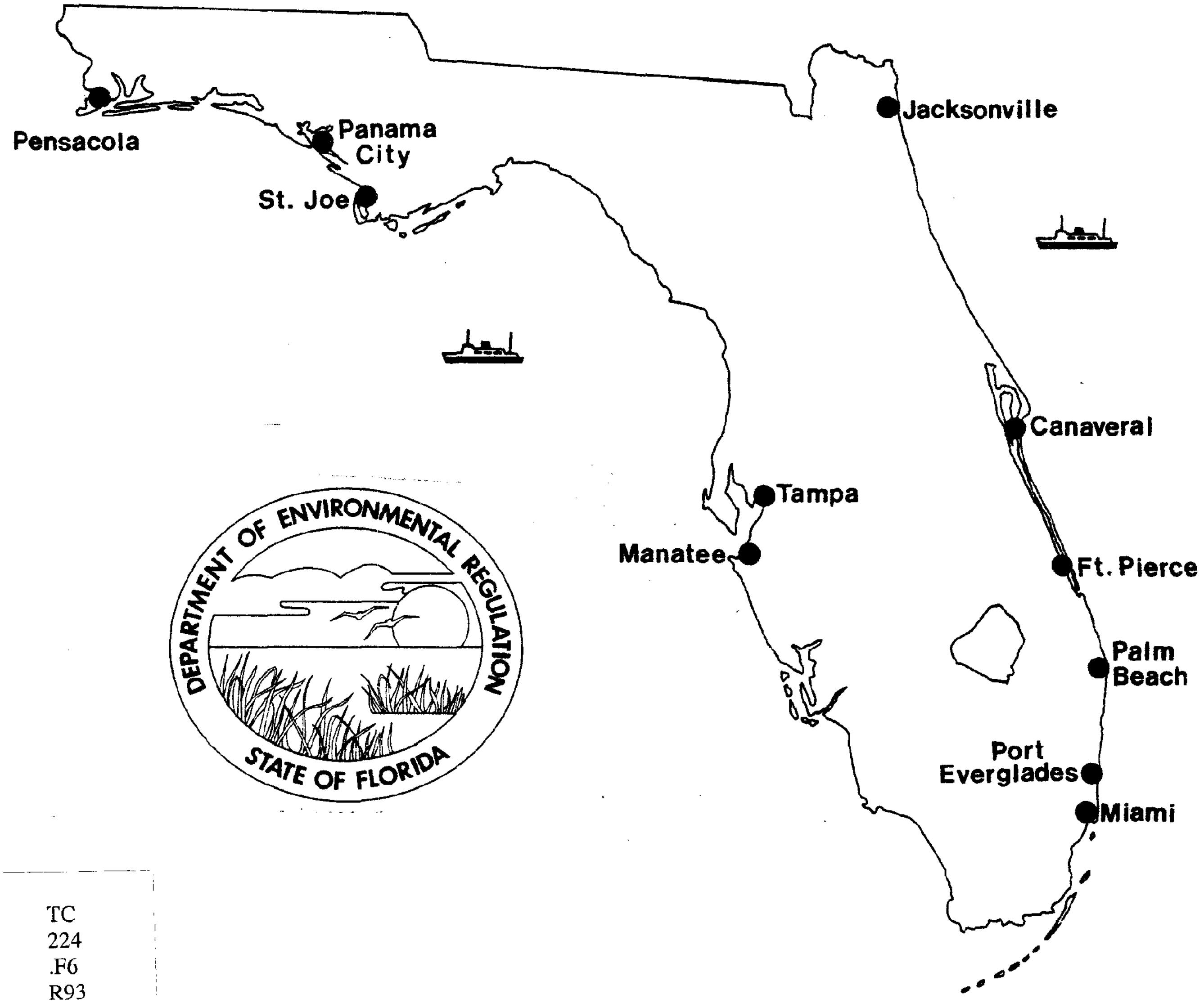

DEPARTMENT OF ENVIRONMENTAL REGULATION
STATE OF FLORIDA

MAY, 1984

DEEPWATER PORTS MAINTENANCE DREDGING AND DISPOSAL MANUAL

A GUIDE TO PLANNING AND ESTUARINE CHEMICAL DATA COLLECTION, ANALYSIS, AND INTERPRETATION

DEPARTMENT OF ENVIRONMENTAL REGULATION
STATE OF FLORIDA

Prepared By: Joseph D. Ryan
Fred D. Calder
Louis C. Burney

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OVERVIEW

An examination of technical and administrative issues involved in regulating port maintenance dredging and disposal activities concluded that the quality of information supporting permit requests, as well as the efficiency of permit administration, could be improved if better technical guidance was provided by DER. Thus, Chapter 17-45, F.A.C. governing the issuance of long-term maintenance dredging permits references planning and quality assurance guidelines contained in this Manual.

The Manual covers three general areas: (1) guidelines for developing long-term port-wide maintenance dredged material management plans; (2) guidelines and supplementary procedures for improving and ensuring the precision, accuracy, and reliability, of water quality and sediment data; and (3) interpretations of these data.

PART ONE
GUIDELINES FOR DEEPWATER PORTS MAINTENANCE DREDGED MATERIAL MANAGEMENT PLANS

Introduction

The purpose of this part of the Manual is to provide guidance to ports regarding the basic planning requirements for receiving long-term maintenance dredging and disposal permits. Chapter 403.816, Florida Statutes provides the legal basis for D.E.R. to issue port maintenance dredging and disposal permits for terms of up to 25 years. Efforts to implement this legislation, however, have led to the realization that long-term permitting cannot be successful without an understanding of long-term port disposal needs and proposed measures for meeting these needs in an environmentally sound manner.

Historically, port maintenance dredging and disposal problems in Florida have been addressed on a piecemeal basis. However, changing socio-economic conditions, environmental constraints, and port operational considerations now dictate that maintenance dredging and disposal activities be treated not only with a greater degree of importance, but also with a broader, long-term perspective. The future viability of ports in Florida will depend, in part, upon their ability to develop long-term solutions to problems associated with maintenance dredging and disposal operations.

Dredged Material Disposal Planning Requirements of DER Rule 17-45.19

In order to receive the full benefits of a long term permit, Section 17-45.19 requires development of a Long-Term Port-Wide Maintenance Dredged Material Management Plan. This plan must demonstrate that the applicant will have the capability for disposal of projected volumes of dredged material in an environmentally sound and efficient manner for the requested life of the permit. It also must provide a perspective of total navigation system disposal needs in order to anticipate effects of proposed dredging and disposal operations. Each plan must contain at least five elements as specified by Subsection 17-45.19(b):

1. Projections of volumes of dredged material according to physical and chemical characteristics of the sediments;

2. Assessment of existing and anticipated dredged material disposal capabilities, including contained disposal, beach renourishment, ocean disposal, and other appropriate methods;

3. Assessment of methods for maximizing service life of disposal sites;

4. Assessment of environmental protection needs and methods for addressing the identified needs;

5. Identification and assessment of dredging and disposal alternatives to meet projected needs; and

6. Proposed strategies for long-term management of maintenance dredged material.

Relationship of the Disposal Plan to the Long-Term Permit

Submission of the Plan and its approval by the Department are requirements for entry into Phase II of the long-term (up to 25 years) permit. The Plan is a key factor in administering long-term permits in that it serves three basic functions needed to integrate a long-term perspective into the permit process.

1. It provides for an understanding of anticipated disposal conditions and their relationship to the applicant's permit request, including: (a) providing for permits to be based on projections of port-wide dredging, disposal, and environmental protection needs; (b) identifying long-term disposal capabilities and limitations; and (c) identifying options for meeting future disposal needs in a manner that minimizes adverse environmental impacts.

2. It provides a mechanism for confirming the accuracy of assumptions and projections of disposal capabilities on which Phase II of the permit is based.

3. It provides a sound basis for anticipating port operation needs associated with maintenance dredging and disposal, and facilitates cost-effective and timely actions toward meeting those needs.

The degree of effort required to satisfy these planning requirements depends largely upon the magnitude and complexity of maintenance dredging and disposal problems experienced by each port. For those ports having short navigational systems, minor shoaling and few disposal problems, the requirements can be met in a relatively simple, straightforward manner. In such cases, certain tasks listed in these guidelines will not be applicable. However, for other more complicated navigational situations, most if not all of the stated tasks will be necessary. Under such circumstances, appropriate commitments of time and expense must be allocated to the planning effort.

In order to avoid unnecessary expense and delays in completing required plans, early consultation and active coordination with the department is recommended.

RECOMMENDED APPROACH FOR DEVELOPING DEEPWATER PORT MAINTENANCE DREDGED MATERIAL MANAGEMENT PLANS

TASK I: INVENTORY AND ASSESSMENT OF PORT-WIDE MAINTENANCE DREDGING AND DISPOSAL CONDITIONS, VOLUMES, AND CAPABILITIES.

OBJECTIVE: To assemble information regarding water quality, dredged material characteristics, dredging volumes and disposal capabilities for developing a perspective of port-wide problems and opportunities associated with maintaining required navigational depths.

SUBTASK I-A: IDENTIFY PORT-WIDE MAINTENANCE DREDGING CONDITIONS

A. Identify and Map Those Harbors, Channels, Berths, Turning Basins and Spoil Disposal Sites Subject to the Provisions of Sections 403.021(9)(b) and 403.061(26)(b), F.S.

B. Determine Sediment Characteristics By Reach (cut), Berth(s), and Turning Basin(s).

1. Physical characteristics:

   (a) Grain size.
   (b) Specific gravity.
   (c) Settling rates.
   (d) Atterburg limits.
   (e) Void ratios.
   (f) Bulking factors.
   (g) Consolidation properties.

2. Chemical characteristics (in accordance with EPA/Corps of Engineers guidelines and supplementary procedures provided in Parts Two and Three of this Manual).

   (a) In consultation with DER, identify parameters for analysis.
   (b) Determine metal to aluminum ratios as referenced in Part Two of this Manual (Supplementary Field and Laboratory Procedures).
   (c) Conduct elutriate tests (as appropriate subsequent to consultation with DER).

C. Determine Water Quality Characteristics in Dredge Areas By Reach (cut), Berth(s), Turning Basin(s), And At Disposal Outfall Receiving Waters.

1. Physical characteristics:

   (a) Depth.
   (b) Temperature.
   (c) Currents and tidal regime.
   (d) Dissolved oxygen.
   (e) Turbidity.
   (f) Conductivity.

2. Chemical Characteristics - Identify parameters in consultation with DER and analyze in accordance with EPA standard procedures and supplementary procedures provided in Parts Two and Three of this manual.

D. Identify Natural Resources Adjacent To Channels And Other Pertinent Areas Of The Navigational System.

1. Marine grassbeds, reefs, oyster beds, clam beds, etc.

2. Relationship of natural resources to defining dredge area mixing zone(s) as referenced in Section 17-45.18.

SUBTASK I-B: IDENTIFY PORT-WIDE DISPOSAL CONDITIONS

A. Describe Existing Dredging Methods (clamshell, hydraulic pipelines, sidecaster, hopper dredge) By Reach (cut), Berth(s), or Turning Basin(s).

B. Determine Quantities of Dredge Material and Frequency of Required Dredging By Reach (cut), Berth(s), Turning Basin(s), and Sediment Type.

1. Historical dredging volumes.

2. Frequency of required maintenance dredging.

3. Volumes of existing material needing to be dredged.

4. Projected volumes by sediment type including anticipated volumes from any new dredging projects (estimate for at least 10 years).

C. Identify Specific Sediment and Water Quality Problem Areas Within The Port Navigational System.

1. Organize information collected in Task I into a format which facilitates an understanding of water quality characteristics and the quantities, characteristics, and distribution of sediments.

2. Identify and discuss reaches (cuts), berths or turning basins containing sediments with physical or chemical characteristics which may present problems during dredging or disposal.

   (a) Identify extent and approximate volume of fine materials (silt and clay having a grain size less than 125 microns).

   (b) Identify extent and approximate volumes of sediments having contaminant (metals, hydrocarbons, nutrients) concentrations in amounts equal to or exceeding the levels specified in DER Rule Section 17-45.17 and as indicated in Part Two of the Manual.

3. Identify existing water quality problem areas (areas which do not meet state standards as specified in Chapter 17-3, F.A.C.) including background water quality adjacent to disposal sites and particular problems associated with disposal operations.

4. Evaluate projected volumes of dredged material according to suitability for disposal.

   (a) Volumes needing to be contained in confined disposal areas.

   (b) Volumes suitable for beach renourishment.

   (c) Volumes suitable for ocean disposal in EPA approved or interim approved areas.

   (d) Volumes suitable for open water disposal (e.g., sidecasting at inlets).

   (e) Volumes suitable for disposal by other methods (e.g., habitat creation).

D. Identify Natural Resource Concerns Associated With Existing Disposal Site Operations, Including The Following:

1. Marine grassbeds, reefs, oyster beds, clam beds, and fishery habitat.

2. Marshes, mangroves, and other wetland areas.

3. Mosquito breeding areas.

4. Rookeries, bird resting areas, etc.

5. Relationship of natural resources to defining dredge area mixing zone(s) as referenced in Section 17-45.18.

SUBTASK I-C: ASSESS EXISTING DISPOSAL CAPABILITIES AND LIMITATIONS

A. Description Of Each Disposal Site Used By The Port (containment sites, beaches, offshore, etc.):

   1. Physical description.

   2. Status of use.

   3. Permit status.

B. Remaining Capacity And Estimated Service Life Of Existing Containment Sites, Taking Into Account:

   1. Consolidation of dredged material.

   2. Required ponding depth, freeboard, dike stability, retention times, and other considerations for meeting effluent quality requirements.

   3. Relationship to port development plans.

   4. Ultimate use of the sites.

C. Volumes Presently Approved For Beach Renourishment.

D. Volumes Approved For Disposal At EPA Approved Or Interim Approved Ocean Disposal Sites.

E. Volumes Disposed In Other Ways.

F. Compare Projected Dredge Volumes With Existing Disposal Capabilities And Identify The Magnitude Of Projected Shortfalls In Port-Wide Capabilities.

G. Identify Timeframes In Which Disposal Capabilities Will Be Exhausted, Including The Following Considerations:

   1. Service life of containment sites.

2. Permit expiration dates.
3. Easement expiration dates.
4. Limitations on beach renourishment and ocean disposal.
5. Other governmental approvals and constraints.

TASK II: GENERAL ASSESSMENT OF ALTERNATIVE APPROACHES TO MEETING DISPOSAL SHORTFALLS

OBJECTIVE: To gain an understanding of the relative merits of approaches for correcting anticipated disposal shortfalls.

SUBTASK II-A: ASSESS WAYS TO MAXIMIZE THE USE OF EXISTING CONTAINMENT SITES.

A. Explore Options For Improving The Management of Dredged Material, Including At Least The Following Considerations:
    1. Accelerated dewatering/consolidation of spoil material.
    2. Segregation of material.
    3. Removal of consolidated material to maintain capacity.
B. Assess Potential For Expanding Site Capacity, Including:
    1. Raising dikes.
    2. Enlarging area of containment site(s).
C. Assess Anticipated Effects Of Each Option On The Following (Apply information provided in SUBTASKS I-A&B):
    1. Hydrographic effects.
    2. Water quality effects.
    3. Natural resource effects.
D. Assess Ability of Alternatives to Meet Overall Port Disposal Needs.
E. Preliminary Selection of Preferred Alternative(s) For Maximizing Use Of Existing Containment Sites.

SUBTASK II-B: ASSESS OPTIONS FOR ACQUIRING NEW CONTAINMENT SITES

A. Screen Potential Sites In Terms of Physical and Environmental Suitability.

1. Site Description(s), including size, location, configuration, topography, etc.

2. Physical and operational constraints:

   (a) Distance from dredging areas.
   (b) Potential for meeting projected capacity shortfalls.
   (c) General geotechnical and engineering considerations.
   (d) Dredge equipment limitations.

3. Environmental constraints:

   (a) Water quality considerations.
   (b) Natural resource considerations associated with the proposed disposal area, such as aquatic resources, wetland areas, wildlife habitat, etc.
   (c) Potential mosquito breeding problems.
   (d) Hydrographic considerations.

4. General assessment of ownership and land use considerations, including:

   (a) Present uses and ownership of the sites.
   (b) Existing adjacent land uses and conflicts.
   (c) Potential conflicts with adjacent land uses.
   (d) Availability of sites.
   (e) Governmental constraints such as zoning, land use plans, environmental regulations.

5. Conceptual design and general assessment of costs:

   (a) Preliminary acquisition costs.
   (b) Conceptual engineering design, including estimated improvement costs.
   (c) Estimated operational and site management costs, including consideration of conceptual site management program, e.g., methods for maximizing service life of site(s), site maintenance, etc.
   (d) Scheduling and funding considerations.

6. Assess ability of alternatives to meet overall port disposal needs.

B. Preliminary Selection of Preferred Alternative Containment Site(s).

SUBTASK II-C: PRELIMINARY ASSESSMENT OF OPTIONS FOR USING EXISTING OFFSHORE (OCEAN) DISPOSAL SITE(S)

A. Status of site:

1. Size of site.
2. Status of approvals for site.
3. Designated dredge areas/projects approved for disposal at site.
4. Restrictions and other conditions contained in federal and state approvals.

B. Operational Constraints Involved In Expanded Use of Existing Offshore Site(s):

1. Distance.
2. Equipment limitations.
3. Transportation costs.

C. In Consultation With The Corps of Engineers, EPA, and DER, Identify Environmental Constraints Involved In Expanded Use of Existing Offshore Site(s), Including The Following:

1. Suitability of dredged material.
2. Sufficiency of existing environmental studies.
3. As appropriate, determine studies needed for expanded use of existing site(s).
4. Approximate timeframe for obtaining needed federal and state approvals.

D. Assess Ability of Option(s) To Meet Overall Port Disposal Needs.

E. Preliminary Determination of Feasibility For Expanded Use Of Offshore Disposal Site(s).

SUBTASK II-D: PRELIMINARY ASSESSMENT OF OPTIONS FOR NEW OFFSHORE (OCEAN) DISPOSAL SITE(S).

A. Summarize Need for New Offshore Disposal In Relation To Other Existing Disposal Alternatives.

   1. Compare the volumes to be accommodated by preliminary preferred disposal alternatives with projected disposal shortfalls to identify ocean disposal needs.

   2. Develop preliminary strategies for inclusion of offshore disposal as an intergral part of satisfying port-wide disposal needs.

B. Consult With The Corps of Engineers, EPA, and DER Regarding Feasibility Of Designating New Offshore Site(s).

   1. Identify priority concerns.

   2. Identify tentative schedule for carrying out necessary investigations and securing approvals.

SUBTASK II-E: PRELIMINARY ASSESSMENT OF POTENTIAL FOR BEACH RENOURISHMENT

A. Determine Suitability of Dredged Material.

B. Determine Suitability of Beach Disposal Area, Including the Following Considerations:

   1. Erosion conditions and wave climate.

   2. Sand transport/induced shoaling.

   3. Status of state, federal, and local approvals for existing disposal areas.

   4. Identify concerns associated with using new beach disposal areas with Dept. of Natural Resources, Dept. of Environmental Regulation, and Corps of Engineers.

C. Identify Operational Constraints, Including the Following:

   1. Distance from dredging area(s) and associated transportation costs.

   2. Equipment limitations.

D. Assess Ability of Beach Disposal To Meet Overall Port Disposal Needs.

E. Preliminary Determination of Feasibility for Beach Disposal.

SUBTASK II-F: PRELIMINARY ASSESSMENT OF POTENTIAL FOR HABITAT CREATION.

A. Identify Type(s) of Desired Habitat.

B. Identify Priority Concerns.

C. Identify Tentative Schedule for Carrying Out Necessary Investigations and Secruing Approvals.

SUBTASK II-G: EVALUATE RELATIVE MERITS OF ALTERNATIVES AND PROPOSE STRATEGIES FOR CORRECTING ANTICIPATED DISPOSAL NEEDS.

A. Compare Preferred Alternatives In Terms of Meeting Port-Wide Disposal Needs To Determine Priority Disposal Strategies.

B. Propose Overall Approach Outlining The Function That Each Preferred Alternative Plays In Meeting The Following Needs:

1. Capacity needs related to:

   (a) Maximizing use and service life of existing containment sites.
   (b) Acquiring and developing new containment sites.
   (c) Use of beach nourishment
   (e) Ocean disposal.
   (e) Other disposal methods.

2. Environmental protection needs related to:

   (a) Long-term protection of water quality.
   (b) Minimizing adverse impacts on natural resources.
   (c) Preventing mosquito breeding problems.

3. Socio-economic considerations, including minimizing land-use conflicts.

C. Provide Necessary Information On Maintenance Dredging and Disposal Capabilities To Allow Entry Into Phase II of the Long-Term Permit.

1. Provide information on disposal limitations, such as capacity shortfalls, anticipated site service life, and other critical milestones.

2. Provide assurances that capability will exist to dispose of maintenance dredged material in an environmentally sound manner for the requested term of the permit.

D. Develop Disposal Site Acquisition and Development Schedule To Meet Anticipated Shortfalls.

TASK III: ESTABLISH ACTIVE COORDINATION WITH THE CORPS OF ENGINEERS, ENVIRONMENTAL PROTECTION AGENCY, FLORIDA DEPT. OF NATURAL RESOURCES AND FLORIDA DEPT. OF ENVIRONMENTAL REGULATION

OBJECTIVE: To assure necessary coordination with govenmental agencies having related responsibilities during plan development and implementation.

A. Establish Agreement on General Planning Approach, Confirm Volumetric Calculations, Verify Environmental Details and Clearly Define Responsibilities During Plan Development.

B. Confirm Feasibility of Strategies for Meeting Disposal Shortfalls.

C. Confirm Schedule for Acquisition and Development of Needed Disposal Sites.

D. Establish Protocol for Routine Coordination During Plan Implementation.

TASK IV: DEVELOP AND IMPLEMENT A DREDGED MATERIAL TRACKING SYSTEM

OBJECTIVE: To develop and implement an efficient and reliable system for data storage and retrieval regarding dredged material. The purpose of this system is to provide an accounting for dredged material and disposal sites managed by the port in order to verify disposal capabilities specified in long-term permits.

A. Volumes and Types of Material Removed From the Navigation System.

B. Volumes and Types of Material Disposed in Containment Sites.

C. Volumes and Types of Material Disposed Offshore, On Beaches, Or By Other Means.

D. Estimated Remaining Capacity and Service Life of Containment Sites.

E. Results of Environmental Monitoring

1. Performance of site management practices.

2. Environmental conditions.

TASK V: PLAN IMPLEMENTATION.

OBJECTIVES: To carry out the agreed upon strategies and schedule for disposal site acquisition and development; provide ongoing review and evaluation of dredge material management capabilities as specified in the long-term permit; and provide coordination with governmental agencies having related responsibilities.

A. Conduct Detailed Work According to Schedule Established in Tasks III and IV.

B. Confirm Projected Volumes and Site Capacities and Expected Site Performance Through the Tracking System.

   1. Recordkeeping.

   2. Ongoing monitoring and evaluation of volumetric projections, remaining site capacity and site performance.

C. Updating and Revision of Plan as Necessary to Reflect Monitoring Results, Unforseen Events, New Information, Technological Improvements, etc.

D. Coordination with DER Long-Term Permit Requirements, DNR, Corps of Engineers, and EPA.

PART TWO

GENERAL ESTUARINE PROCESSES AND PROCEDURES FOR INTERPRETING CHEMICAL RESULTS

1.0 Background

After numerous problems were uncovered regarding the accuracy of existing data on the environmental conditions in Florida's deepwater ports, it was recognized that guidelines were necessary to supplement the EPA Methods for Chemical Analysis of Water and Wastes (1982a) and the joint EPA/Corps Procedures For Handling and Chemical Analysis of Sediment and Water Samples (1981).

State, federal, and local environmental agencies base most dredging-related decisions on water and sediment data that are collected in or adjacent to port navigation systems. Consequently, it is essential that reliable data-gathering, analytical and interpretive procedures be employed in order to identify potential environmental problems that could result from maintenance dredging operations.

Spatial and temporal changes in the environmental chemistry at each port may be substantial. Thus, adequate characterizations of these fluctuations require that field collections and laboratory analyses be performed uniformly throughout all data-gathering events. Implementation of such an approach will help distinguish natural variability from real problems resulting from dredging operations. Field collection techniques must be uniform, and laboratory analyses should be carried out using best available yet cost-effective procedures for ensuring precision and accuracy of the results. To accomplish these goals, it is imperative that field collection techniques minimize sample contamination and that analytical procedures for working in the estuarine environment are adopted.

The need for implementing the aforementioned procedures arose after a review by DER of permit files, pertinent academic publications and public agency reports containing water, sediment and elutriate chemical results on the navigational systems of Jacksonville, Tampa, Manatee, and Pensacola. This initial screening revealed that these data are replete with problems and suggested that most of the environmental data on these estuarine areas are unreliable for one of more of the following reasons:

- Most of the existing physical and chemical data appear to be statistically unreliable since replicate samples were rarely taken during field collections. As a result, sample means and the variability within a set of samples could not be determined according to the data gathering approach used.
  This is a serious problem since the spatial heterogeneity of chemicals encountered in the estuarine environment is potentially great and a single sample is not representative of actual background estuarine chemical conditions.

- Failure to record exact station locations and other relevant information was a common problem encountered during the file review. This deficiency severely limits the usefulness of the existing data base. As an example, salinity, which plays an important role in the physical behavior of many contaminants, was rarely recorded at the time water samples were collected. Seldom were any records made of the tidal phase during which samples were collected. Thus, estuarine dynamics, which play such an important role in the distribution of chemical species in estuarine environments, were largely ignored in most studies.

- Elevated concentrations were reported for numerous contaminants, especially in the water column. These values are atypical of levels reported in the scientific literature for most southeastern U.S. estuaries. This suggests that either estuarine waters in Florida are more polluted than the literature indicates or simply that these data are inaccurate. Typical problems that can lead to such inaccuracies include sample contamination in the field and lab, or analytical interference (e.g., salts) that can occur during laboratory analyses.

- The DER review found high variability among the results of many studies. In most of the surveys conducted prior to the Deepwater Ports Study (DER, 1983; DER, 1984), field collection methods apparently were not uniform and rarely documented. The variability of estuarine chemical data is not surprising since only recently have standard field and laboratory methods been made available by federal agencies (USEPA-COE, 1981).

° Because general agreement on appropriate analytical methods has evolved only recently, the great variability observed in the historical data also suggests that laboratory procedures (extractions, analyses, and sample storage practices) may have been inadequate. In most cases, laboratory methods employed during earlier studies were not referenced. More importantly, it is apparent that the methods previously employed for water column analyses were not suitable for saline waters due to interference associated with chlorides and other salts. Also, detection Limits were often too high for making decisions regarding the degree to which water and sediments were contaminated.

In summary, the review of estuarine water and sediment chemical data indicated that field and lab procedures currently being employed by many commercial and regulatory laboratories are not uniform and are often inadequate to characterize the environmental chemistry of an estuary. Therefore, it is difficult to assess the existing environmental quality of port navigation systems and to assess the effects of dredging and disposal operations using these data. Problems with these data have caused delays in issuing permits and increased costs for providing followup data. In any case, the limitations of these data make it virtually impossible to characterize historical water and sediment quality trends that have occurred in port navigation systems.

Based on the preceeding, there is a strong need for promoting consistency and accuracy in future estuarine chemical sampling and analytical programs designed for securing reliable data on dredging-related impacts. Accordingly, the department has developed this supplementary set of field collection and analytical laboratory procedures to be used in conjunction with other recent regulatory publications (USEPA, 1979; 1982a; USEPA-COE, 1981). It is anticipated that the uniform set of guidelines contained in this manual will promote consistent collection and analytical methods for securing information on estuarine chemistry. These guidelines will in turn provide improvements in the reliability of the data and allow meaningful data comparisons to be made for the navigational areas of Florida's ports and estuaries. Results obtained from incorporating these improvements will help identify common environmental concerns at each port, accelerate regulatory reviews and provide appropriate regulatory approaches that are responsive to environmental problems.

2.0 GENERAL ESTUARINE CHEMISTRY

2.1 Water Column Chemistry

The estuarine water column is an important transition zone in the geochemical cycle. Metals, nutrients, and organic matter are continually being released from the land as a result of natural phenomena such as erosion and weathering, and are subsequently transported downstream to the estuary.

When freshwater mixes with brackish, estuarine water, a number of physical and chemical processes occur that affect the fate of river-borne chemicals. While most river water ranges from acidic to neutral and has low ionic strength, the composition of seawater is much more alkaline, and shows less variability in the concentration of major chemical constituents. Increases in pH and ionic strength (elevated concentrations of ions such as Na^+, Mg^{++}, Cl^- and $SO_4^=$) associated with seawater change the solubility of a number of substances in the water column. Additionally, increases in pH and ionic strength may also lead to physical changes (e.g., destabilization of colloids) that enhance flocculation and precipitation of many materials in estuaries. As a result, many of these substances are removed from the estuarine water column to the sediments during mixing. A good review of the dynamics of particle associations and their behavior in coastal environments is given by Olsen et al. (1982).

Particles such as clays and hydrated iron oxides traveling in river water can readily adsorb many chemical species from solution. As fresh water enters more saline waters, some of the material that was previously adsorbed to these particles (both natural and toxic anthropogenic materials) may once again be released into solution.

In addition to natural sources, metals and toxic organics may also be introduced to estuaries as a result of anthropogenic activities. Many of these potentially deleterious chemicals have the same fate as natural materials and estuarine sediments generally act as a sink for many of these constituents (see Section 2.3). Remobilization of estuarine sediments (e.g., dredging), may therefore, be a real threat to the estuarine biota since such activities may re-distribute these previously sequestered contaminants into the water column. Potential environmental problems arising from dredging activities are summarized in subsection 3.1 and in Appendix 6.

2.2 Organic Compounds in Estuaries

While the exact composition of organic constituents present in estuarine waters is poorly known, the major portion of organic matter (both dissolved and particulate) in estuaries is derived from riverine inputs and *in situ* biological production. Concentrations of these naturally occurring organic compounds can be as high as several parts per milion (mg/l) in the water column (Beck *et al*, 1974). By comparison, most anthropogenic inputs to an estuary are small and localized.

Utilization of organic matter by estuarine microorganisms results in oxygen consumption (i.e., oxidation). During warm periods, natural oxygen depletion of estuarine waters may result in extremely low dissolved oxygen concentrations. The organic matter in the water is said to exert an oxygen demand on the water column which is referred to as the biochemical oxygen demand (BOD). Although the BOD of most estuarine waters is generally less than 5 mg O_2/liter and results from the presence of natural organic compounds, anthropogenic nutrient inputs may lead to higher BOD values since such inputs stimulate increased biological production. For instance, typical organic matter released from municipial sewage treatment plants contains readily oxidizable compounds and may place a large BOD on portions of the estuary.

Natural organic compounds in aqueous environments are predominantly derived from degradation of adjacent terrestrial and aquatic plants. Once these materials have become incorporated into estuarine sediments, they can be rapidly oxidized. The natural organic component of estuarine sediments has a fairly constant nitrogen to carbon ratio of about 0.14 (Russell-Hunter, 1970). Ratios exceeding this value suggest an anthropogenic source of organic material entering the estuary.

Toxic organics such as phenols, petroleum hydrocarbons, and chlorinated hydrocarbons (e.g., PCB's and pesticides) have low solubilities in natural waters. In general, these compounds accumulate in sediments shortly after being introduced into estuarine waters. Once in the sediments, petroleum hydrocarbons and pesticides degrade at variable rates, depending on their structural complexity. For example, highly chlorinated pesticides such as toxaphene, mirex, chlordane, and DDT (and its break down products DDE, DDA, etc.) may persist for some time. Polychlorinated biphenyls (PCB's) are also extremely stable and exhibit little degradation in the estuarine environment.

2.3 Sediment Chemistry

Estuarine sediments contain detrital, natural authigenic, natural organic, and anthropogenic components. The relative importance of these four components varies geographically. The detrital component is composed of material derived from the drainage basins of rivers and streams that empty into the estuary. This material consists mostly of mineral phases (e.g., quartz, feldspars, carbonates, clay minerals and other silicates) resulting from physical weathering of the adjacent drainage basin. In general, such material has a homogeneous or consistent composition from drainage basin to drainage basin.

The most abundant authigenic materials in estuarine sediments are hydrated iron oxides. Iron, which is abundant in lateritic soils of the southeastern United States is weathered from the drainage basins of rivers and delivered to estuarine areas in solution. Upon mixing with seawater, the iron in freshwater precipitates out of solution as hydrated oxides and accumulates in estuarine sediments.

Characteristics of the anthropogenic components of estuarine sediments are difficult to predict. They will depend on the degree of industrialization and urbanization of the estuarine area and its drainage basin. Based on results obtained from DER's Deepwater Ports Project(DER, 1983; DER, 1984) the anthropogenic components detected in estuarine sediments of Florida appear to be localized and are therefore distributed heterogeneously throughout a given estuary.

The detrital component is by far the most quantitatively important constituent of estuarine sediments. In the absence of anthropogenic inputs, estuarine sediments may be considered deposits composed of grains of detrital minerals with fairly uniform amounts of hydrated iron oxide and natural organic additions. The detrital component will be influenced by physical processes that produce either fine or coarse grain sediment. Typically, coarse grain detrital sediments are composed predominantly of quartz and feldspar which have low metal concentrations and are resistant to to mechanical breakdown. Fine grain sediments are richer in clay minerals and contain greater concentrations of metals and hydrocarbons.

It is widely known that estuarine sediments act as a trap for upland-derived pollutants and in general, the pollution climate of an estuary will be reflected in the sediments rather than the water column. Thus, the major effects of maintenance dredging will occur as a result of redistributing these sediments and sediment-associated pollutants. A grasp of sediment chemistry is fundamental to understanding potential environmental problems resulting from dredging operations. This should not, however, preclude water quality analyses since background estuarine water quality conditions should be established. Characterizations of existing water quality then make it possible to assess the effects of dredging and disposal site dewatering activities on background levels of the receiving estuarine waters. Collection of this information helps identify environmental problems, take corrective action to minimize any degradation that might occur, and subsequently, to ascertain the efficiency of such control measures employed at dredge and disposal sites.

2.4 Sediment Chemistry and Data Interpretation and Their Relationship to Section 17-45, F.A.C.

As discussed in Section 2.2, the sediments reflect the chronic pollution climate of estuaries. Consequently, Section 17-45.17 provides sediment criteria for anticipating sediment behavior during dredging, selecting appropriate equipment and practices, and determining the need for testing and monitoring. The discussions in the following Section provide guidance for applying the criteria and making other decisions related to specific testing and permit actions.

3.0 DATA INTERPRETATION TOOLS

The concentration of chemicals detected in estuarine water and sediment samples is usually reported in terms of absolute concentrations. However, unless these concentrations can be related to the physical, chemical and other natural processes that predominate in a particular estuary, they are useless for understanding the pollution climate of that estuary. For a proper evaluation of estuarine data, it is crucial that ancillary data (e.g., salinity, dissolved oxygen) be collected simultaneously with water and sediment chemical samples.

For evaluating the significance of metal levels in sediments, it is useful to work within the framework of natural metal abundances. As an example, metal to aluminum ratios are particularly useful for identifying environmental problems since the relative proportions of metals in continental rocks and sediments have been found to be surprisingly consistent from one area to another

(Turekian and Wedepohl, 1961; Taylor, 1964; Martin and Meybeck 1979; Martin and Whitfield, 1983). Metal to aluminum ratios for a number of elements are given in Table 1 and a more extensive list is provided in Appendix 1. Sediment grain size is also important not only for evaluating sediment chemistry, but for understanding and estimating potential problems related to turbidity and resuspended bottom material.

A discussion of interpretive approaches focusing on metals, nutrients, hydrocarbons, biochemical oxygen demand, turbidity, and suspended solids are outlined in the following sections. By interpreting sediment data as described in Section 3.1, guidance is provided for applying Section 17-45.17, F.A.C. Additionally, these interpretive tools will distinguish between natural and polluted sediments, assist in determining appropriate dredging and disposal practices, and aid in assessing water quality degradation and other detrimental environmental effects.

3.1 SEDIMENTS

3.1.1 Sediment Grain Size

Sediment grain size is an important qualitative predictor of sediment chemistry. Fine grain estuarine sediments usually contain elevated concentrations of metals and hydrocarbons whereas lower levels are observed in coarse grain sediments. Fine grain sediments have greater concentrations because they are more enriched in organic matter and clay minerals (which are rich in metals). Additionally, fine grain sediments have greater surface areas and thus provide numerous binding sites for these chemicals.

Information on the mean grain size of sediments to be dredged is useful for assessing potential environmental impacts; for establishing best dredging and disposal practices; for providing reasonable assurance that State water quality standards will be met; and for determining the need for additional information regarding potential environmental impacts associated with dredging.

As described in DER Rule 17-45.17, sediment grain size is divided into three broad categories:

1) very fine sand, silt and clay (grain size less than .125 mm in diameter)
2) fine to medium sand (0.125 to 0.5 mm)
3) coarse sand and larger materials (greater than 0.5 mm).

This classification will enable the data reviewer to better distinguish natural versus anthropogenic inputs of contaminants and allow an assessment of potential environmental impacts from dredging these sediments. Section 2.3 in Part Three of this manual explains a simple calculation for determining mean grain size of a sediment sample.

3.1.2 Interpretation of Reported Metal Concentrations in Sediments

As mentioned in subsection 2.3, natural estuarine sediments have several components that are dominated by a detrital fraction. Metal concentrations will generally be controlled by the detrital component which is primarily derived from physical weathering of materials out of the adjacent drainage basin. As these detrital materials enter the estuary, many are removed from the water column during mixing processes (Section 2.1) and become incorporated into estuarine sediments. In general, fine grain sediments contain the highest concentration of these metals. Thus, elevated metal concentrations detected in estuarine sediments may represent naturally occurring levels that simply reflect the composition of the proximate drainage basin. Natural material from the earth's surface has been found to be uniform in the relative abundance of metals (Turekian and Wedepohl, 1961; Taylor 1964; Martin and Meybeck, 1979; Martin and Whitfield, 1983). Additionally, a farily constant ratio is observed for a particular metal to aluminum in continental rock and sediments (Appendix 1). Because aluminum is so abundant, aluminum concentrations are not likely to be greatly affected by anthropogenic inputs. Other metals less abundant than aluminum, however, may be enriched considerably as a result of anthropogenic inputs. Consequently, the use of metal to aluminum ratios is an extremely useful approach to environmental studies since aluminum is the most abundant metal in the earth's crust and thus, in sediments of crustal origin (e.g., estuarine sediments). In natural estuarine sediments, the metal to aluminum ratio would be expected to be fairly constant regardless of the grain size or the absolute metal concentration. Calculation of the metal to aluminum ratio therefore, normalizes sediment grain size and helps eliminate interpretive problems encountered when dealing with coarse and fine grain material.

For fine grain sediments, the metal-to-aluminum ratio appears to hold and provides a strong geochemical basis for interpreting results of metal analysis of estuarine deposits. Figure 1 shows this relationship for one metal, chromium. The stippled area shows the values of total chromium and the chromium to aluminum ratio expected for natural, or uncontaminated sediments. A method for distinguishing between metal concentrations resulting from natural processes and for those released by man-induced activities is carried out as follows.

First, the metal to aluminum ratio (based on the sample mean of triplicate results) is calculated for each metal for a given sampling station. Mean sediment grain size should be determined for each station according to the method described in Part Three, Section 2.3.

For <u>fine grain material</u> (sediments having a mean grain size less than .125mm in diameter), plot the metal to aluminum ratio on the abscissa (y axis) against the concentration of that metal on the ordinate (x axis) of the appropriate graph in Appendix 2. The area below y_1 marks the natural metal to aluminum ratio for that metal; the area to the left of x_1 represents the concentration of the metal observed in natural or unpolluted fine grain sediments.

If the plotted value lies outside the stippled area, then the sediment sample is considered to be polluted and an elutriate test is then required for that sediment. Such a test will help determine whether or not the metal could be released during dredging. If the test shows a release of the metal, then appropriate dredging or disposal practices will be required. Plotted points

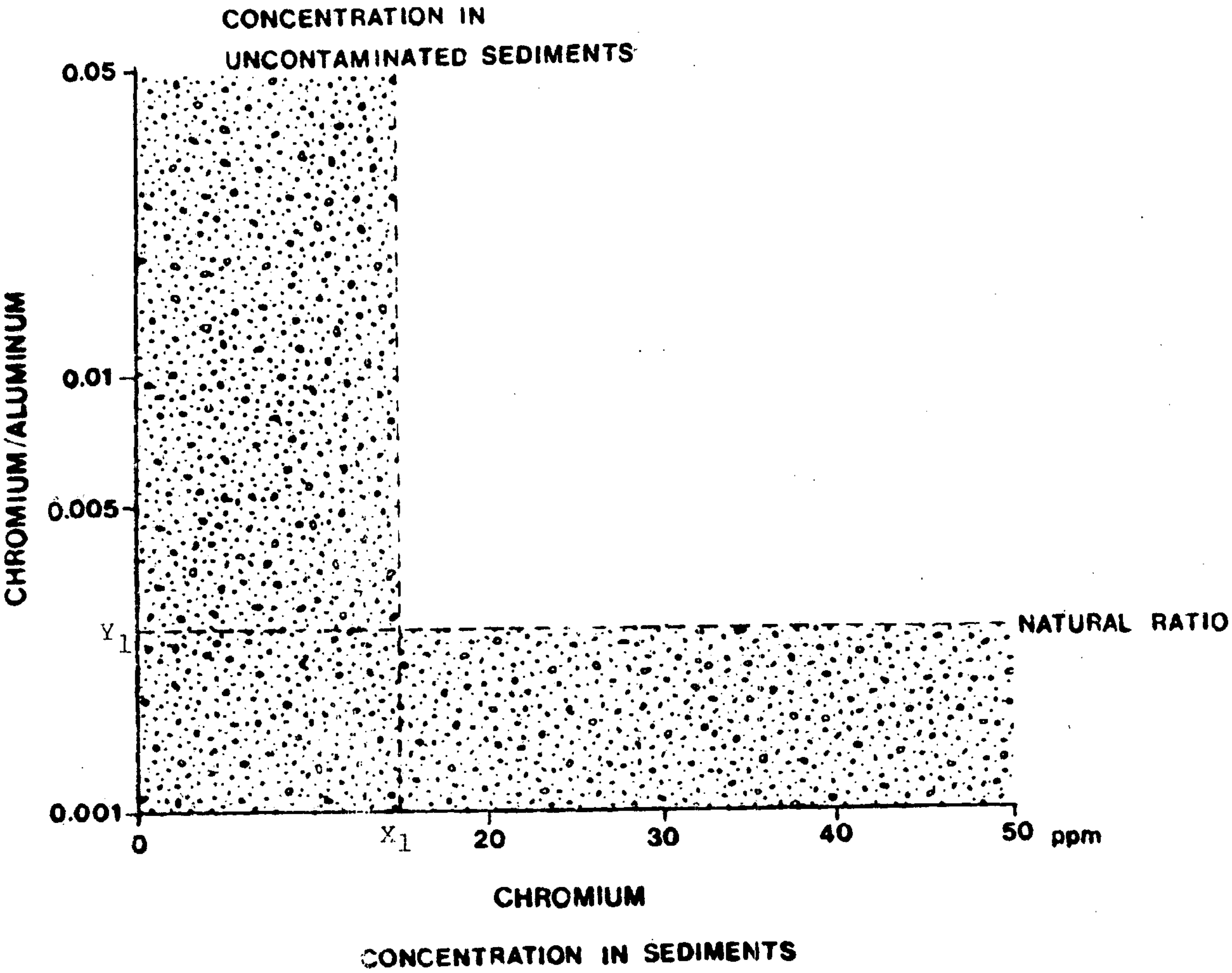

FIGURE 1: Sample Graph of the Chromium to Aluminum Ratio Versus Total Chromium Concentration Reported In Natural Sediments. Values Falling Outside The Stippled Area Are Considered To Be Representative of Polluted Sediments, Whereas Those Values Plotted within the Stippled Area Are Considered Natural Levels For Chromium.

(X_1= 15 PPM; Y_2=.002).

falling below the y_1 intercept are deemed unpolluted and no further testing is suggested for that metal. Similar figures for other metals of concern are given in Appendix 2. Metal concentrations and ratios falling within the stippled areas of the figures in Appendix 2 would be expected to pose no environmental problems.

Fine to medium sands and coarse grain natural sediments (sediments whose mean grain size is greater than .125mm in diameter) are low in metal-rich detrital minerals, but metal-rich natural authigenic phases (e.g., iron oxides) are often more quantitatively important to the total metal concentration. Consequently, the metal to aluminum ratio may be much higher than the natural ratios given in Appendix 1, and therefore Table 1 should be consulted. In order to overcome this deficiency, data obtained from DER's Deepwater Ports Study have been used to define natural metal concentrations in natural, coarse grain sediments (greater than .125mm in diameter) and are listed in Table 1. Sediments having a metal concentration that is less than the value given in column 2 of Table 1 are deemed natural. Sediments that contain metal concentrations greater than the value in column 2 but have metal to aluminum ratios less than that listed in column 3 are also deemed natural. Consequently, no further testing is required for a metal that meets these criteria.

Metal concentrations found in coarse grain material that do not fit into the categories outlined above are deemed polluted, and additional testing (e.g., elutriate tests) or monitoring is required. If a pollutant is released during the elutriate test,

TABLE 1

CRITERIA FOR DETERMINING METAL CONTAMINATION IN COARSE GRAIN ESTUARINE SEDIMENTS.

Sediments having concentrations less than the levels listed are considered uncontaminated and no additional testing is necessary. Sediments having metal concentrations greater than those listed in column 2 but having a metal to aluminum ratio below that listed in column 3 are also deemed uncontaminated.

Sediments are "flagged" as being potentially contaminated if the observed values exceed the levels shown in both Columns 2 and 3, and further testing or monitoring is warranted.

METALS	CONCENTRATION (ppm)*	METAL TO ALUMINUM RATIO
Arsenic	1.0	2.4×10^{-4}
Cadmium	0.5	8.3×10^{-6}
Chromium	15	2.6×10^{-3}
Copper	5	9.5×10^{-4}
Lead	9	2.1×10^{-4}
Silver	0.1	2.4×10^{-5}
Nickel	20	9.1×10^{-4}
Mercury	0.20	9.7×10^{-7}
Zinc	40	8.5×10^{-4}

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* Cutoff values were determined from results generated from the DER Deepwater Port Study (1982, 1983) by plotting metal concentration against mean grain size (N=88 for each metal). These concentrations represent the intercept of the trend line for coarse grain sediments (>0.1mm diameter). It should be noted that most of these concentrations are considerably lower than the EPA Overboard Disposal Criteria.

then appropriate dredging techniques will be required to minimize environmental degradation in the estuary.

As discussed above, potential problems associated with a metal in sediments to be dredged can be evaluated based on metal concentration and metal to aluminum ratio. However, potential environmental problems associated with turbidity might also exist during a dredging event, and sediment grain size must be determined. If a large percentage of fine grain materials is encountered, then appropriate dredging techni- ques must be employed to reduce turbidity and suspended material.

3.1.3 Nutrients in Sediments

Nitrogen, phosphorus, carbon and silicon generally comprise the nutrients that are growth-limiting for photosynthetic organisms. Each of these elements is ubiquitous in the estuarine environment and reflect natural and man-induced inputs to the system.

When excessive nutrients are introduced into an estuary, a number of detrimental processes may occur. Under these conditions, growth of phytoplankters is stimulated, and dense phytoplankton blooms follow. As these plants die and are processed by other organisms, respiration may exceed photosynthesis in the water column and oxygen depletion will follow. While this specific relationship is well documented, much less is known about the indirect relationship between nutrient enrichment and its effect on predators at different trophic levels. Recent studies of the Chesapeake Bay suggest that the decline of important fisheries and submerged aquatic in the Bay may be a result of nutrient enrichment (USEPA, 1982b).

In most of Florida's estuaries, nitrogen is the limiting nutrient for growth. Consequently, an excessive nitrogen input to the system may produce a range of deleterious effects. Nitrogen occurs as nitrite, nitrate, organic nitrogen (measured as Total Kjeldahl Nitrogen), and ammonia. Of these, ammonia can be critical to the survival of estuarine organisms since it can be toxic or stimulatory to the biota, depending on which ionic form is present.

The release of nitrogenous compounds in effluent from disposal operations is well documented. Windom (1973) reported large nutrient increases during disposal activities in his study of five southeastern estuaries. Algal growth was significantly greater when dredged material was placed in experimental receiving waters. A similar trend in elevated nitrogen concentrations has been documented in the effluents from estuarine disposal sites by the U.S. Army Corps of Engineers Waterways Experiment Station (Hoeppel, 1982). These findings are consistent with the department's Deepwater Ports Study which indicated that ammonia is released from organically-enriched estuarine sediments during elutriate tests (DER, 1983). Thus, nitrogen compounds in sediments should always be considered a potential problem during dredging and disposal operations.

Information on Total Kjeldahl Nitrogen (TKN) and Total Organic Carbon (TOC) in estuarine sediments provides a basis for evaluating the potential release of nutrients and potential oxygen demand associated with dredging a given sediment. During the DER Deepwater Ports Study, sediments were typically found to have TKN to TOC ratios ranging from 0.1 to 0.2 (Appendix 3). These results agree with TKN to TOC ratios reported for natural estuarine sediments (Russell-Hunter, 1970). Ratios greater than approximately 0.15 coupled with high TOC values suggest that sediments may release nutrients during dredging.

It should be noted that natural fine grain sediments can contain high TOC and TKN concentrations. Sediments with naturally high TOC and TKN may pose potential problems during dredging due to nutrient release or oxygen demand. Consequently, an elutriate test or operational monitoring maybe required to determine the release of these potentially deleterious compounds. This will provide a better understanding of the effects of nitrogen releases during dredging and assist in improving dredging and disposal site management practices.

3.1.4 Hydrocarbons

Hydrocarbons comprise both natural and synthetically derived compounds that can adversely affect estuarine biota and cause public health problems. Like metals, organic compounds tend to settle out of the estuarine water column and become trapped in sediments. Again, because of greater surface areas, fine grain sediments generally contain the highest concentration of hydrocarbons. Not surprisingly, dredging fine materials could remobilize toxic organic materials that are potentially deleterious to estuarine biota.

While a bulk sediment test for assessing potential impacts of excessive hydrocarbons in sediments is not currently available (Dr. Pat Parker, personal communication), hydrocarbon-rich sediments can be flagged as follows. Sediments containing oil and grease concentrations greater than 300 parts per million are deemed unnatural and should be subjected operational monitoring. Similar precautions should be taken when the sediment ratio of Total Kjeldahl Nitrogen to Total Organic Carbon approaches 0.05. Values falling below this ratio suggests that elevated hydrocarbon concentrations are present and further testing is required.

3.1.5 Turbidity, Transparency, and Total Solids (Suspendable and Settleable)

While the terms turbidity and solids are often used interchangeably, they reflect measurements of different conditions in the water column. Turbidity measures the scattering and absorption of light resulting from the presence of suspended matter in the water column, including biotic and abiotic components. The total suspended solids (TSS) measurement, expressed in milligrams per liter, represents the non-soluble particulate matter in the water column.

In any case, increased turbidity and solids levels are characteristic effects of dredging operations. The most serious concern of dredging associated with these effects relates to the reduction of the compensation point in the water column[1]. As stated by the National Academy of Sciences (1973): "The combined effect of color and turbidity should not change the compensation point more than 10 percent from its seasonally established norm, nor should such a change place more than 10 percent of the biomass of photosynthetic organisms below the compensation point" and "aquatic communities should be protected if the following maximum concentrations of suspended solids exists:

High level protection	25/mg/liter
Moderated protection	80/mg/liter
Low level of protection	400/mg/liter
Very low level of protection	over 400/mg/liter"

Priest (1982) has summarized the ranges of suspended solids created by different dredges. TSS ranged from several hundred mg/l downstream for a cutterhead to a maximum of 500 mg/l for clamshell dredges. These levels approach concentrations that could be deleterious to estuarine biota. However, little research has been done on dredges as a source of suspended solids, and a better understanding of this relationship is necessary. Similarly, the concentrations and composition of TSS in disposal site effluent has received little attention by researchers. As

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[1] Compensation point marks that point in the water column where photosynthesis and respiration are equal, and usually indicates the lower limit of growth for photosynthetic organisms.

high levels of TSS in effluent are potentially harmful to estuarine plants and animals (Appendix 6), attention must also be given to this aspect of dredging operations.

Currently, there is no adequate method for predicting the impact of dredging and disposal on estuarine biota. Careful professional judgement should be used in estimating the output and effects of turbidity and suspended solids. Monitoring and testing should be performed regularly when TSS and turbidity problems are anticipated, especially in those areas containing seagrass meadows, reefs or other fragile biological areas. However, for these results to be meaningful, background TSS and turbidity levels must be established prior to dredging.

Measurements of photosynthetically active radiance (PAR) or downwelling spectral irradiance should be made in order to address any changes in water column transparency and compensation point that could result from dredging and disposal operations. Calculations of the compensation point should be made before, during and after dredging operations are carried out adjacent to these light-dependent habitats.

For seagrasses, 10% of the surface insolation is usually accepted in the scientific literature as the minimum light requirement for viable seagrass beds. (Van Tine and Wetzel, 1983, R. Lewis, personal communication, and others.) Pursuant to Chapter 17-3.121, F.A.C., ten percent of surface insolation should be maintained at the normal maximum depth at which seagrasses occur in the area to be dredged. Because this depth varies geographically, existing information on the maximum depth of seagrass viability should be determined. Surface insolation or PAR can be measured by a spectroradiometer and from these results, the compensation point can be calculated.

3.1.6 Biochemical Oxygen Demand (BOD)

BOD measures the concentration of oxidizable organic matter. Often, dredging of organically-rich sediments can decrease the amount of oxygen that is available for estuarine organisms to respire. Measurements of BOD provide useful information on potential water quality impacts when used in conjunction with other information on nutrients and organic material in estuarine sediments.

At present, there is no simple procedure for predicting the severity of oxygen depletion associated with dredging and disposal site discharges. Potential environmental problems associated with dredging sediments with a high BOD will require substantial professional judgement that considers the type of organisms present, estuarine flushing/mixing processes, and the duration of the dredging operation, and other pertinent factors.

3.2 Interpretations of Water Quality Data

Concentrations of metals and other substances such as nutrients and TOC in estuarine waters reflect the concentrations of the two end members (fresh water and sea water), and various processes that take place in the water column. The degree of solubility indicates whether the material will be removed from the water column or released from the bottom sediments. If a metal behaves conservatively (no removal or release), its concentration will be a linear function of salinity. Even when metals are found to be nonconservative (removed or released during mixing of fresh and salt water due to natural processes), a consistent relationship to salinity is generally observed (Windom, et al, 1971; Waslenchuk and Windom, 1978; Boyle, et al, 1977; Eaton, 1979). Pertubations of these natural relationships are an indication of other pollution inputs. Information on the salinity of water samples is essential in evaluating anthropogenic influences on water quality. Plotting metal concentrations against salinity should show a consistent pattern, and the appearance of outliers or elevated concentrations between end members (mid-estuary maxima) in such plots may indicate pollutant inputs to the estuary. Appendix 4 shows a typical plot for one metal, lead versus salinity.

Although concentrations of metals in the water column vary from one estuarine system to another, levels are generally low. Any excess due to local input is generally removed rapidly from the water column to the sediments. Metal concentrations in southeastern estuaries have been found to vary as follows: arsenic, from 0.1 to 1 µg/l* (Waslenchuk and Windom, 1978); copper, 0.2 to about 1.0 µg/l; nickel, 0.4 to about 1.0 µg/l; and cadmium, 0.01 to about 0.1 µg/l (Windom, et al, 1982). Iron and manganese concentrations range from 1 µg/l to greater than 100 mg/l (Beck et al, 1974; Windom et al, 1971). Similar concentrations have been observed in other, highly industrialized rivers such as the Mississippi (Boyle, 1983). Mercury concentrations of approximately one ng/l** were recently reported for the St. Johns River (Olaffson, personal communication and Appendix 14) and are consistent with values reported for the southeast Atlantic by Windom and Taylor (1979).

3.3 Overview of the Application of Elutriate Tests in Estimating the Effects of Dredging and Disposal

During maintenance dredging and disposal, impacts on water quality are often related to the release of materials from sediments dispersed during each of the operations. In estimating impacts prior to dredging, the potential of dredged sediments to release pollutants or other degrading materials must be evaluated. Substances which may be released during maintenance dredging of estuarine sediments include toxic metals, organic compounds and biostimulatory/inhibitory substances. Suspended particles may exert an oxygen demand on the water column, and can also reduce light penetration required by photosynthetic organisms. A summary of potential environmental effects associated with dredging is presented in Appendix 6.

The first attempt to establish a basis for evaluating the potential impact of a sediment on water quality during dredging was made during dredging operations in the Great Lakes (U.S. Army Corps of Engineers, Buffalo District, 1969). Laboratory studies suggested a relationship between the bulk chemical composition of

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* parts per billion (ppb)
**parts per trillion (pptr)

sediment and its biostimulatory or toxic potential. As a result of this work, the U.S. Environmental Protection Agency adopted criteria (EPA, 1975) for determining the acceptability of dredge spoil materials for disposal in the nation's waters. The criteria consisted of discrete concentrations of those constituents observed in sediments, above which water quality degradation was predicted to occur during the dredging.

Subsequent to the adoption of these criteria, a number of studies of actual dredging and dredged material disposal operations demonstrated that changes in the quality of receiving waters bore no simple relationship to the bulk chemical composition of the sediment (Windom, 1972; May, 1974; Keely and Engler, 1974; Windom, 1974; Windom, 1975). As a result, Keely and Engler (1974) proposed the use of an elutriate test which consisted of agitating an aliquot of the sediment to be dredged in a given volume of water and measuring the amount of a substance which is released over a prescribed time period. Their rationale for the development of the elutriate test was as follows:

> "...regulatory agencies faced with the legislative requirement of establishing dredged material criteria, must strive to establish meaningful criteria based on the best possible knowledge, and avoid the tendency to set forth criteria that precede the current technical state-of-the-art. Furthermore, regulatory criteria should be based on laboratory procedures that can be performed satisfactorily in routine testing laboratories as opposed to complicated procedures that can only

be conducted in sophisticated research-level laboratories. Finally, in order to be equitable, the criteria should not be prohibitively expensive."

Utimately, this work led to the standard elutriate test (Keely and Engler, 1974; Lee et al, 1975; USEPA-COE,1981) for evaluating the suitability of dredged sediment for open water disposal as required in Section 404 of the Clean Water Act.

The standard elutriate test has met with criticism because the results are dependent on a number of conditions (e.g. filtering, pH, and DO) that may vary during the test. Although the test does not represent actual environmental conditions, it does provide a more realistic estimate of potential water quality problems than does bulk sediment analysis alone.

It is important to note that the elutriate test was not specifically designed to evaluate water quality impacts on waters receiving effluents from confined disposal areas. At the present the U.S. Army Corps of Engineers' Waterways Experiment Station is conducting research to evaluate predictions of contaminant levels in effluents from confinement areas using modifications of the elutriate test (Palermo, 1982).

It may not be possible to closely predict disposal site effluent pollutant concentrations from results of elutriate tests, since duplication of disposal conditions in the laboratory is difficult. However, results of Windom (1974) clearly indicate that the general direction and magnitude of changes in effluent quality (with respect to the receiving water quality) can be estimated from such tests. For several study areas, high levels of nutrients, BOD, DO and low metal concentrations in effluents discharged from spoil disposal areas were predicted by analyzing the aqueous phase of sediment-water suspensions taken directly from dredge pipeline, prior to deposition in the disposal area (Windom, 1974).

Even with the inherent problems in applying the elutriate test, it is presently the most straightforward, cost-effective means for estimating material release to and impact on receiving waters during maintenance dredging. Results of elutriate tests themselves should never be used as standards for evaluating dredging operations using confined disposal. Elutriate testing can, however, serve as a basis for predicting impacts on receiving water and for developing disposal practices during actual maintenance dredging operations. During maintenance dredging, predictions can be verified by monitoring disposal area effluents and these findings can, in turn, be used to modify future predictions.

PART THREE

FIELD AND LABORATORY METHODS

1.0 FIELD COLLECTION PROCEDURES FOR WATER AND SEDIMENT SAMPLES

As discussed in the background section of Part Two, an examination of over ten years of estuarine water quality and sediment information demonstrated considerable variation within and among data sets. For the reasons discussed previously, it was determined that this information was unreliable and inadequate for making environmental decisions.

Paramount to the quality of any data generated from an environmental study is the care taken during field collections and laboratory analyses, particularly when dealing with chemical samples obtained from marine and estuarine systems. While considerable effort often goes into selecting an adequate sample size to address spatial heterogeneity at each sampling area (e.g., representative number of sampling stations), proper collection and handling techniques are often neglected. Consequently, sediment and water samples can be contaminated before arriving at the laboratory for analysis. Thus, the accuracy of such data is questionable and results from the study become essentially meaningless.

A summary of potential problems associated with handling and analyzing each parameter follows. Detailed field and laboratory methods are provided in subsequent sections of the manual. Procedures for collecting estuarine water, bulk sediment, and elutriate samples are designed to minimize sample contamination and alteration of the physical chemical properties. Analytical procedures described represent EPA approved methods with modifications that can be followed easily by most chemical laboratories. Collection techniques for securing information on the physical properties of a sediment sample (e.g., Atterburg limits, settling rates, etc.) are also provided.

A basic list of useful sampling gear as well as a set of guidelines for occupying and securing ancillary information at each sampling station is given in Table 2. It should be emphasized that while the procedures outlined herein should be followed closely, the type of sampling equipment is left to the discretion of the lab or sampling team.

Table 3 lists parameters that could pose a potential environmental threat during dredging operations. Specific parameters to be analyzed should be determined on a port by port basis in consulation with the department. Table 3 also lists detection limits that are expected of participating laboratories. Analytical procedures are referenced in Tables 6 and 7. These techniques are capable of producing detection limits considerably below the limits referenced in Table 3, provided good laboratory practices are maintained. Marine waters generally contain levels of the parameters below the detection limits listed in Table 3.

1.1 COORDINATION OF FIELD SAMPLING AND ANALYTICAL EFFORTS

One of the keys to achieving high quality data is coordination between field sampling and laboratory personnel. Prior to initiation of field sampling, a meeting should take place between the project manager, the field crew chief, and the laboratory pro-

TABLE 2
FIELD EQUIPMENT

Parameter	Field Equipment or Instrumentation	Manfacturer and Model Number
Depth	Graduated, weighted line; recording fathometer	Optional (although fathometer should be sensitive at <15ft depth)
Salinity	S.C.T. Meter	Yellow Springs Instrument Co., Inc. (YSI) Model 33 S.C.T. Meter
	Refractometer	American Optical (AO) Automatic Temperature Compensated Hand Refractometer Model 10419
Conductivity	S.C.T. Meter	YSI Model 33 S.C.T Meter
Dissolved Oxygen	D.O. Meter	YSI Model 57 D.O. Meter
pH	pH Meter	Analytical Measurements Inc., Model 107 pH Meter
Turbidity	Turbidimeter	Hach Chemical Company, Hach Portilab Turbidimeter Model 16800
Transparency	Secchi Disk	Wildco Instruments
Water Chemistry	Peristaltic Pump	Cole Parmer Peristaltic Pump Model 1-7530-20 (high speed)
	Pipette	Automatic Micropipette Disposal Polystrene pipettes
	Water Sampler	All metal Water & Sewage Water Sampler
	Ultrex Ultrapure (HNO_3) Sulfuric Acid (H_2SO_4)	
Temperature	Thermometer S.C.T. D.O. Meters	Standard Armored thermometer YSI Model 33 SCT meter & YSI Model 57 DO Meter
Sediments	Ponar Grab Sampler 23cm x23cm (9"x9")	Wildco Model #1725-010 (approx. 60 lbs.)

NOTE: The equipment listed above is not endorsed by the department, but has proven to be functional during the Deepwater Ports study.

TABLE 3

DESIGNATION OF PARAMETERS TO BE ANALYZED AND REQUIRED DETECTION LIMITS (D.L.)

Parameters	Water Column		Sediment		Elutriate[4]
	Analysis	D.L. (μg/l)[2]	Analysis	D.L. (mg/kg)[3]	
Aluminum (Al)	-	-	x	10.0	x
Arsenic (As)	-	0.1	x	1.0	1
Cadmium (Cd)	x	0.05	x	0.05	x
Chromium (Cr)	x	0.2	x	1.0	x
Copper (Cu)	x	0.2	x	1.0	x
Fluorides (F)	1	100.0	1	1.0	1
Iron (Fe)	x	1.0	x	1.0	x
Lead (Pb)	x	0.2	x	1.0	x
Manganese (Mn)	-	1.0	1	1.0	1
Mercury (Hg)	x	0.1	x	0.1	x
Nickel (Ni)	x	0.2	x	1.0	x
Silver (Ag)	x	0.05	x	0.05	x
Zinc (Zn)	x	0.2	x	1.0	x
Total Kjeldahl Nitrogen (TKN)	x	100.0	x	10.0	x
Total Suspended Solids (TSS)[2]	x	5000.0	-	-	x
Oil and Grease	-	5000	x	20	x
Pesticides (scan)	x	0.01-0.25	x	0.01-0.05	x
Petroleum Hydrocarbons and PAHs	-	10	1	0.5	1
PCBs	1	0.25	x	0.05	x
Phenols	1	0.01-0.5	x	0.05-0.4	1
Nitrate (NO_3)	-	50.0	x	1.0	
Ammonia	x	50.0	x	0.1	x
Total Phosphorus	x	30.0	x	1.0	x
Total Organic Carbon (TOC)	-	1000.0	x	10.0	-
Grain size	-	-	x	-	-
BOD	x	1000.0	-	-	x

x Should be analyzed

- Not applicable

[1] Selection should be made according to port-specific problems with this parameter.

[2] parts per billion (ppb)

[3] Dry basis (ppm)

[4] Elutriate detection limits are identical to water column D.L. with exception of TSS, where D.L. for elutriate test is not applicable.

ject manager. At this meeting, the design of the entire sampling program and sampling schedule should be reviewed.

The chief chemist should review the sampling program design and prepare a list of required sampling containers for each station. A sample custody form (Appendix 11) containing a checklist of all bottles shipped to the field should also be prepared. When the field crew fills a sampling container, it should be noted on the sample custody form that the sample was taken.

Since the field crew does not often have access to proper supplies, reagents and a clean laboratory area for preparation of sampling containers, the responsibility for preparing all sampling containers should lie with the chief laboratory chemist or a designate. It is recommended, however, that the sampling team keep a small container of sulfuric and ultrapure nitric acid on board in the event that sample bottles are accidentally contaminated in the field. Sample bottles should be acid rinsed with the appropriate chemical acid prior to making sample collections (Table 4). Generally, it is convenient for the laboratory personnel to pre-label all sample containers and to pack each station's bottles in a separate styrofoam chest or cooler. This chest can be used to keep the sampling containers organized in the field and for delivery of samples to the laboratory. Each sampling container should be coded (e.g., color codes to denote which preservatives are to be added) to make the field sampling crew aware of the parameters to be analyzed for the sample in that container.

Table 4 shows the sampling containers, preservatives and maximum storage times required for collecting each water para-

TABLE 4

SUMMARY OF SAMPLING AND HANDLING REQUIREMENTS FOR ESTUARINE WATER AND SEDIMENT SAMPLES

Water Samples[1]

Parameter	Container	Preservation	Regulatory Maximum Holding Time[2]
Metals (total)	acid rinsed hard plastic	ultra pure or redistilled HNO_3 to pH<2	6 months
Mercury	acid rinsed glass; glass or telfon cap	ultra pure or redistilled HNO_3 to pH<2	28 days
Phenolic compounds	solvent rinsed glass; TFE-lined cap	H_2SO_4 to pH<2 4°C	28 days
Pesticides and PCB's	solvent rinsed glass; TFE-lined cap	4°C	7 days
Ammonia-N	plastic	H_2SO_4 to pH<2; 4°C	28 days
TKN	plastic	H_2SO_4 to pH<2; 4°C	28 days
TOC	plastic	H_2SO_4 to pH<2; 4°C	28 days
Total Phosphorus[4]	plastic or glass	H_2SO_4 to pH<2; 4°C	28 days
Nitrate	plastic	H_2SO_4 to pH<8; 4°C	48 hours
BOD	plastic or glass	4°C	48 hours
Orthophosphate[4]	plastic or glass	4°C	48 hours
Residue (solids)	plastic or glass	4°C	7 days
Fluoride	plastic	4°C	28 days

TABLE 4 (con't)

Parameter	Container	Preservation	Regulatory Maximum Holding Time
	Sediment Samples[3]		
All parameters	acid and solvent rinsed glass; TFE-lined cap	4°C	48 hours

[1] Source of requirements is Table 105:1, Standard Methods, 15th ed.

[2] Environmental Protection Agency; Proposed Rules, Federal Register 44, No.244, December 18, 1979.

[3] Sediments should be processed within 48 hours. Extracts or digests can be held up to the regulatory holding times for water (above) provided they are properly preserved and stored.

[4] EPA 600/4-82-029.

meter. These items are generally based on the Environmental Protection Agency's proposed rules as outlined in Federal Register 44; 10.244, December 18, 1979. Table 105:1 (An errata page to the 15th edition of Standard Methods) lists these sampling and handling requirements.

1.1.2 REPRESENTATIVE SAMPLING

Several considerations are important for defining the chemical variability within a sampling area, since chemical species are inhomogeneously distributed throughout the estuarine environment.

Heterogeneity within the water column can be determined electronically by measuring conductivity, dissolved oxygen, salinity and pH along a vertical gradient. If the variability is great, then a decision must be made whether a more costly vertical chemical sampling profile is needed. In most cases, however, chemical species are short-lived in estuarine waters, and answers regarding the existing pollution climate of a port lie in the sediments. Thus, mid-depth water column sampling appears to be adequate for determining existing water quality conditions at a port. Additionally, one high salinity station (greater than 32ppt) should be sampled offshore so that sampling handling and analytical techniques (e.g. blanks, spikes) may be checked in the lab.

Sediment chemistry is generally much more spatially heterogeneous than water chemistry, and therefore it is more difficult to obtain a representative sample. Essentially, the greater the chemical inhomogeneity, the larger the sample size required to define the entire sampling area adequately. Sediment characteristics such as texture and color are good indicators of uneven distribution. Consequently, a good field sampling program should retain enough flexibility to readjust station locations according to information obtained from field observations. Samples should be collected near known point source discharges as well as in "clean" areas in order to distinguish worst-case from background chemical conditions.

All water and sediment samples must be collected in triplicate in order to account for spatial heterogeneity and to ensure statistical reliability of the results obtained from the sampling program. Obviously, a single value for a given parameter provides no information on the variability within the system. Similarly, for duplicate samples, if two different values are generated, the actual background concentration of that parameter still remains unknown.

A meaningful sampling program, for regulatory purposes, cannot be accomplished solely by obtaining data on mid-depth water chemistry at several locations within the port. Rather, the greatest sampling effort should be directed toward understanding the environmental chemistry of estuarine sediments.

1.2 FIELD SAMPLING PERSONNEL AND EQUIPMENT

Based on field experience during DER's Deepwater Port Study, it was found that three field technicians can effectively operate a sampling program using methods similar to those described in this document. It is imperative that careful notes of field conditions and all *in situ* recordings be made at each station.

Basic field sampling equipment is listed in Table 2 showing manufacturer model number. Designated equipment is not necessarily endorsed, but DER field personnel have found the listed equipment to perform satisfactorily during the initial deepwater port sampling programs. Note that although a winch-davit- snatch block system is extremely helpful for deploying the peristaltic pump tubing, ponar and corers utilized in sampling, such a system is certainly not essential to the project.

The all metal sewage and water sampler is optional, although it is an excellent device for minimizing contamination problems associated with collecting organic water samples. If this sampler is not used, pesticide and phenol samples may be collected from mid-water depths using the peristaltic pump with Teflon or silicone tubing. Tygon tubing should <u>not</u> be used to collect hydrocarbon or other organic water samples.

1.2.1 Occupying the Station

The following procedures should be followed when occupying a sampling station:

1. Before leaving berth, an inventory of all bottles and equipment should be made. *In situ* meters should be turned on at least fifteen minutes prior to being used to equilibrate with the ambient temperature.

   The location of proposed stations should be plotted on a nautical chart, although exact locations of these sites may be "fine-tuned" once the boat is on station. To the extent possible, sampling stations should be co-located with navigation markers.

2. When approaching a station, the following observations should be recorded:
   - ° location of channel and range markers in the vicinity of the station;
   - ° channel width and depth as indicated on nautical chart;
   - ° frequency of ship traffic in the area including recent passages;
   - ° tidal stage (e.g., ebb, flood, slack);
   - ° direction and estimated velocity of the current; and
   - ° presence of any non-point pollution sources.

3. To locate a designated sampling station relative to the existing dredged channel, the boat is positioned along a transect across the channel locating slopes, toes, and other physical features. Care should be taken to note channel traffic and avoid potential safety problems in the sampling areas.

Once the sampling site has been determined from the fathometer recordings, a weighted station locator buoy is dropped into that portion of the channel in which samples are to be collected. Commencing several hundred meters from the existing channel, begin a transect for recording bottom depths with the fathometer that would bisect the channel perpendicularly, as shown in Figure 2.

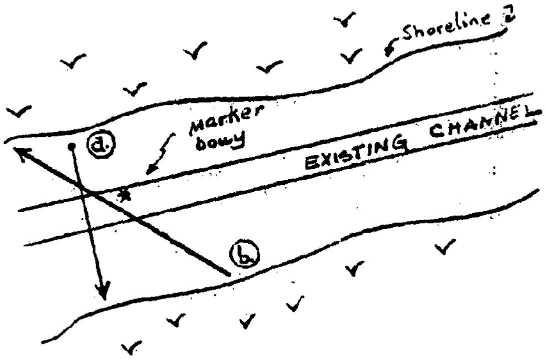
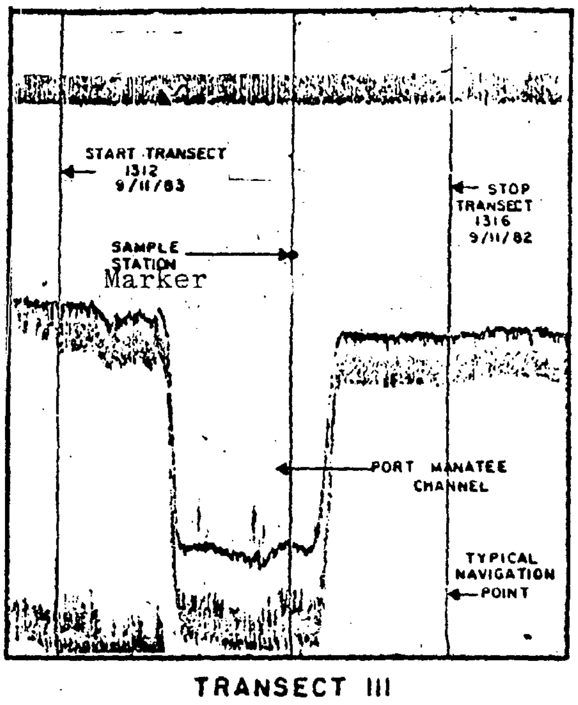


FIGURE 2: Typical Pattern for Running a Transect Across Navigation Channel.

If the channel is located near shore, begin the transect near the shoreline and terminate at the opposite shoreline. Indicate the location of the station marker buoy on the sensing paper as the fathometer electrode passes over it (Figure 3). Compass heading, rpm, drift rate of the boat, as well as starting and end-points of the transect should also be penciled on the fathometer's recording paper.

FIGURE 3: Fathometer Printout Showing Station Marker Location Relative To Channel, Transect Limits, and Channel Depth and Profile.



A second transect is then run at 45° angle across the channel, beginning either at the adjacent shoreline or, if the shoreline is too far from the station, several hundred meters from the channel if the shoreline is too far from station.

4. Noting velocity and direction of the current, drop the bow anchor so that when anchor is set, the boat will be near the station marker buoy and within the dredged channel. Wind direction and velocity will determine if a stern anchor is necessary to maintain a position within the channel.
5. After anchoring, tilt the outboard engine to the up position to help prevent contamination of water samples by oil, grease or gasoline.
6. Using magnetic bearings on landmarks (radio towers, water tanks), locate and mark the station location on the appropriate nautical chart.
7. Verify water depth using both the recording fathometer and lead line.
8. Record date, time of day, water depth, meteorological conditions, and general observations in the vicinity of the station (e.g., distance from outfalls, point pollutions sources, etc.) on the appropriate data sheet (Appendix 3).
9. _In situ_ recording meters which have been allowed to warm up should be calibrated according to manufacturer's instuctions at this time.

1.3 WATER COLUMN SAMPLING

Water samples can be collected with either discrete samplers (e.g., approved metal-sampling Kemmerer bottle) or a pump (e.g., peristaltic or magnetic) as long as the equipment and accessories are constructed of a non-contaminating material (e.g., Teflon®, silicone). Discrete samplers can, however, be easily contaminated when the open bottle passes through surface water which contains metals and low molecular weight organic compounds. In some cases, contamination may be minimized by avoiding visible surface slicks or by selecting a sampler with a large surface to volume ratio (EPA-COE, 1981).

Potential contamination associated with discrete samplers can be overcome, however, by using a peristaltic pumping device for making water collections. Collecting tubes or hoses should be constructed of silicone, Teflon® or some other inert material. Packing and lubricants used in some pumps are also a potential contamination source, and precautions should be taken if such equipment is used. The key to minimizing contamination in any of these pumps is to flush the system thoroughly prior to sample collection. Peristaltic or magnetic-type pumps have proven to to be reliable and are strongly recommended for obtaining uncontaminated water samples. Again, it should be emphasized that because boat exhaust can be a source of lead and other metals, the engine should be turned off and raised out of the water during water column sampling.

1.3.1 Peristaltic Pumping System

The peristaltic pump operates on a 12 volt marine or automobile battery. One end of tubing is attached to the intake of the pump while the remainder of the tubing is tethered to a weighted polypropylene line that is lowered to a mid-depth position in the water column (Figure 4-a). Preparation for water sampling using the peristaltic pump is as follows:

1. Swing the davit to the outboard position and secure.

2. Locate the peristaltic pump near the davit and connect the electrical (+,-) leads to a 12V automobile or marine battery.

3. If not done earlier, insert the pump head in the peristaltic pump housing.

4. Remove the pump head cover using a screwdriver and wrap the tubing around the pump head rollers so that two feet of tubing (the outflow end) extends from the pump head. Lubricate the pump head rollers using an inert lubricant such as Teflon® or silicone spray. This is done by removing the pump head cover and spraying the rollers. Each time the pump head is lubricated, the tubing should be shifted so that a different section of tubing passes over the rollers. (NOTE: Silicone or Teflon sprays may contain organic diluents or impellers. Consequently,

they should not be used where organic samples could be contaminated).

5. If not done previously, insert the intake end of the tube into a four-inch cube of wood with one-half inch hole drilled through the center for the line (Fig. 4b). Another one-half inch hole should have been drilled perpendicular to and slightly offset from the line hole to allow passage of the tubing. This block should be placed on the line, approximately one foot above the weight. Secure the tube from contamination by covering the openings with twist-tie wraps (e.g., Whirlpac®). The intake end should extend two to three inches from the wooden block. Attach a plastic-coated weight to the end of the line passing through the wooden block.

6. Attach the plastic-coated 10 kilogram weight to the polypropylene line (e.g., 3/8 inch) supporting the silicon tubing-block assembly and secure the line in the snatch block on the davit (Figure 4a). Secure the free end of the line. Hang the weighted end overboard and lower equipment into the water. The line should be clearly marked in one meter increments to ensure accuracy in sampling depth.

7. Lower the plastic coated weight to mid-water depth. If the current is greater than 1.5 knots, the tubing must be

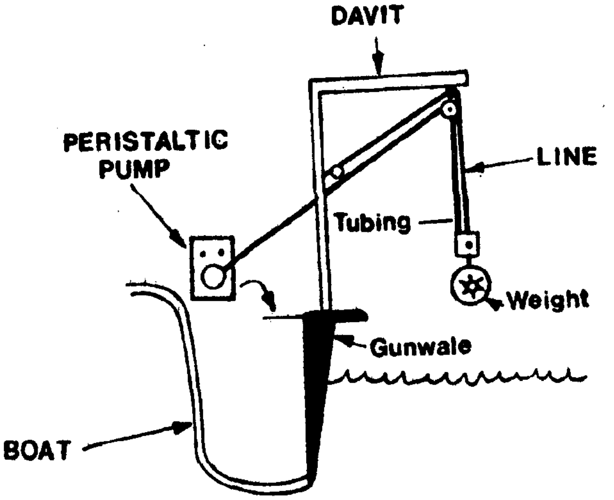


FIGURE 4a: Basic water and sediment sampling apparatus for use in a small boat. Line, tubing and weight (see Fig 4b) are lowered to mid-depth to carry out water column sampling. Device is also useful for collecting sediment samples.

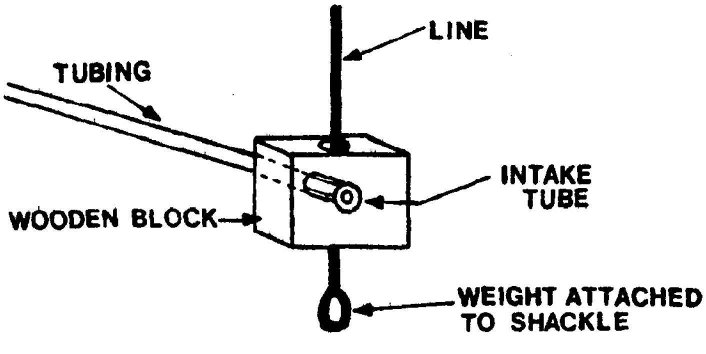


FIGURE 4b: Wooden block with attached polyproylene line, weight, and influent end of tubing to be lowered to mid-depth for water column sampling.

secured to the polypropylene line with duct tape at three to five foot intervals. If a strong current is present, deflection of the scope or angle of the weighted line must be minimized in order to ensure that mid-water sampling occurs. If the current is too strong for the weight, either attach a second weight or simply wait for slack tide.

8. Start the pump by pushing the switch to the forward position. If the pump is functioning properly it should prime and begin pumping water in about thirty seconds. Flush the pumping system and empty water into a plastic bucket for a minimum of two minutes before taking the first sample (water temperature can be measured in the bucket). Be sure to keep fingers and other objects away from the effluent opening of the tube to prevent contamination of the sample.

9. Flush each sample container twice with water from the peristaltic pump.

10. Collect each sample in the appropriate container (refer to subsections 1.3.2 through 1.3.8). Also record mid-water turbidity, pH, salinity and temperature readings as specified in Section 1.4.

11. When sampling is complete, shut the pump off and allow excess water to drain from the system.

12. Retrieve the weighted line so that the weight is hanging just below the water's surface and cleat the line. Secure a Whirlpac® or baggie over the effluent tube, being careful not to touch the end of the tube with fingers or against the hull (gunwale, deck, etc.).

13. Secure a Whirlpac® over the intake end of the tube after all residual water has drained from the tube, taking precautions not to touch the end of the tube.

14. Swing the plastic-coated weight into the boat and release the line from the cleat. The line can then be removed from the snatch block on the davit.

15. Secure the pump (pump head attached) and tubing.

16. Release davit lock, swing inboard and secure.

17. Preserve samples with appropriate reagents as described below.

1.3.2 Metals

Flush hard plastic bottles twice with pumped water and fill each replicate bottle, leaving sufficient room to add ultrapure nitric acid after sampling is completed. In order to minimize contamination, it is important not to touch the outflow end of the pump effluent tube and to keep fingers away from the mouth of the bottle in the field and while acidifying samples. The effluent end of the tube tube should not be allowed to touch or fall inside the sample bottle. Should a sample become contaminated, wash the bottle using a 5 ml solution of ultrapure nitric acid (HNO_3) and 10 ml of distilled water. Again, flush the bottle several times with water from the pump and collect another sample. Once a sample is collected add 0.5 ml of Ultrex ultrapure nitric acid to each sample bottle. If an automatic pipette is used, caution should be taken to avoid drawing acid into the pipette housing, as sample contamination will result when the acid encounters the housing. Clearly mark each sample bottle with a permanent marker (preferably twice in order to prevent confusion if erasures occur). Metal samples do not need to be stored on ice. Because high salinity water outside the port area is considered cleaner than distiller water used as a blank in laboratories, an offshore high salinity station should be established for collecting blank water.

1.3.3 BOD/TSS

Flush three soft plastic bottles twice with pumped water and then fill each bottle completely. Mark each bottle legibly using a permanent marker and store on ice.

1.3.4 Ammonia

While the pump is still running, flush three soft plastic bottles twice and then fill bottles, leaving enough volume to add sulfuric acid at the end of the sample collection period. After sample collection (either on the boat or immediately after returning to shore), fix each sample using 0.5 ml concentrated sulfuric acid (H_2SO_4). Avoid aerating the sample prior to acidification Caution should be exercised when using the automatic pipette to avoid sample contamination since contact with acid will destroy certain working parts of the pipette and the resultant leachate will enter and contaminate the sample.

1.3.5 Fluorides

Fluorides samples, if necessary (e.g., Ports of Tampa, Manatee or any other port that could have a fluoride problem),are collected in plastic bottles along with BOD and TSS during the water sampling program. Samples do not require acid fixation or iced storage.

1.3.6 Phosphorous

Total phosphorous and/or phosphate samples are collected in soft plastic bottles. Total-P samples are treated according to procedures described for ammonia in Section 1.3.4. No preservatives are required for orthophosphate. After all samples have been collected, secure the peristaltic pump system as discussed previously.

1.3.7 Pesticides

Particular caution must be exercised during the collection of pesticide samples since there are numerous potential contamination sources present. On the boat such problems may be overcome by employing an all-metal sewage and water sampler (available from COLE-PARMER or other scientific supply houses). To collect a sample for pesticide analysis, affix a glass bottle to the hand-held water and sewer grab sampling device (Figure 5). Loosen the cap slightly and attach the suction cup to the top of the cap.

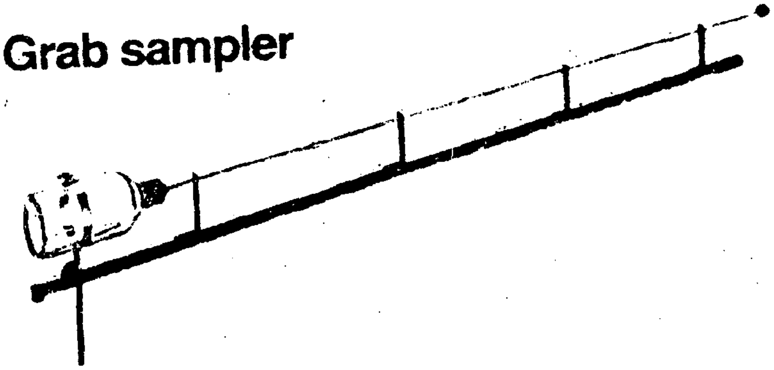


FIGURE 5: WATER COLUMN SAMPLER FOR ORGANICS.

Thrust the device into the water so that the sample container is five to six feet beneath the surface (a rope or line should be attached to the device if excessive currents are encountered). Open the container and when the bottle is approximately one-half full (judging from the release of air bubbles), retrieve the jar, agitate to flush, and empty back to water. Again, thrust five to six feet below surface, allow the sample jar to fill and retrieve sample. Repeat the sequence so that three samples are obtained. Examine each bottle cap to be sure an aluminum foil liner is present. If no foil is present, place a clean piece of foil over the mouth of the jar and screw on the lid. Clearly label each bottle by placing a piece of duct tape on the outside of each jar and marking with a permanent marker. Jars should also be marked with a wax pencil. No acid fixation is required but each bottle should be stored on ice. Plastics must not come in contact with the sample.

1.3.8 Phenols

Affix a glass jar to the water and sewer sampling device as described in the previous section. Thrust the device to a depth of five to six feet and again, allow the jar to fill partially. Retrieve, agitate in order to flush bottle, and empty the jar. Thrust the device to the same depth and allow the jar to fill with water sample. Repeat the sequence so that three samples are obtained. Add 1.0 ml of concentrated sulfuric acid (H_2SO_4) to each bottle (this should be done at the same time metal samples are preserved), using a glass pipette to measure the volume of acid delivered. Be sure that each bottle cap has an aluminum foil or teflon liner. If such a liner is missing, place a piece of foil over the bottle mouth and tighten the cap.

1.3.9 Salinity Measurement

Salinity is measured using a temperature compensated refractometer. Salinity and ph should be measured BEFORE and AFTER water column sampling. Samples should be collected using the peristaltic pump and placed in a rinsed cup for measurement. The refractometer must be calibrated before use by pouring distilled water onto the reading plate. The instrument should display zero salinity on the indicator scale. If the value is not zero the instrument should be adjusted according to the manufacturer's instructions.

1.3.10 pH Determination

pH is measured in the field using an analytical field pH meter. Mid-depth water samples are collected in a styrofoam cup or plastic bucket with the peristalic pump. Before using the instrument, it must be calibrated according to the manufacturer's instructions.

1.4 IN-SITU DATA COLLECTION

1.4.1 Salinity, Conductivity and Temperature

Measure salinity, conductivity and temperature at the beginning of mid-water column sampling. In-situ measurement of these parameters is easily accomplished using an approved SCT meter (e.g., Yellow Springs Instrument, Inc., Model 33 with a 50-foot probe cable or other comparable equipment by following the manufacturer's operation procedures explicitly). Instruments should be calibrated prior to use at each station and turned on fifteen minutes before sample collection begins. Care must be taken to establish correct null points (zeroes). Additionally, the instrument's sensitivity and accuracy should be verified by using a known standard reference sample.

The SCT cables should be marked in increments to facilitate calculating depths. In most cases it may be easier to lower SCT and D.O. cables at the same time and take simultaneous readings.

Once all readings are taken and recorded, the SCT mode control dial should be turned to the OFF position. The probe should be rinsed with distilled water and the cable rewound on the cable holder. The instrument and probe should be stowed so that they are well-cushioned and will receive the least possible shock once the boat is underway. The instrument and probe should not be left exposed to the sun for more than a few minutes before use.

1.4.2 Dissolved Oxygen

Dissolved oxygen (D.O.) can be measured using either the Winkler titration method or an EPA approved dissolved oxygen meter.

Dissolved oxygen values are determined for surface, mid-depth and bottom waters by lowering the probe to the desired depth and recording the indicated values. If the D.O. meter is used, the instrument should be turned on for at least 15 minutes before use to equilibrate with ambient air temperature. Calibration in an air calibration tube is highly recommended.

Occasionally, an air bubble will form under the probe membrane. When this occurs, the membrane must be removed. Care should be taken to ensure that the membrane is not covering the silver sensor rod of the probe. A small O-ring holds the membrane in place. Holding the probe so that the membrane end is up, use a pipette to fill the central cavity with KCl solution. A kit containing KCl crystals and membranes should be on board the boat at all times. Proper techniques for membrane replacement are shown diagramatically in the service kit (e.g., YSI 5034).

1.4.3 Water Temperature

Surface, mid-depth and bottom water temperatures may be determined using the SCT meter and the D.O meter as described previously. Mid-depth water temperature can be verified with a standard thermometer by collecting mid-depth water using the peristaltic pump. The thermometer should remain in the shade for at least one minute prior to reading temperature.

1.5 SEDIMENT SAMPLING METHODOLOGY

1.5.1 Deployment of Bottom Sampler

Sediment samples can be collected with a remotely-operated grab device (ponar, KB corer, Eckman) or using diver-operated cores. The choice between a corer or a grab sampler depends upon the type of dredging project in the port. Sediments for a new work or harbor deepening project should, of course, be collected with a coring device. In maintenance projects, vertical stratification is less likely and deep coring devices usually are not necessary. Sediments that have accreted in these areas since the last maintenance dredging operation are essentially homogeneous due to reworking by ship traffic. Thus, grab samplers are sufficient in most cases. An evaluation of various grab samplers presented in Appendix 7 and 8 (EPA/Corps,COE, 1981) suggests that a ponar dredge is considered the best sampling device for collecting sediments in maintenance projects. A recent study by DER found no difference for the concentration of cadminum and lead in sediments collected with ponar and core samplers.

Attach a one-half inch, nonstretch (e.g., Dacron) line to ponar dredge or corer (an Eckman dredge may also be used, although the sample volume is much smaller). Place the line through the snatch block on the davit. Secure the line to a nearby cleat. With assistance, carefully cock the ponar and lift it overboard. Lock the davit in the outboard position as a safety measure. Remove the line from the cleat and begin lowering the ponar to the bottom. Better samples are usually obtained if the ponar is dropped from 3 to 5 feet above the substrate. Once ponar is on the bottom pull on the line abruptly to trip the release mechanism. If the sediment to be sampled is exceptionally hard, additional weight (e.g., plastic coated 5 kg weights) can be attached atop the ponar line.

1.5.2 Sample Collection

Retrieve grab sampler (e.g., ponar or corer) with the winch or by hand. When sample is well above gunwale of the boat, unlock davit and carefully swing the ponar inboard. Care should be taken to keep hands and feet clear from equipment so that if the sampler accidentally falls, no injuries will result. Once inboard, lower the sampler into a rectangular Teflon® pan. If the ponar is used, the pan should have low sides and should be larger than the ponar so that the device can be easily opened once inside of the pan.

The ponar must remain low in the pan so that when the jaws of the ponar are opened, the sample will slip out of the ponar and into the pan without mixing.

Hydrocarbon and metal samples may be collected separately (as described in Sections 1.5.3 and 1.5.4) or placed together in one glass sample jar, provided that sediments are transferred from pan to jar using a utensil made of an inert material. Often, metal molds are used to manufacture plastic or Teflon® spoons/spatulas. Such utensils should be soaked in nitric acid prior to initial use in order to remove any potential surface contaminants. When placing sediments in sample bottles, extreme caution should be taken to avoid removing any sediments that have come into contact with metal ponar.

If a coring device is used to collect sediment metal samples, the corer must employ a noncontaminating insert sleeve or be constructed of an inert material. Samples of the top 6-8 inches of the core should be placed in the collecting jar. If desired, a vertical chemical profile can be obtained by placing 6-8 inch sections of the cored sediment into separate bottles.

1.5.3 TSS, TOC, Metals, Grain Size, Specific Gravity, and BOD

Using NON-METALLIC utensil, remove the oxidized layer (if present) from one-half of the surface of the sample. The oxidized layer may only be about one-sixteenth inch thick. Rinse the utensil between samples and be sure to prevent contact between the utensil and foreign substances (e.g., boat, hands). Care should be taken not to scrape the bottom of the pan or collect sediments that were in contact with the metallic ponar dredge. Fill a one quart plastic jar with sediment from the Teflon® or plastic pan ensuring that no air bubbles remain in the jar after it is filled. Tighten the cap so that an airtight seal is formed. Clearly mark each sample bottle with a permanent marker and store the samples in an ice slurry.

1.5.4 PCB, Pesticides, Oil and Grease, and Phenols

Using METALLIC utensils (or utensils made with an inert material), remove the oxidized layer from the remaining half of the sample remaining in the pan. Fill a glass jar (e.g., one quart) with sediment from the pan. Care should be taken not to scrape the bottom of the plastic pan and avoid sediments that are in contact with the ponar dredge. Legibly mark each sample bottle with a permanent marker on duct tape attached to the outside of the jar with a permanent marker. Store the sample bottles on ice.

1.5.5 Replicates

Repeat Sections 1.5.2, 1.5.3,and 1.5.4 in order to obtain triplicate samples.

1.5.6 Settling Rates and Atterberg Limits

A coring device (e.g., KB corer) is used to collect samples for Atterburg Limits, settling tests, and trace metals. If used for collecting metals, then a Lexan or other type of noncontaminating sleeve should be inserted into the steel core in order to prevent sample contamination. This corer will not penetrate bottom sediments composed of firm sand or sand with rock fragments. Secure the corer to the line. Place the line through the snatch block of the davit and cleat the free end. Swing the davit to the outboard position and secure (similar to preparing for deployment of water sampling equipment as depicited in Figure 4a). With assistance from crew members lift and hang the corer overboard. Set the corer triggering device. Slowly lower the corer to the bottom and release the line, holding it above the water-sediment interface. Attach the tripping messenger to the supporting line and release the messenger (tie a knot in the line to mark approximate depth so that collection of successive samples at the station is facilitated). If the bottom sediment is either fine grained or soft, the core barrel will slide through the material under its own weight. When the bottom material is firm, the core may have to free fall for the last two or three feet of water depth in order to penetrate the sediment and fill the core barrel. Drop the messenger device in order to trigger the corer's plunger and retrieve the core sampler with the crew's assistance and/or using a winch. Retrieval should cease when the top of the coring device is at the water surface so that sample is not lost. In order to facilitate collection of an intact sampler, a crew member then reaches overboard, places a hand over the bottom of the core barrel and lifts the bottom of the core barrel and lifts the core device inboard. Record the composition (e.g., texture, color, and layering of each core sample) and estimated penetration depth. The sample can then be extruded into a plastic pan. Homogenize the sample, then place into a plastic one quart jar and seal. Clearly mark the sample jar with a permanent marker. Store samples away from heat or direct sunlight.

1.5.7 Sample Inventory

Before leaving a station, an inventory should be conducted to ensure that all necessary samples have been collected. A sample checklist is presented on the field data sheets shown in Appendix 9 and the custody form in Appendix 10.

2.0 LABORATORY METHODS

2.1 Laboratory Sample Handling Procedures

A sample custodian should be designated prior to the delivery of samples to the laboratory. This person should have a copy of the entire sampling design and list of bottles that were sent to the field and will be responsible for receiving, checking and storing laboratory samples.

Samples should be brought into the laboratory and unpacked immediately. The samples which are to be analyzed for unstable parameters should be immediately refrigerated, frozen or prepared for analyses. All samples should be checked for proper identification and logged into the sample registry book. The sample custody form should be checked to ensure that every sample container was filled and safely transferred to the laboratory.

Any missing samples or problems should be noted in writing on the sample custody form (Appendix 10), by the custodian who should make daily checks to see that all samples are processed within the required holding times.

To insure internal accountability in carrying out analyses, the laboratory project manager or designate should prepare all job assignments.

2.1.1 Quality Assurance Project Plan

The laboratory should have an established quality control program which is based on quality control requirements as stated in DER's proposed quality assurance guidelines. The laboratory performing the analyses must be approved by the Department of Environmental Regulation for the parameters included in the sampling program. Additionally, the QA plan should address the items denoted in EPA/QAMS-005/80.

Upon completion of the analyses, the laboratory should prepare a quality control report which (1) explains the quality control assurance project plan, (2) provides precision and accuracy data which were generated on the analyzed samples, and (3) stipulates whether the quality control data are within acceptable standards to the department. A list of detection limits that will be required is given below.

PARAMETER	WATER COLUMN[1]	SEDIMENTS[2]
Aluminum	-	10.0
Arsenic	0.10	1.0
Cadmium	0.05	0.05
Chromium	0.20	1.0
Copper	0.20	1.0
Iron	1.0	1.0
Lead	0.20	1.0
Mercury	0.10	0.1
Silver	0.05	0.05
Zinc	0.20	1.0
Pesticides & PCB	0.01-0.25	0.01-0.25
Hydrocarbons & PAH	0.01-0.50	0.05-0.40
Nickel	0.20	1.0

A more detailed listing is given in Table 3 on page III-4.

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[1] Measured in micrograms per liter (ppb)

[2] Measured in milligrams per kilogram (ppm) on a dry basis

As an absolute minimum, the following quality control measure shall be taken with each group of samples analyzed:

1. A reagent blank should be run.

2. Duplicate analyses should be made on 10% of all samples, and precision data should be reported in the quality control report.

3. At least one audit or reference sample (EPA, NBS or other source) should be run and reported in the quality control report. This audit sample (water or sediment) should be within the same concentration range as the samples that are being analyzed.

4. Spiked samples should be run for appropriate parameters in order to address analytical accuracy. At least 20% of the samples must be spiked with an appropriate standard in order to address accuracy. The concentration of the spike should be large enough to increase the analyte's concentration by at least 50%, but not more than 200% above the original sample concentration. If the sample concentration is less than three times that of the analyte, then a spike of two to three times that detection limit is appropriate.

5. Printouts from all AA and GC analyses should be kept on file in the event that any problems with the data arise.

2.1.2 PROCEDURES

EPA approved procedures, when available, should be used for analyses. The recommended procedures for water and sediment are summarized in Tables 5 and 6. Other procedures may be used, provided it can be demonstrated that the procedure gives acceptable results and detection limits in saline waters.

2.1.3 Analytical Procedures for Determining Metal Concentrations In Saline Water

The detection limits for metals required to determine if Florida Class III water standards are being met can be obtained in saline samples only by procedures that will reduce the salt matrix interference. If the sample is analyzed directly by atomic absorption furnace techniques, matrix interferences from the salt will result in values 10 to 20 fold higher than the actual concentrations of most metals. These erroneous values in most cases will show ambient levels higher than Florida Class III water standards. For this reason, extraction-chelation procedures should be used for determining cadmium, chromium, copper, iron, lead, nickel, silver and zinc concentration in water. Applying this procedure to acidified, nonfiltered samples gives results which represent the total dissolved and weak acid-leachable particulate metals.*

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*Samples should not be filtered in the field unless a high level clean room is available on board the sampling boat.

A recommended method for extraction-chelation is the procedure of Kinrade and VanLoon (1974). This method is similar to the extraction-chelation procedure listed in EPA-600/4-79-020 and EPA/CE-81-1, except that two chelating agents are utilized and a specific pH is maintained for the extraction. Iron and zinc should be determined on the MIBK extracts by either flame or furnace atomic absorption. The remaining metals should be determined on MIBK extracts by furnace techniques unless high levels of trace metals are known to be present in the sample. In this case, ICP or flame AAS may be acceptable.

Since chromium must be converted to the hexavalent form prior to extraction, it is extracted at a lower pH than the remaining metals and a separate extraction is required. The method to be used for chromium extraction and analysis should be EPA-218-3 (EPA-600/ 4-79-020).

A gaseous hydride technique should be used for analysis of antimony and arsenic (EPA 206.3-600/4-79-020).

Accurate mercury analyses in seawater will require careful work. Mercury samples should be collected in glass bottles as described in section 1.3.2 and acidified with Ultrex HNO_3. At the laboratory, care should be taken to prepare mercury samples in a clean working area (e.g., Class 100 to 1000 Clean room with Class 100 work benches), since atmospheric mercury may be a potential source of contamination in many laboratories (e.g., where COD or TKN samples are analyzed).

Either of two analytical methods are recommended. The first procedure involves placing samples in bulb stoppered silica flasks, adding a 1% $K_2Cr_2O_7$ solution (1 ml/100g), and setting the sample aside for 24 hours. Samples are then U.V. irradiated for 4 hours under a 1 kw lamp. Mercury concentrations are then determined by cold vapor atomic absorption after $SnCl_2$ reduction and preconcentration on gold (Friemann and Schmidt, 1982; Olafsson, 1981, 1982). This method may not be appropriate when elevated levels of hydrocarbons are present in the water column (Appendix 12).

The second recommended technique is that used by Windom and Taylor (1979). This method employs cold vapor atomic absorption analysis on a 200 ml water sample. Five percent (w/v) $KMnO_4$ is added until the sample maintains the permanganate color for 15 minutes. Further oxidation is accomplished by adding 2 ml of 5% (w/v) potassium disulfate. The analyte is allowed to stand 30 minutes. Two ml of 12% (w/v) NaCl-hydroxylamine hydrogen sulfate are then added to eliminate any excess in oxidizing materials. Finally, 10 ml of 10% (w/v) SnCl in 3.N H_2SO_4 is added. The bottle should then be fitted to a closed aeration apparatus for cold vapor AAS.

The detection limit for each of these methods is in the nanogram per liter (parts per trillion) range which is below the State water quality standard of 0.1 part per billion mercury.

All sample preparation steps and extractions should be made in an isolated clean room on Teflon® coated benches. Special steps should be taken to avoid contamination and to reduce contaminants which may be present from chelation, pH adjustments or chemicals required in the extraction procedure.

TABLE 5

LABORATORY PROCEDURES FOR WATER SAMPLES

Parameter	Analytical Method*		Special Procedures
Aluminum	EPA 202-1	AA-flame	
Antimony	EPA 204-2	AA-hydride	
Arsenic	EPA 206-2	AA-hydride	
Cadmium	EPA 213-2	AA-furnace	Note 1
Total Chromium	EPA 218-3	AA-furnace	Note 2
Copper	EPA 220-2	AA-flame	Note 1
Fluoride	EPA 340.2	Potentiometric	
Iron	EPA 236-1	AA-flame	Note 1
Lead	EPA 239-2	AA-furnace	Note 1
Mercury	EPA 245-5***	Cold vapor	
Nickel	EPA 249-2	AA-furnace	Note 1
Silver	EPA 272-2	AA-furnace	Note 1
Zinc	EPA 289-1	AA-flame	Note 1
Chlorinated Pesticides	EPA 608**	GC-EC	Note 3
PAH	EPA 610**	GC-FID	
PCB	EPA 608**	GC-EC	Note 3
Phenols	EPA 604**	GC-EC and FID	Note 4
Ammonia	EPA 350.3	Potentiometric	
BOD	EPA 405.1	5 Day -20°C	
Nitrate	EPA 353.3	Cadmium reduction	10cm light path
Phosphate	EPA 365.2	Ascorbic Acid	10cm light path
Total Phosphorus	EPA 365.2	Persulfate digestion Ascorbate	10cm light path
TKN	EPA 351.3	Digestion Potentiometric	
Total Solids	EPA 160.2	Gravimetric -105°C	Note 5
TOC	EPA 415.1		

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* EPA - Methods of Chemical analysis of Water and Waste (EPA-600/4-79-020).

** EPA Gas Chromatographic Methods - Federal Register 44, No.223, December 3, 1979.

***Refer to methods described in section 2.1.3.

TABLE 5 (cont.)

Notes:

1. APDC - DDDC chelation (pH 5.0) - MIBK extraction method is utilized on 200 ml sample. (Kinrade and Van Loon (1974), Analytical Chemistry 46 (No. 13): 18-94.
2. Sample (100 ml) is oxidized by EPA 218-3 method, followed by APDC - DDDC chelation (pH 2.4) and MIBK extraction.
3. Sample (750 ml) is extracted with methylene chloride. Florisil cleanup is required for some samples.
4. Acidified sample (750 ml) is extracted with methylene chloride. Extract is analyzed by GC - FID. 2-Propanol extracts of chlorinated phenols are analyzed by EC detector for increased sensitivity.
5. Samples (5 ml) are analyzed by ampule technique or by another comparable instrument. Organic carbon is oxidized to CO_2 by persulfate, and CO_2 is then measured by IR.

TABLE 6

LABORATORY PROCEDURES FOR SEDIMENT SAMPLES

Parameter	Analytical Method*		Special Procedures
Aluminum	EPA 202-1	AA-flame	Note 1
Antimony	EPA 204-2	AA-hydride	Note 2
Arsenic	EPA 206-2	AA-hydride	Note 2
BOD	EPA 405.1	5 Day -20°C	Note 3
Cadmium	EPA 213-2	AA-furnace	Note 1
Total Chromium	EPA 218-3	AA-furnace	Note 1
Copper	EPA 220-2	AA-flame	Note 1
Fluoride	EPA 340.2	Potentiometric	water extraction
Iron	EPA 236-1	AA-flame	Note 1
Lead	EPA 239-2	AA-furnace	Note 1
Mercury	EPA 245-5	Cold vapor	Note 4
Nickel	EPA 249-2	AA-furnace	Note 1
Silver	EPA 272-2	AA-furnace	Note 1
Zinc	EPA 289-1	AA-flame	Note 1
TKN	EPA 351.3	Digestion potentiometric	Note 5
Oil and Grease	EPA 413.1	Gravimetric	Note 6
Chlorinated Pesticides	EPA 608**	GC-EC	Note 7
PAH	EPA 610**	GC-FID	Note 8-A
PCB	EPA 608**	GC-EC	Note 7
Phenols	EPA 604**	GC-EC and FID	Note 8
Ammonia	EPA 350.3	Potentiometric	
Phosphate	EPA 365.2	Ascorbic Acid	Note 9
Nitrate	EPA 353.3	Cadmium reduction	Note 10
Total Phosphorus	EPA 365.2	Persulfate digestion Ascorbate	Note 11
Total Solids	EPA 160.2	Gravimetric -105°C	
TOC	EPA 415.1		Note 12
Grain Size	ASTM-19-D422;Pettijohn (1967)		Including hydrometer
Specific Gravity	ASTM-19-D854		
Atterberg Limits	ASTM-19-D423 and D424		

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* EPA - Methods of Chemical analysis of Water and Waste (EPA-600/4-79-020).

** EPA Gas Chromatographic Methods - Federal Register 44, No.223, December 3, 1979.

TABLE 6 (con't)

Notes:

1. 0.5 to 1.0g of sediment is weighted out into a teflon capped digestion vial (5 ml of 48% HF) and 10 ml conc. HNO_3 are added and slowly heated to dryness (6-8 hours). 5 ml of conc. HNO_3 is added and the vials are allowed to sit for two hours. Beakers are then capped and digested on low heat for 48 hours. Caps are removed and nitric acid is then taken off (to near dryness) and five additional ml of HNO_3 and 1 ml of perchloric acid are added. The vials are heated until the white perchloric acid fumes subside. If necessary, additional increments of HNO_3 and percloric acid are added to complete digestion. The sediment is then brought up with 1 ml conc. HNO_3 and 9 ml of redistilled demineralized water and analyzed by atomic absorption.

2. The digest from note 1 is analyzed by the AA-hydride technique.

3. Wet sediment samples are weighted into BOD bottles and diluted to 300 ml.

4. Samples are digested with sulfuric and nitric acid and potassium permanganate in an autoclave prior to cold vapor analyses.

5. Wet samples are digested in a Kjeldahl flask, distilled, and ammonia is then determined by potentiometric method.

6. Gravimetric - extraction with Fluorocarbon-113.

7. Samples are extracted by techniques in "Interim Methods for Sampling and Analysis of Priority Pollutants in Sediments and Fish Samples". US - EPA-October, 1980. Extracts are cleaned up by florisil column chromatography prior to GC-EC analyses.

8. Sample is extracted with methylene chloride (pH 2) and analyzed by GC-FID or GC-EC (chlorinated phenols).

8-A. Sample is extracted with methylene chloride (pH2) and analyzed by GC-FID.

9. Water extractable phosphates.

10. Water extractable nitrates or ammonia.

11. Sample is digested with persulfate and digest is analyzed by ascorbic acid technique.

12. Sediment is analyzed by ampule technique (e.g., OI instrument).

At least 10% of all samples should be extracted and analyzed in duplicate. Standards should be analyzed for every ten samples. These standards should be obtained by diluting EPA low level audit samples from ten to twenty times the instruction supplied with the sample, since the EPA standard is based on polluted water.

2.2 Procedures for Performing Elutriate Test on Sediments

The elutriate test is a simulation of dredging and disposal activities whereby water and sediment collected from the dredging site(s) are combined to approximate the properties of a dredge slurry. The elutriate is the water which is separated from the slurry after filtration through a 0.45 micron filter. The water is then analyzed as an indicator of contaminant levels released during the dredging process.

The dredge site samples should be collected according to procedures for water and sediment collection described in previous sections of this text. The site water sample should be unpreserved and stored at 4°C until processed. The storage period prior to elutriate test should be as short as possible in order to minimize changes in the characteristics of the sample water. It should be noted that the advantages of conducting the elutriate test in a clean well-equipped laboratory far outweigh the advantages of on-site testing. Every effort should be made to avoid contamination of site water and sediment samples during collection and when performing the elutriate test. Non-contaminating samplers, storage bottles, test vessels, homogenizing utensils and high purity, analytical grade reagents should be used.

The elutriate test procedure used should be performed according to methods outlined in Procedures for Handling and Chemical Analysis of Sediment and Water Samples, (EPA-COE, 1981). Four parts water and one part wet sediment (volume/volume) are vigorously shaken for thirty minutes and allowed to settle for one hour prior to centrifugation and the 0.45 micron filtration step (for most sediments centrifugation is not required, since a one hour settling time will separate the sediment from the liquid base). After filtration, the elutriate is sorted, preserved and analyzed according to the same procedures that would be used for a water sample. The site water is filtered and analyzed as a blank for the elutriate.

The sediment should be sampled in triplicate and the elutriate test should be conducted in triplicate. The blank water should also be analyzed in triplicate, and the average of the triplicate results should be reported as the concentration of the standard elutriate.

2.3 Grain Size Determination

Sediment grain size is a useful tool for interpreting the potential environmental effects of dredging operations in estuaries. While coarse grain sediments may occassionally be a problem, dredging of fine material is almost always a concern. Because fine grain sediments contain elevated concentrations of potential contaminants, including metals, nutrients and hydrocarbons (see Section 2.0 of Part Two), their remobilization and resuspension can be a threat to estuarine biota.

Although the exact correlation between grain size and a particular chemical is site specific, a relationship between metals and sediment type has been observed: metal concentrations are much higher in fine grain sediments. Consequently, grain size analyses are required in DER Rule 17-45.17 to assess potential problems associated with dredging metal-contaminanted sediments. Determination of mean grain size is a crucial part of determining potential problems, and procedures for calculating grain size (Pettijohn, 1960) are described below.

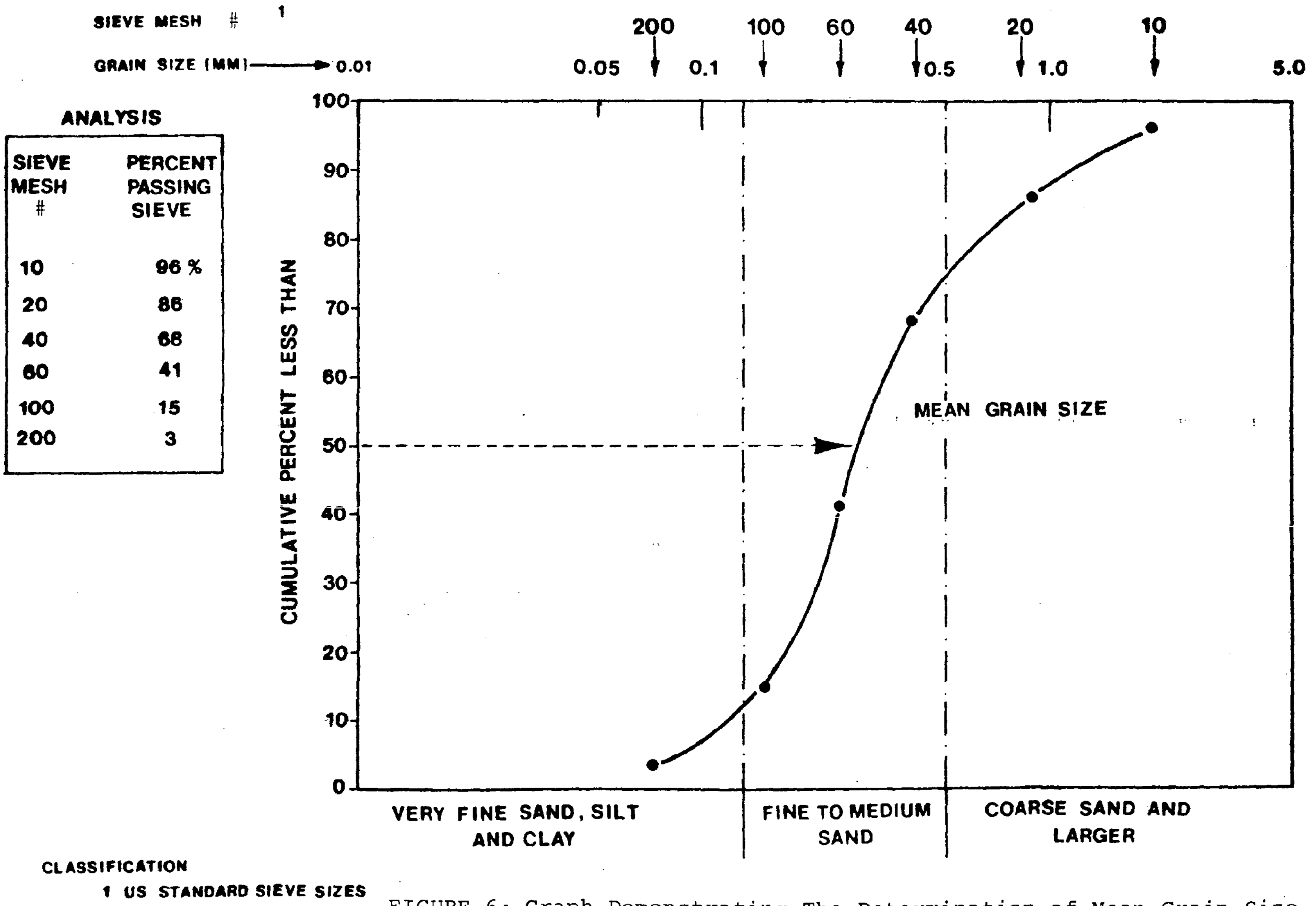
To determine mean sediment grain size, two aliquots of each sediment are collected. Both are weighed and only one is dried at 50°C to determine percent moisture. The second aliquot is wet sieved successively through U.S. standard meshes numbers 10, 20, 40, 60, 100 and 200. The material collected is dried and weighed on each sieve. The percent, P, should be determined for the sediment passing each mesh using the following equation:

$$P = \frac{W_T(1-M)W_S}{W_T(1-M)} \times 100$$

where W_T is the wet weight of the sediment aliquot passed through the sieves, M is the percent mositure of the sediment calculated from the first aliquot, and W_S is the dry weight of the material retained on the given sieve.

Although Table 1 in DER Rule 17-45.17 indicates only three sieve sizes for determining acceptable dredging practices when metals are present at elevated levels, a reliable method for determining mean grain size requires that sediments be passed through a minimum of six sieves in order to obtain a representative mean. Results of these measurements are then plotted on a semilogrithmic scale as shown in Figure 6, and read as mean grain size of the sediment according to the curve obtained from the grain size data.

After mean grain size has been determined for a sediment sample, the metal to aluminum ratio should be calculated according to the procedure described in Section 3.1 of this manual. This information is then compared to the criteria contained in Table 1 of DER Rule 17-45.17. Additionally, mean grain size will be employed for determining the potential environmental effects of resuspending fine grain material into the receiving water column via dredging and disposal site operations.



ANALYSIS

SIEVE MESH #	PERCENT PASSING SIEVE
10	96 %
20	86
40	68
60	41
100	15
200	3

FIGURE 6: Graph Demonstrating The Determination of Mean Grain Size.

REFERENCES

AMERICAN PUBLIC HEALTH ASSOCIATION (1975)...Standard Methods for the Examination Water and Wastewater Including Bottom Sediments and Sludges, 15th Edition. American Public Health Association, New York, N.Y.

BECK, E., J.H. Reuter, and E.M. Perdue (1974)..."Organic and inorganic geochemistry of some Coastal Plain rivers of the southeastern United States". Geochim. Cosmochim. Acta, 38:341-364.

BOYLE, E. and S.S. Huestad (1983)..."Aspects of the surface distribution of copper, nickel, cadmium, and lead in the North Atlantic and North Pacific". IN: TRACE METALS IN SEAWATER; C.S. Wong et al (Eds), pp. 379 - 394 Plenum Press.

BURTON, J.D. (1976)..."Basic Properties and Processes of Estuarine Chemistry." In: ESTUARINE CHEMISTRY, J.D. Burton and P.S. Liss (eds.).

EATON, A. (1979)..."Observations on the geochemistry of soluble copper, iron, nickel, and zinc in the San Francisco Bay estuary". Environ. Sci. Technol., 13:425-432.

FRIEDMANN, P. and D. Schmidt (1982)..."Determination of Mercury in Seawater by Cold Vapour Atomic Absorption Spectrophotometry." Frenenius Z. Anal. Chem. 313:200-202.

FLORIDA DEPARTMENT OF ENVIRONMENTAL REGULATION (1983)...Deepwater Ports Maintenance Dredging Study: Ports of Jacksonville, Tampa, Manatee, and Pensacola.(2 volumes).

_______ (in preparation)...Deepwater Ports Maintenance Dredging Study: Ports of Miami, Palm Beach, Ft. Pierce, Canaveral, Everglades, and Port St. Joe.

HEAD, P.C. (1976)..."Organic Processes in Estuaries" In: Estuarine Chemistry, J.D. Burton and P.S. Liss (eds).

HOEPPEL, R.E. (1982)..."Contaminant Remobility in Diked Containment Areas." Environ. Intl. 7:119-141.

KEELY, J.W. and R.M. Engler (1974)..."Discussion of Regulatory Criteria for Ocean Disposal of Dredged Materials: Elutriate Test Rationale and Implementation Guidelines" Miscellaneous Paper D-74-14, U.S. Army Engineers Waterways Experiment Station, Vicksburg, Miss.

KINRADE, and VanLoon (1974)..."Solvent Extraction for use with Flame Atomic Absorption Spectrometry" Anal. Chem. 46:18-94.

LEE, G.F., M.D. Piwoni, J.M. Lopez, G.M. Mariani, J.S. Richardson, D.H. Homer, and F. Saleh (1975)..."Research Study for the Development of Dredged Material Disposal Criteria"...Tech Rept. D-75-4. U.S. Army Engineers Waterways Experiment Station, CE; Vicksburg, MS.

MAY, E.B. (1973)..."Environmental effects of hydraulic dredging in estuaries". Ala. Mar. Resources Bull.,9:1-15.

MARTIN, J. and M. Meybeck (1979)..."Elemental Mass Balance of Material Carried by Major World Rivers." Marine Chem. 7:178-206.

_________ and Whitfield (1983)..."The significance of river inputs to the ocean." In: Trace Metals in Seawater.

National Academy of Sciences, National Academy of Engineering (1973)... water quality criteria 1972. EPA Ecol. Res. Series EPA-R3-73-033, U.S. Environmental Protection Agency, Washington, D.C. 594 pp.

OLAFSSON, J. (1981)..."Report on the ICES Intercalibration of Mercury in Seawater for the Joint Monitoring Group of the Oslo and Paris Commissions. In: Reports on ICES Intercalibrations of Mercury and Cadmium in Sea Water. pp. 1-25 Coop Res. Rept. No. 110, ICES.

____________ (1982)..."An Intercalibration for Mercury in Seawater." Marine Chemistry 11:129-142.

OLSEN, C.R., N.H. Cutshall and I.L. Larsen (1982)..." Pollutant Particle Associations and Dynamics in Coastal Marine Environments: A review." Marine Chemistry 11:501-533

PALERMO, M.R. (1982) "Prediction of contaminant levels in dredged material disposal area effluents". Study Plan. U.S. Army Engineer Waterways Experiment station, Vicksburg, Miss. Priest (1981).

PETTIJOHN..."Sedimentary Petrology." Harper and Rowe.

PRIEST, W.I. (1981)..."A Study of Dredging Effects in Hampton Rhoads, Virginia." USACOE Special Report in Applied Marine Science and Ocean Engineering No. 247, 266p.

RUSSEL-HUNTER, W.D. (1970)...Aquatic Productivity. Macmilliam, New York; 306 p.

TAYLOR, S. (1964)..."Abundance of chemical elements in the continental crust: A new table". Geochim. Cosmochim. Acta 28: 1273-1285.

TUREKIAN, K.K., Wedepohl (1961)..."Distribution of the elements in some major units of the earth's crust". Geol. Soc. Am. Bull. 72:175-192.

U.S. Army Corps of Engineers, Buffalo District (1969) "Dredging and Water Quality Problems in the Great Lakes".

USEPA-USACOE (1981)..."Procedures for Handling and Chemical Analysis of Sediment and Water Samples". Tech. Report EPA/CE-81-1, 478 pp. USEPA (1981).

USEPA (1982a)..."Methods for chemical analysis of water and wastes". Environmental Support Laboratory, USEPA, Cincinnati, Ohio.

USEPA (1982b) The Chesapeake Bay Program Technical Studies: A Synthesis 634p. U.S. Printing Office 1983-606-490.

WASLENCHUK, D. and H. Windom (1978)...Factors controlling the estuarine chemistry of arsenic. Estuar. Coast. Mar. Sci. 7:455-462. Windom, H.L. (1973)

WINDOM, H.L (1973)..."Processes Responsible for Water Quality Changes During Pipeline Dredging in Marine Environments." In: Proceedings, World Dredging Conf. V, Wodcon Assoc.

_______ (1974)..."Processes responsible for water quality changes during pipeline dredging in marine environments" IN: Proc. World Dredging Conf.V, Hamburg Germany, Symcon, San Pedro, Calif. pp. 761-787.

_______ (1975)... "Water quality aspects of dredging and dredge spoil disposal in estuarine environments". In: Estuarine Research,Vol. 2 (Cronin, L.E., ed.) Academic Press, New York, p. 559-591.

_______ K. Beck, and R. Smith (1971)..."Transport of trace metals to the Atlantic Ocean by southeastern rivers". Southeast. Geo. 12:169-181.

______ and F. Taylor (1979)..."The flux of mercury in the South Atlantic Bight". Deep Sea Res. 26A: 283-292.

______ G. Wallace, R. Smith, N. Dudek, M. Maeda, R. Dulmage and F. Storti (1982)..."Behavior of copper in southeastern United States estuaries". Marine Chemistry, 12 (1983): 183-193.

VAN TINE, R.F and R.L. Wetzel..."Structural and functional aspects of the ecology of submerged aquatic macrophyte communities in lower Chesapeake Bay." Special Report No. 267 in Applied Marine Science and Ocean Engineering, Virginia Institute of Marine Science.

APPENDICES

APPENDIX 1

NATURAL ELEMENT ABUNDANCES AND METAL TO ALUMINUM RATIOS IN SEDIMENTARY MATERIAL[1]

ELEMENT	AVG. ABUND. IN CRUSTAL MATERIAL[2]	AVG ABUND. IN CARBONATE ROCK[2]	NATURAL METAL TO Al RATIO[3]
Al	82,300	4,200	1.0
Sb	0.2	0.2	4.76×10^{-5}
As	1.8	1.0	2.38×10^{-4}
Ba	425	10	5.16×10^{-3}
B	65	20	4.76×10^{-3}
Br	2.5	6.2	1.48×10^{-3}
Cd	0.2	0.035	8.30×10^{-6}
Cs	3.0	1.0	2.30×10^{-4}
Cr	100	11	2.60×10^{-3}
Co	25	0.1	2.30×10^{-5}
Cu	55	4.0	9.50×10^{-4}
F	625	330	--0.08--
Ga	15	4.0	9.50×10^{-4}
Ge	1.5	0.2	4.76×10^{-5}
Au	0.01	0.01	2.30×10^{-6}
I	0.5	1.2	2.86×10^{-4}
Fe	56,300	3,800	--0.90--
Pb	12.5	9.0	2.14×10^{-3}
Li	20	5.0	1.20×10^{-3}
Mn	950	1,100	--0.26--
Hg	0.08	0.04	9.50×10^{-6}
Mo	1.5	0.40	9.50×10^{-5}
Ni	75	20	4.76×10^{-3}
P	--	400	--0.95--
Rb	90	3.0	1.09×10^{-3}
Sc	22	1.0	2.67×10^{-4}
Se	0.05	0.08	1.90×10^{-5}
Si	--	0.1	2.30×10^{-5}
Ag	0.07	0.1	2.38×10^{-5}
Sr	375	610	--0.145--
Th	9.6	1.7	4.04×10^{-4}
Sn	2.0	1.0	2.38×10^{-4}
U	2.7	2.2	5.24×10^{-4}
V	135	--	3.28×10^{-5}
Zn	70	20	4.76×10^{-3}

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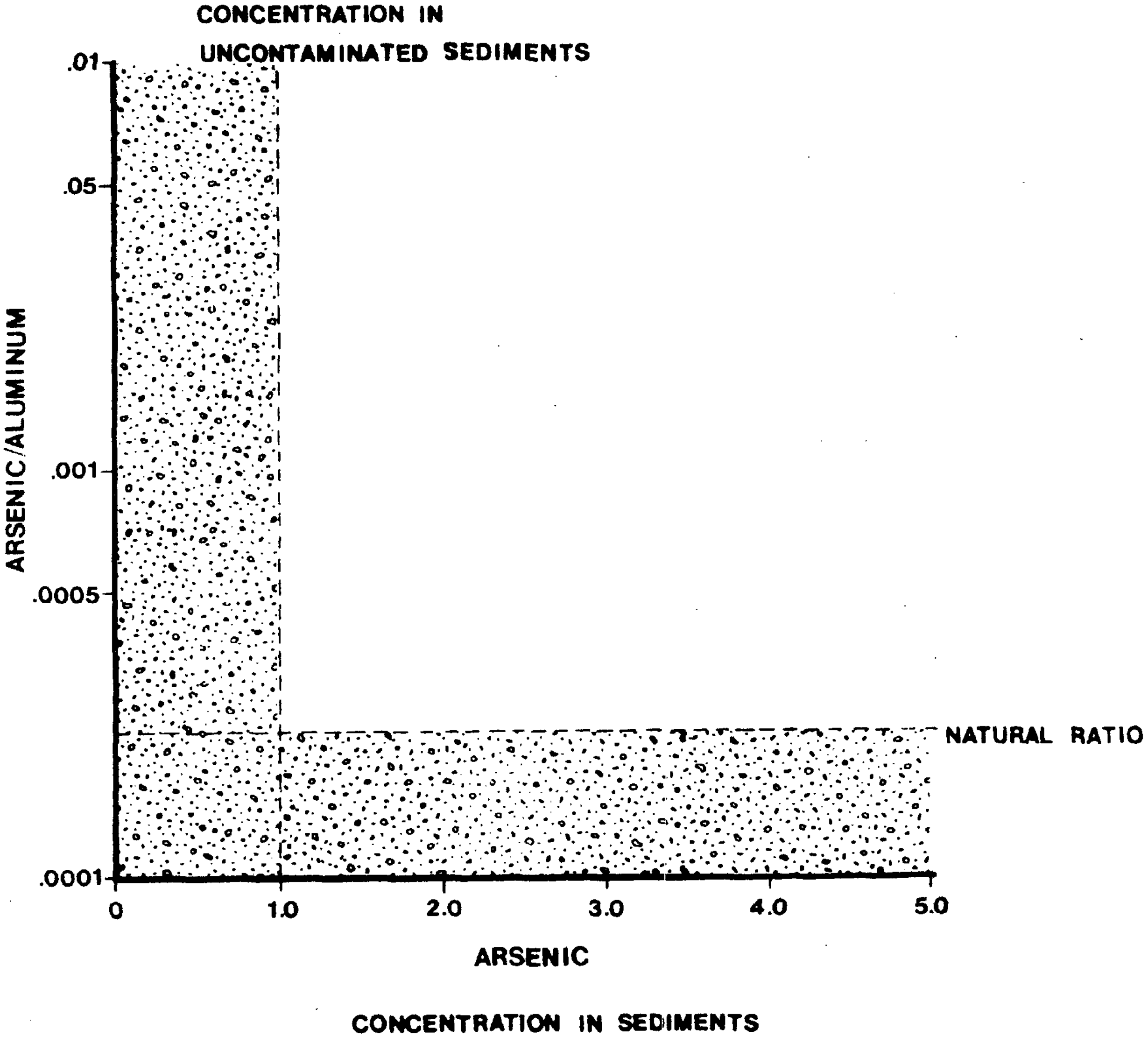
[1] References: Turekian and Wedepohl (1961); Taylor (1964); Martin and Meybeck (1979)

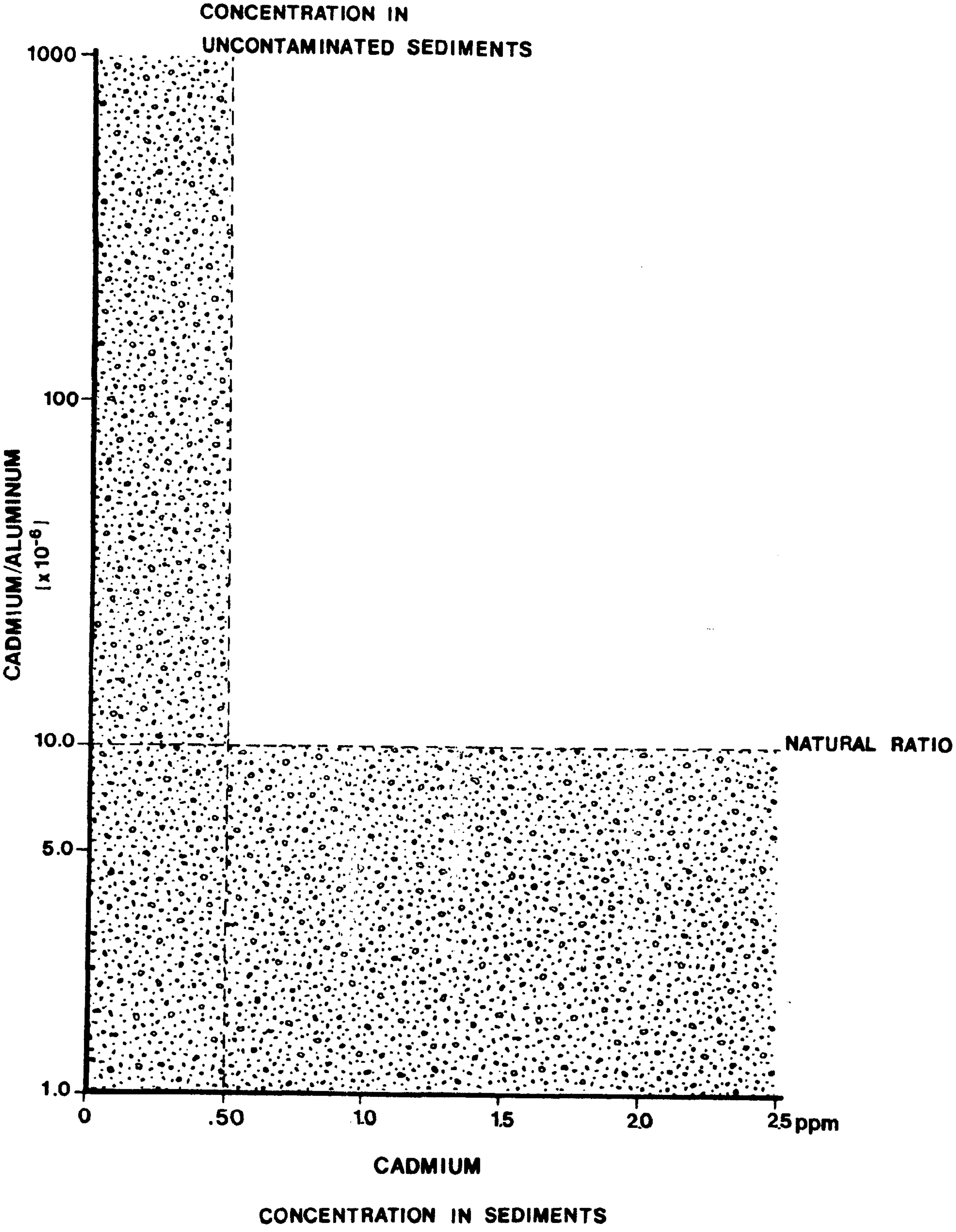
[2] All abundances are in parts per million

[3] Based on highest ratio of carbonate or crustal material

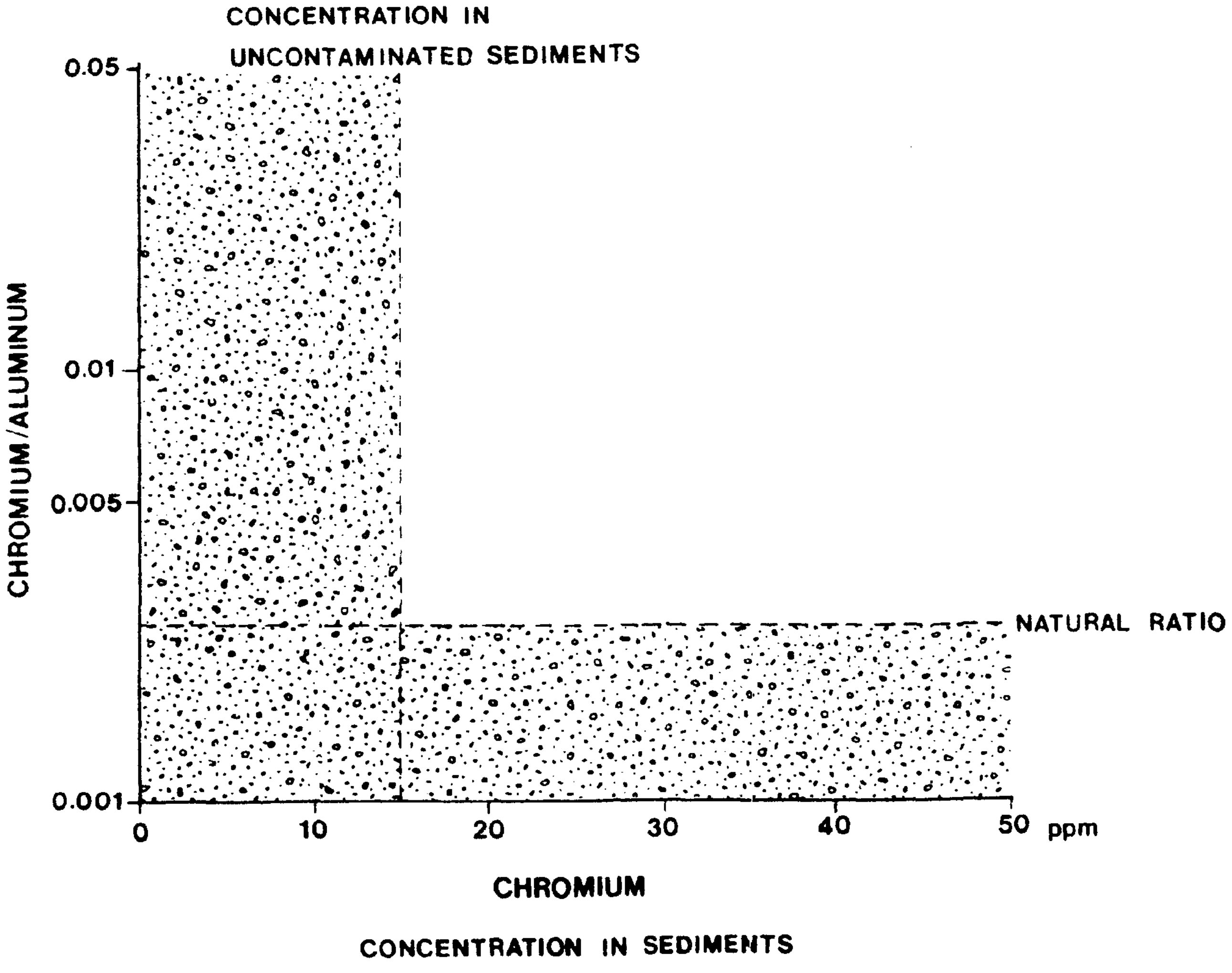
APPENDIX 2a: Graph Representing Arsenic to Aluminum Ratio Versus Total Arsenic Concentration in Sediments. Outliers From the Stippled Area Suggest Anthropogenic Inputs of Arsenic.



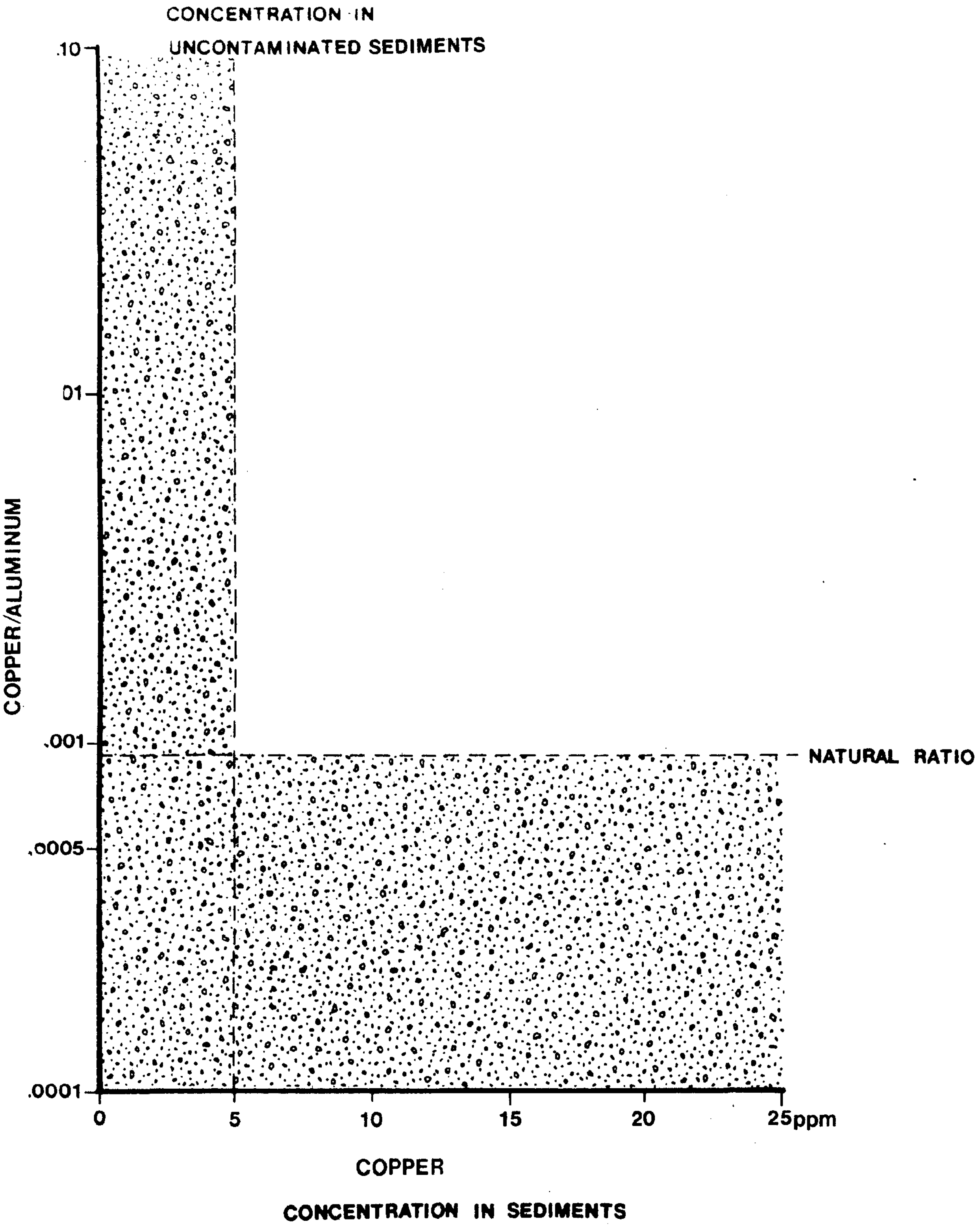
APPENDIX 2b: Graph Representing Cadmium to Aluminum Ratio Versus Total Cadmium Concentration. Outliers From the Stippled Area Suggest Anthropogenic Inputs of Cadmium.



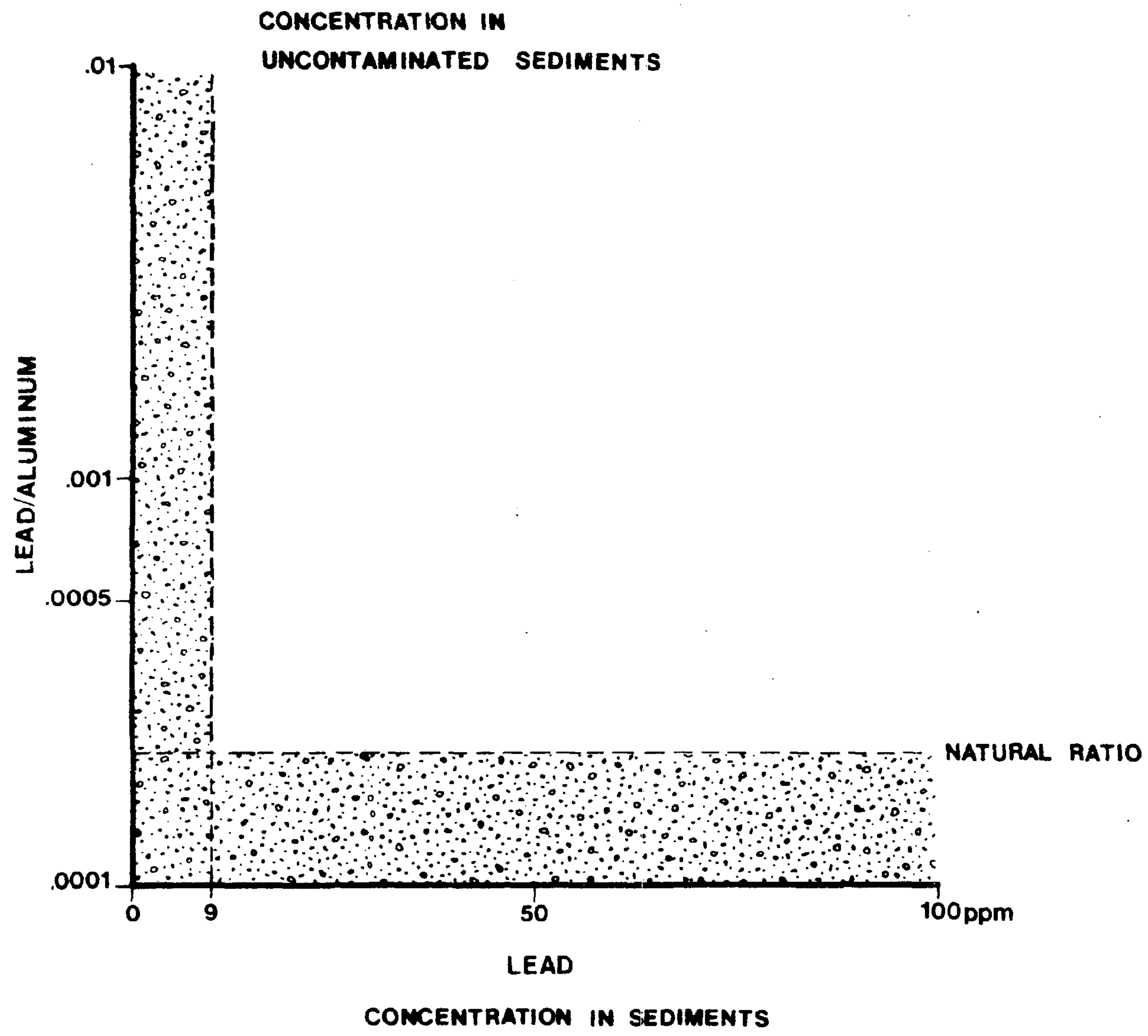
APPENDIX 2c: Graph Representing Chromium to Aluminum Ratio versus Total Chromium Concentration in Sediments. Outliers Suggest Anthtropogenic Inputs of Chromium.



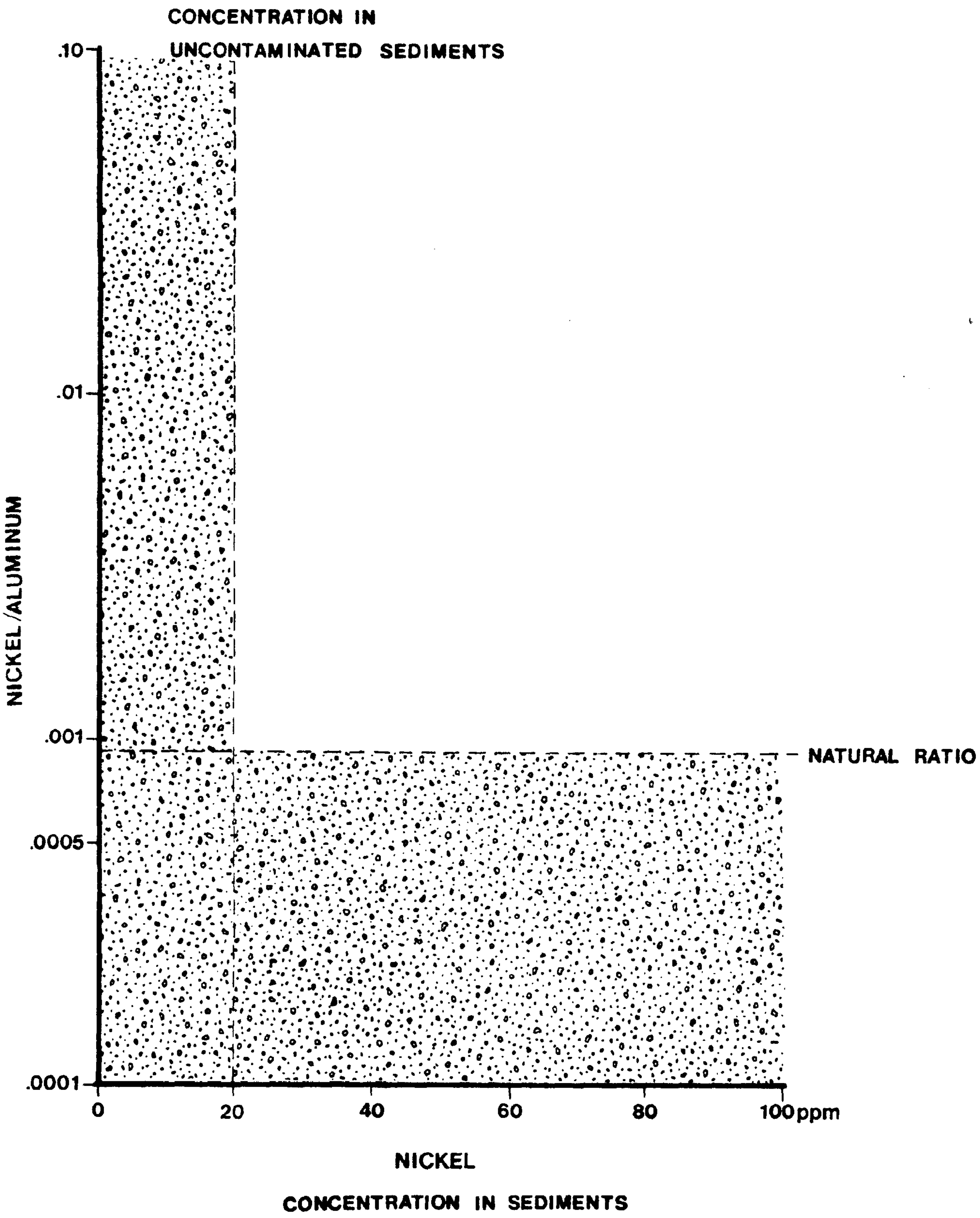
APPENDIX 2d: Graph Representing Copper to Aluminum Ratio versus Total Copper Concentration in Sediments. Outliers From the Stippled Area Suggest Anthropogenic Inputs.



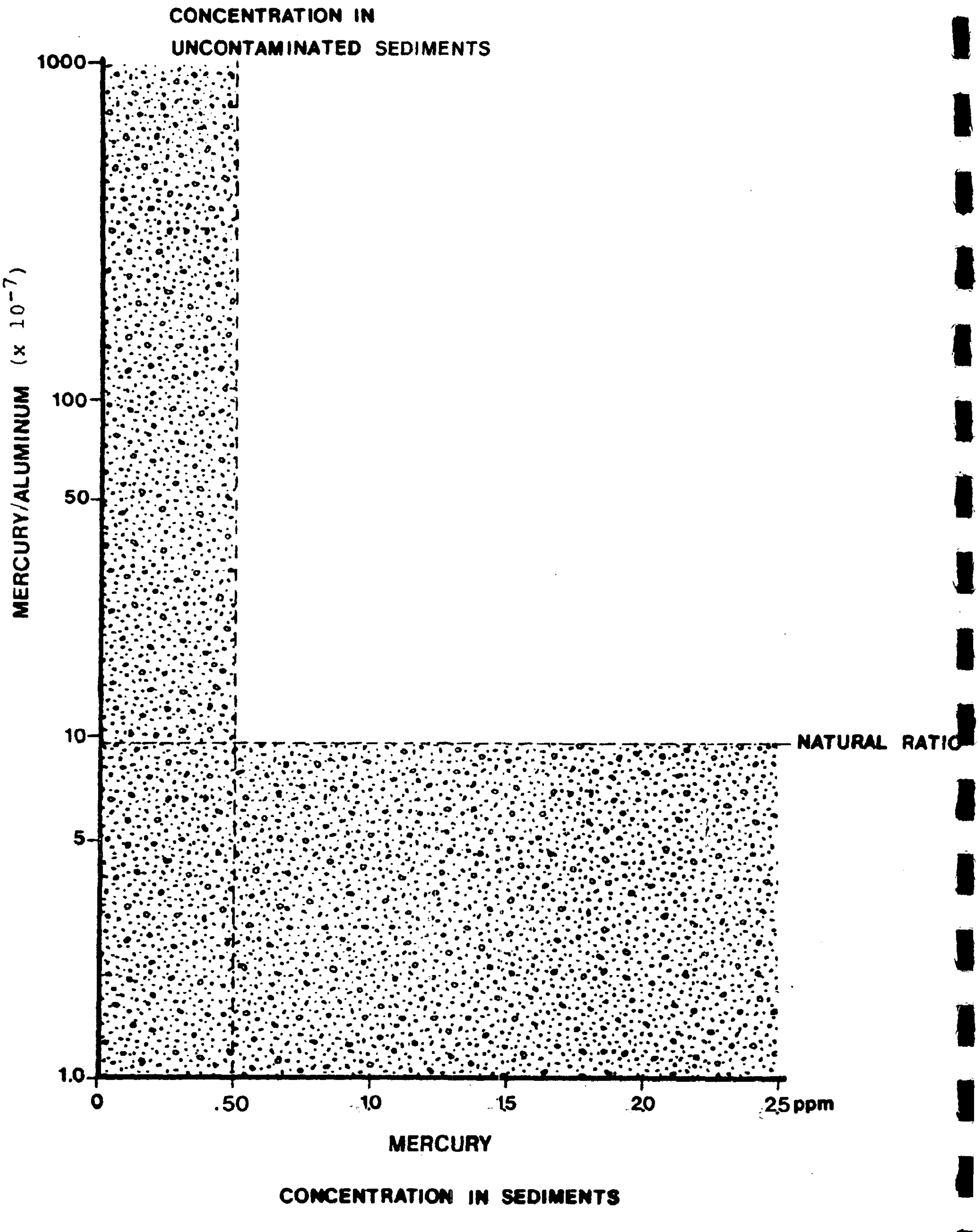
APPENDIX 2e: Graph Representing Lead to Aluminum Ratio Versus Total Lead Concentration in Sediments. Outliers Suggest Anthropogenic Inputs of Lead.



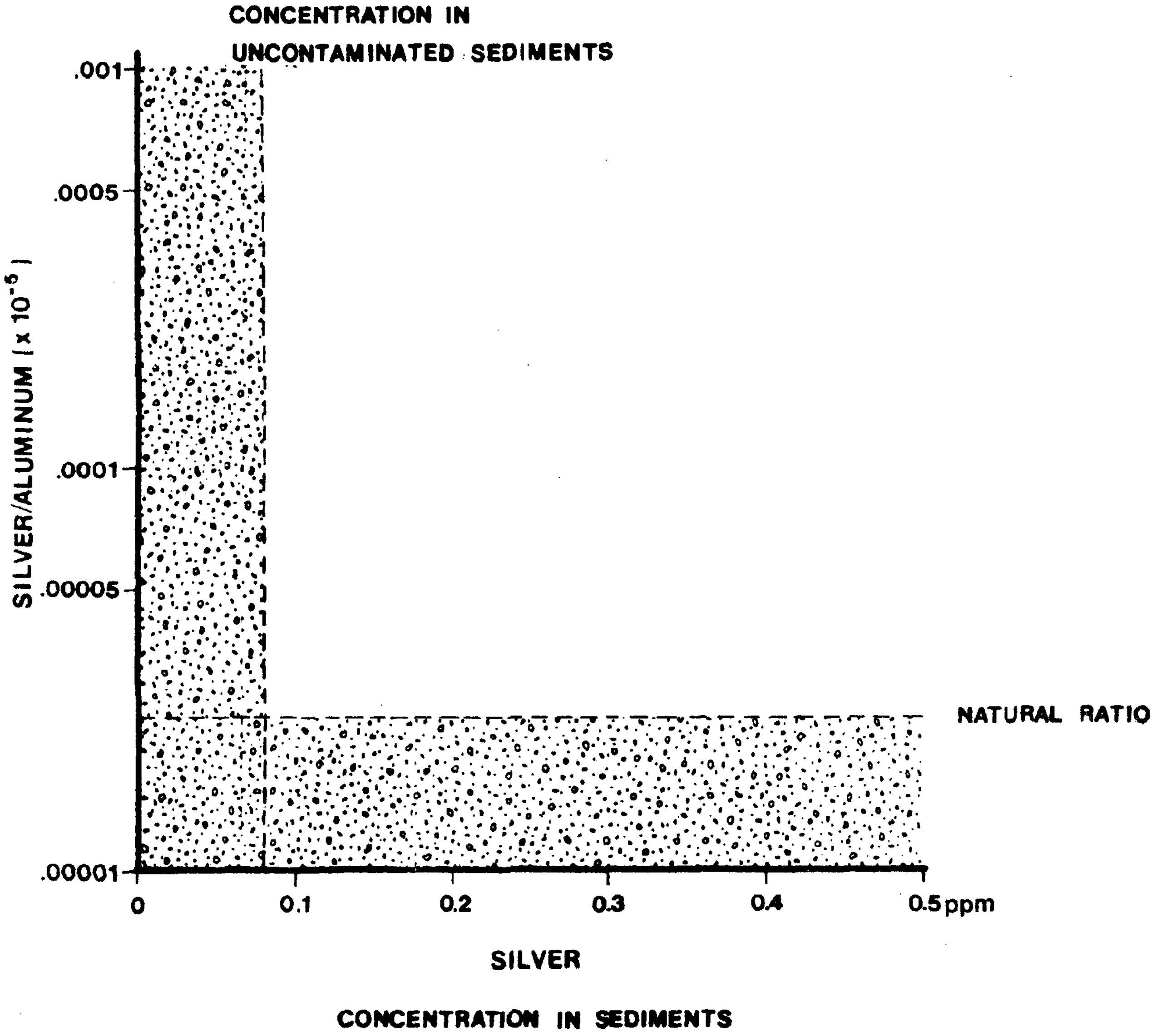
APPENDIX 2f· Graph Representing Nickel to Aluminum Ratio Versus Total Nickel Concentration in Sediments. Outliers Suggest Anthropogenic Inputs of Nickel.



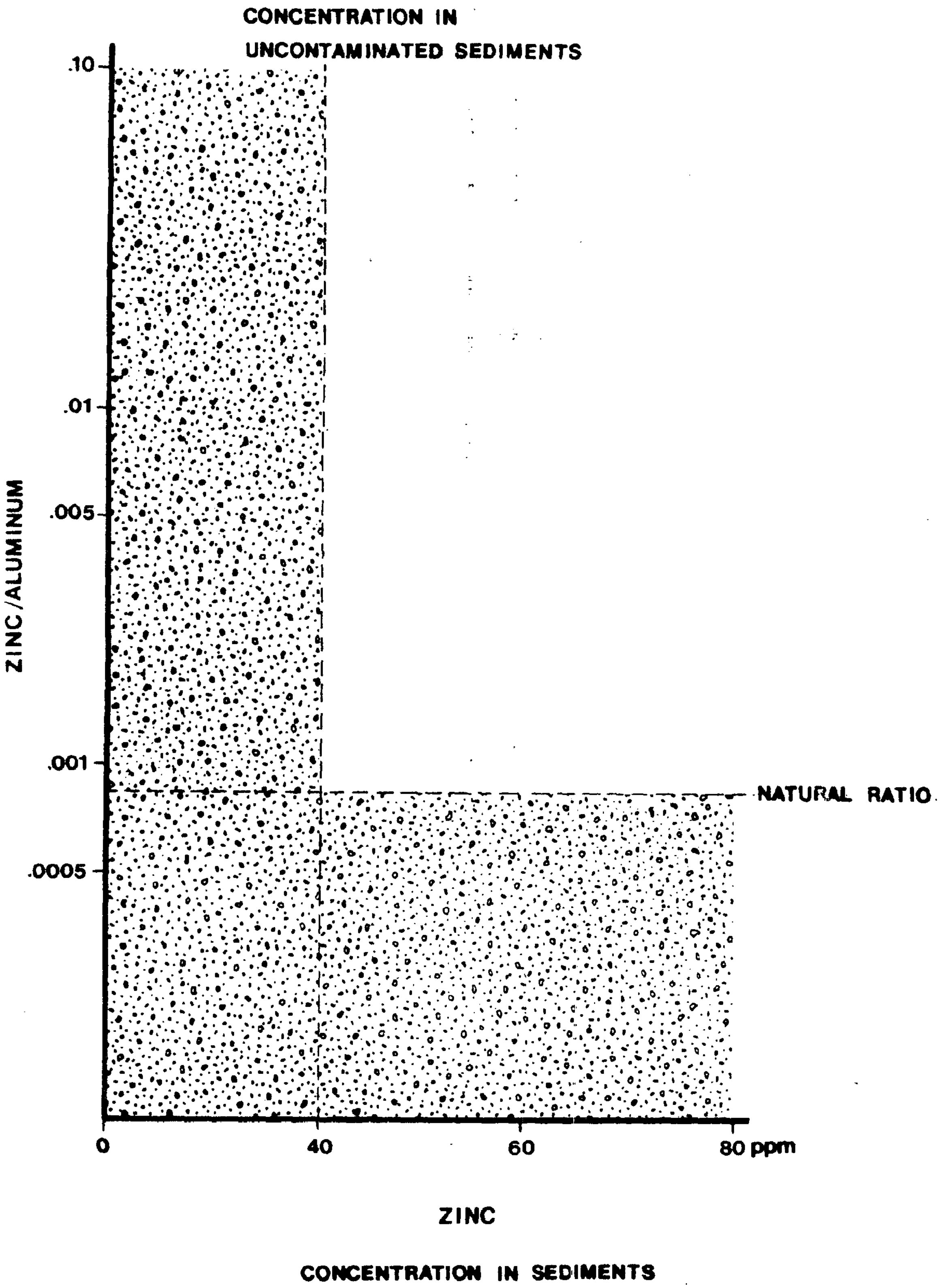
APPENDIX 2g: Graph Representing Mercury to Aluminum Ratio versus Total Mercury Concentration in Sediments. Outliers From the Stippled Area Suggest Anthropogenic Inputs.



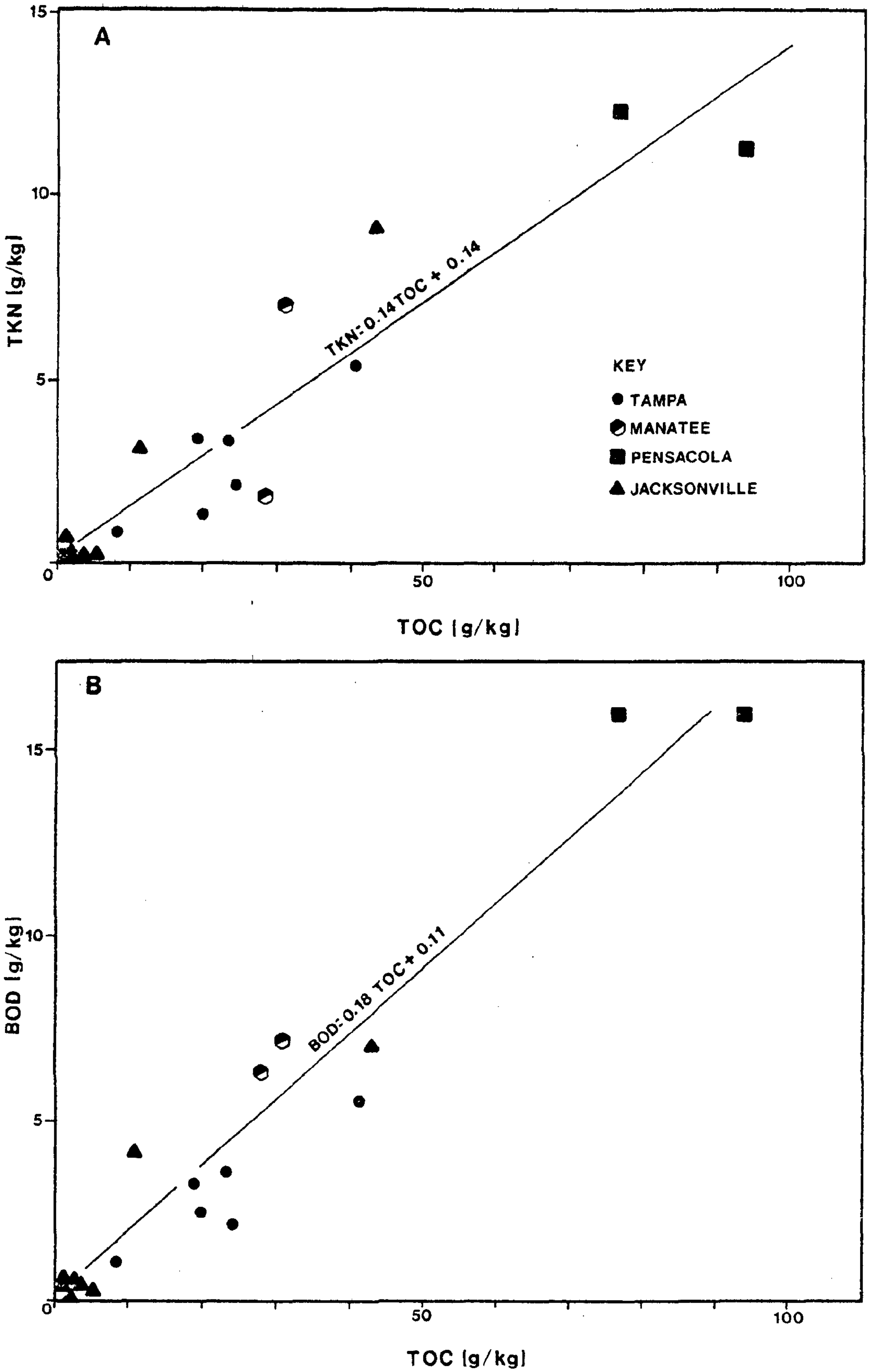
APPENDIX 2h: Graph Representing Silver to Aluminum Ratio versus Total Silver Concentration in Sediments. Outliers From the Stippled Area Suggest Anthropogenic Inputs of Silver.



APPENDIX 2i: Graph Representing Zinc to Aluminum Ratio Versus Total Zinc Concentration in Sediments. Outliers From the Stippled Area Suggest Anthropogenic Inputs.

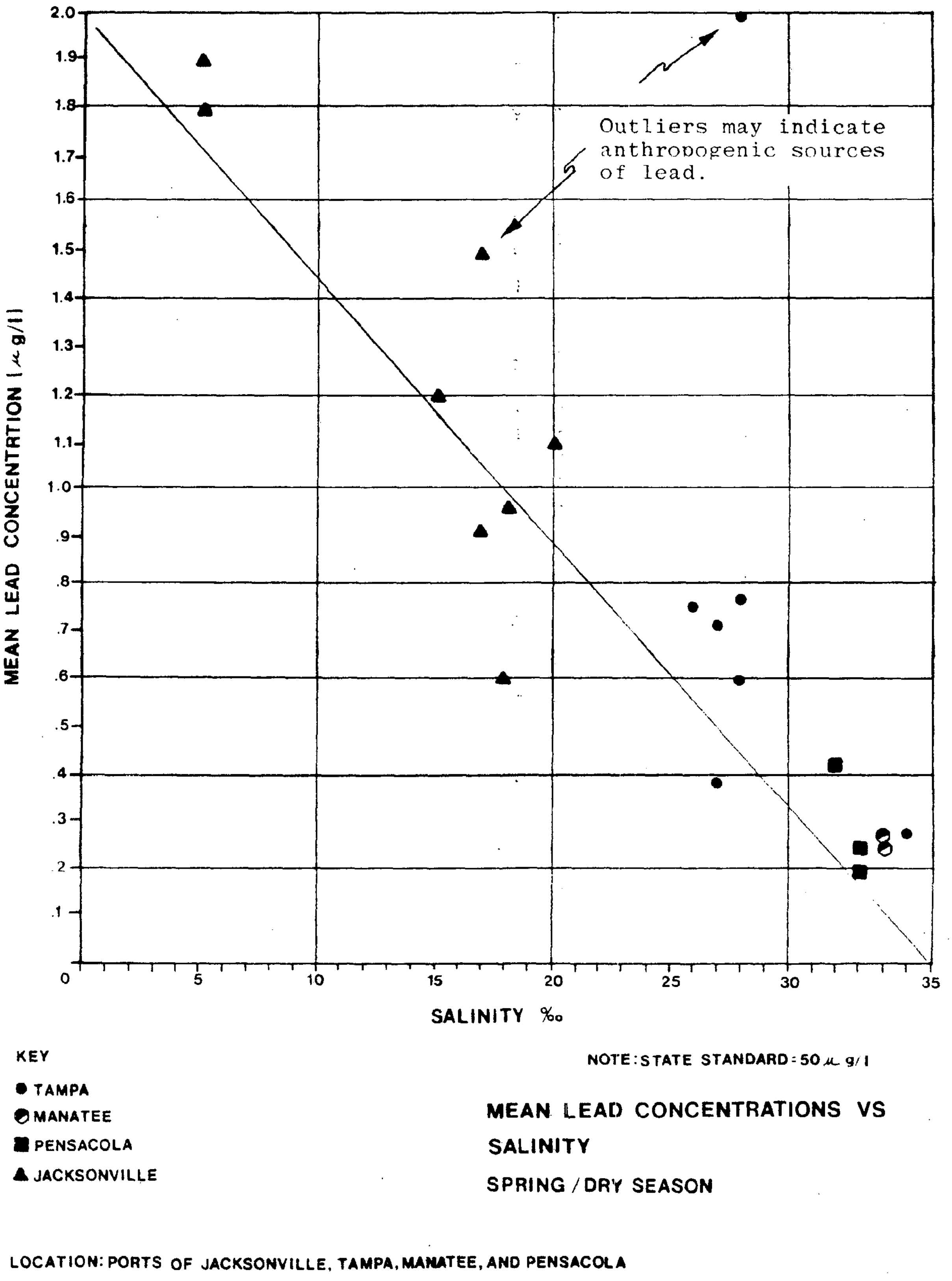


APPENDIX 3: RELATIONSHIP BETWEEN TKN,BOD, AND TOC



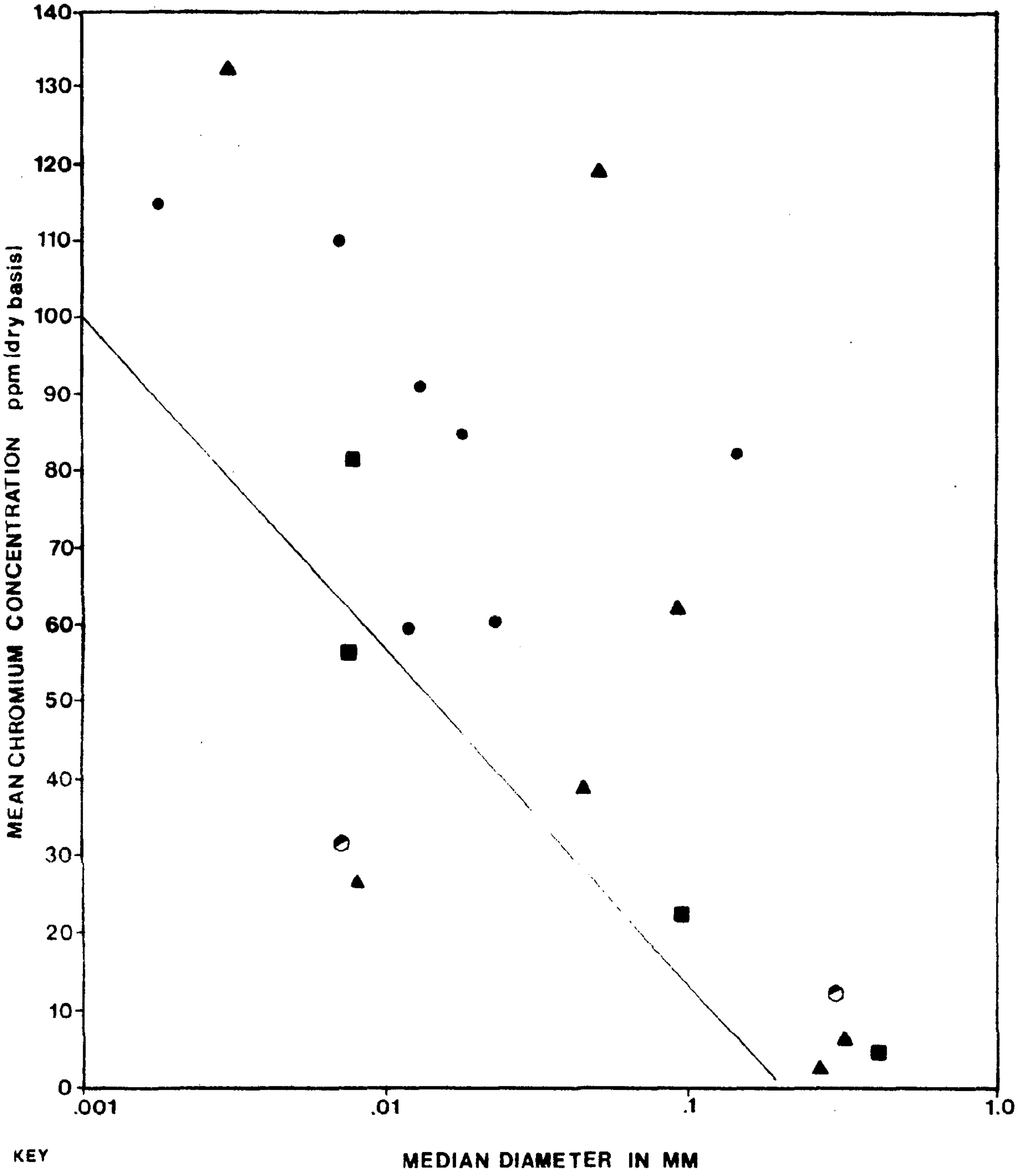
TKN and BOD versus TOC **SPRING / DRY SEASON**

LOCATION: PORTS OF JACKSONVILLE, TAMPA, MANATEE, AND PENSACOLA



APPENDIX 4: Graph of the conservative behavior of lead in four estuarine areas in Florida (DWP,1983). The theoretical line represents this trend. Outliers (above) this line may indicate anthropogenic lead inputs to the system.

APPENDIX 5: Relationship between one metal (chromium) and mean grain size. The theoretical line represents the natural relationship for chromium and coarse grain sediments.



MEAN TOTAL CHOMIUM CONCENTRATION

VS. MEDIAN DIAMETER OF SEDIMENT

FALL/WET SEASON

LOCATION: PORTS OF JACKSONVILLE, TAMPA, MANATEE, AND PENSACOLA

APPENDIX 6

SUMMARY OF POTENTIAL BIOLOGICAL IMPACTS ASSOCIATED WITH DREDGING IN ESTUARIES

Habitat	Impact at Dredge Site	Impact at Disposal Site
WATER COLUMN	Direct impacts of dredging may include increased turbidity, Total Suspended Solids (TSS), and the release of nutrients. These impacts are most likely to have an adverse effect on planktonic organisms. Turbidity and TSS reduce light penetration essential for phytoplankters that are important in plankton-based food webs. Turbidity problems at a hydraulic dredge site are generally not as great as turbidity associated with return waters at the disposal site, since deeper channels are generally biologically depauperate. However, turbidity generated by dredging methods (e.g., hopper dredges) that do not offer as much control over the dispersal of fine material present the greatest concern in most dredging operations. Nutrients can stimulate biological production, which in turn creates greater BOD and lower dissolved oxygen concentrations in the water column. They can be acutely toxic(e.g., NH_3) to estuarine biota. Solubilization of toxic substances released at the dredge head is also a problem that could lead to bioconcentration of metals, hydrocarbons and other toxins by estuarine biota.	Impacts adjacent to disposal sites are qualitatively the same as for the dredge site, but certain impacts, especially those associated with nutrients, turbidity and TSS, problems may be far greater than at the dredge site. Solubilization of toxic compounds is also a concern in disposal site discharge waters since these compounds may be taken up by estuarine biota.

APPENDIX 6 (cont)

Habitat	Impact at Dredged Site	Impact at Disposal Site
ESTAURINE BENTHIC COMMUNITIES	Increased turbidity and TSS loads can clog breathing and feeding (e.g., filter feeders) mechanisms, or direclty smother live bottom areas. Resuspended contaminants can be oxidized and microbially-activated (e.g., via bioalkylation processes) so that they can be incorporated into estuarine food webs via bioaccumulation processes. Additionally, bottom areas can be disrupted in such a way to cause difficulties for larval settling in the area.	Impacts are the same as for dredge site, although disposal site littoral areas are generally shallower and more productive than are deep navigation channels. Thus, potential impacts could be much greater on benthic communities and dredging could negatively affect more species and individuals. Diked disposal areas situated in estuarine waters will eliminate productive benthic habitats, disrupt trophic relationships, and reduce overall pollutant-assimilation capacity of bottom areas (i.e., by eliminating microflora).
SEAGRASS MEADOWS	Chronic impacts of dredging involve increased turbidity and TSS and can reduce the light penetration crucial to seagrass survival. Additionally, dredging of fine materials can blanket grassbeds, disrupt osmotic processes or suffocate epibiota that are important components of grassbed food webs; relocation and deposition of these fine sediments can inhibit rhizomes from rooting in newly-deposited dredged material. Nutrient releases can produce localized plankton blooms which reduce water transparency and light penetration; nutrients also stimulate seagrass epiphyte and macroalgae (e.g., encrusting algae) growth, which in turn reduces sunlight reaching grassblades.	Qualitative impacts are essentially the same as those at dredging site, but since disposal site discharge waters generally enter shallower areas, the potential for each of these problems is considerably greater if grassbeds are adjacent to spoil site. Side casting operations are particularly deleterious to seagrasses. Diked disposal areas constructed in grassbeds will eliminate productive submergent wetlands and destroy food, shelter, and habitat required by estuarine biota that depending on these nursey areas to complete their life cycle.

Habitat	Impact at Dredge Site	Impact at Disposal Site
Coral Reefs	Decreased light penetration due to increased turbidity and TSS will reduce photosynthesis carried out by symbiotic zooxanthellae, eventually killing corals. Dredge spoils can clog feeding and breathing mechanisms of the corals, and calcification rates may also be depressed by interference with these processes. Nutrients released from the dredging operation can stimulate microalgal growth which can also kill corals. Consequently, food, shelter, and habitat function of these reef systems will be reduced or even eliminated.	The effects of disposal can have the same qualitative impacts as those discussed for dredging. Dredge spoils can clog feeding and breathing mechanisms of the corals, and calcification rates may also be depressed by interference with these processes. Nutrients released from the dredging operation can also kill corals. Consequently, food, shelter, and habitat function of these reef systems will be reduced or even eliminated. Side casting is extremely deleterious to coral reef communities due to blanketing and smothering of biota.
Barrier Islands	Channel maintenance dredging through or around barrier islands can alter hydrodynamic regimes and reduce shoreline stability.	Improper spoiling on barrier island beaches (i.e., renourishment) can eliminate productive bottom areas, outcrop habitats, and shoreline vegetation which export nutrient-rich detrital material to adjacent estuary areas.
Worm Reefs	Suspended and settable materials clog feeding and respiratory mechanisms. Nutrients released to these fragile communities can stimulate growth of encrusting algal species which cover worm reefs and destroy colonies.	Direct disposal on reefs eliminates food, shelter, and habitat for biota by smothering actions. Side casting produces increased suspended and setteable solids that clog feeding and breathing mechanisms. Nutrients stimulate undesireable macroalgal growth over reef habitat.

Appendix 6 (cont)

Habitat	Impact at Dredge Site	Impact at Disposal Site
TIDAL FLATS, MARSHES AND NON-TIDAL WETLANDS	Direct impacts of dredging include complete elimination of these productive tidal habitats whose primary function is to provide food, habitat and shelter for estuarine biota. Bottom areas also sequester pollutants (microbially-mediated) and convert them to a biologically-usable form. Dredging would destroy the systems that carry out these vital processes.	Diked disposal areas located in tidal flats will have impacts similar to those noted for dredging operations. Diking and burial will eliminate these valuable habitats.

APPENDIX 7a

Operational Evaluation of Grab Samplers*

Grab	Trigger System Reliability
Franklin Anderson	Good, but perhaps too sensitive on hard sand and gravel bottom.
Dietz-LaFond	Poor, unless area of trigger foot is increased to at least 50 cm^2. Triggering may often be impossible in very soft mud unless the foot has been modified.
Birge-Ekman	Good. Triggered by messenger weight dropped from surface, normally consistent but can be affected on soft bottoms if sampler is allowed to settle for too long before dropping the messenger.
Petersen	Fair to good, though tends to be a little oversensitive on hard sand and gravel bottoms.
Ponar	Good, though like the Petersen, tends to be a little oversensitive on gravel bottoms.
Shipek	Good, though some slight settlement may occur before triggering on very soft materials. Sampler may fail to trigger when lowered gently on soft bottoms. By lifting and dropping the trigger weight a few centimeters after bottom contact, abortive casts may be avoided. The slight movement of the inertial trigger weight has no other effect on the sampler.
	Jaw Shape, Design, and Cut
Franklin-Anderson	Poor. During the first stages of closure and when under the greatest pressure of springs and weight, the jaw shape loosely follows the arc of cut. However, the degree of fit becomes progressively worse as the closing pressure is reduced. Because each jaw is semicylindrical in shape, sample displacement is necessary within it if anything near maximum capacity is to be achieved.
Dietz-LaFond	Poor. As for Franklin-Anderson.
Birge-Ekman	Excellent. Jaw shape exactly follows arc of cut and almost no sample displacement occurs.
Petersen	Poor. Comments as for Franklin-Anderson, except that, instead of the reduction in closure pressure

(Continued)

*After USEPA/COE (1981)

(Sheet 1 of 4)

APPENDIX 7b

Grab	Jaw Shape, Design, and Cut
Petersen (Continued)	being produced by slackening of tensional springs, the same result is effected by reduced leverage on the scissor arms mounted across the hinge line.
Ponar	Excellent. Jaw shape exactly follows arc of cut and almost no sample displacement occurs.
Shipek	Excellent. As for Ponar. In addition, the rotation of the bucket is extremely rapid. In most cases the rotational shear is far greater than the sediment shear strength, thus the cutting action is very clean (producing minimal disturbance), particularly in soft clays, muds, silts, and sands.
	Preservation and Protection from Washout
Franklin-Anderson	Fair, but the tightness of closure is largely dependent upon the lack of grains trapped between the edges of the jaws. Providing a tight fit between the two jaws is obtained, the sample is well shielded against washout. If the jaws are kept open by material trapped between the jaws, washout can be severe or total.
Dietz-LaFond	Fair. Comments as for Franklin-Anderson.
Birge-Ekman	Good, except when the sampler is used in very coarse or shelly sediment. Under these conditions, material may be trapped between the jaws, preventing their closure. In this case, washout may be severe. The jaws are so designed that they slightly overlap one another, thus a slight imperfection of closure can be tolerated.
Petersen	Good. Comments as for Birge-Ekman.
Ponar	Good. Comments as for Birge-Ekman. In addition to the overlap jaws, this sampler has a pair of metal side plates, mounted close to the moving side faces of the jaws. These plates further reduce the possibility of washout.
Shipek	Excellent. The great advantage of the Shipek, over all of the other samplers described, is

(Continued) (Sheet 2 of 4)

APPENDIX 7c

Grab	Preservation and Protection from Washout
Shipek (Continued)	that the bucket closes with its separation plane aligned in the horizontal rather than in the vertical. Good samples can be retrieved even when bucket closure is prevented by pebbles or similar material, even 2 to 5 cm across. With the bucket properly rotated, washout is completely avoided.

	Stability
Franklin-Anderson	Fair. Despite the weight of this grab, it tends to "stream" at an inclined angle under conditions of rapid ship drift or fast water flow. Provided lowering conditions are calm and stable, the sampler will hold upright during the initial sampling process; if, however, the line is allowed to slack, the sampler will fall over.
Dietz-LaFond	Poor. This sampler is very sensitive to "streaming" and will rarely operate in the vertical position unless used in ideal conditions. Its tendency to maintain an inclined attitude during descent sometimes results in a failure to trigger.
Birge-Ekman	Fair. Despite the light weight of this sampler and its tendency to "stream," its wide base gives good stability and stance once it has come to rest on the sediment floor. Under poor sampling conditions, however, it becomes impossible to operate because: (a) the sampler, due to its light weight, is continually being lifted and dropped and "streamed" along the bottom, and (b) any slack in the line, particularly near the sampler, is likely to impede the proper function of the triggers' messenger weight. It tends to roll over after triggering on all but soft bottoms.
Petersen	Good. This is a heavy sampler with a wide base line (when the jaws are open). It maintains a near vertical descent under all conditions, but after sampling it tends to fall over (unless on a soft bottom).

(Sheet 3 of 4)

(Continued)

APPENDIX 7d

Grab	Stability
Ponar	Very good. Comments as for Petersen; because of its weight and wide baseline (when jaws are open), this grab has a good vertical descent under most conditions and has a stable stance on the bottom. The presence of the fixed side plates prevents the grab from falling over after jaw closure and helps in preserving a near perfect bottom sample.
Shipek	Excellent. Despite the large size of this sampler, its weight ensures a near perfect vertical descent even under conditions of rapid drift or fast water flow. The sampler is also very stable even on bottom slopes 20 degrees or more. This stability ensures the minimum possible disturbance of the sample material.

(Sheet 4 of 4)

APPENDIX 8

Operational Suitability of Corers and Grab Samplers*

Sampler	Characteristics
Benthos Gravity Corer	Cores of 3 m or less in soft clays, muds, or sandy silts. Particularly suitable for studies of the sediment/water interface, for studies on depositonal sediment structures.
Alpine Gravity Corer	Cores of 2 m or less in almost all sediment types. The rugged nature of this corer lends itself to general usage. For studies involving sediment structure or large volumes of material, the corer is unsuitable; for studies of a pilot nature, or to prove the suitability of an area for piston coring, this gravity corer is excellent.
Phleger Corer	Cores of 0.5 m or less, in almost all sediment types. Particularly suited to bottom materials containing a high percentage of fiberous organic material. The low cutter angle, the narrow wall thickness and high point loading, and the extremely sharp cutter, make it very suitable for sampling shallow lacustrine and estuarine deposits, marsh deposits, and thin peat beds.
Multiple Corers	Still under investigation.
Franklin-Anderson Grab	Suitable for obtaining material for bulk sample analysis. Works best in soft clays, muds, silts, and sands. Will occasionally obtain a good gravel sample. Material of no use for structural or other specific analyses.
Dietz-LaFond Grab	Can be used for general sampling but not recommended for any particular use. Of all the samplers tested, this pattern proved to be the least suitable.
Birge-Ekman Dredge	Suitable for soft clays, muds, silts, and silty sands. This sampler should be used under calm water conditions, typically in small lakes or restricted areas. The lack of sample disturbance, square cross section, and moderate penetration make this sampler suitable for detailed studies (i.e. biological and geochemical) of the top 2 to 3 cm of bottom sediment. Because of its light weight and easy handling, it is well suited to small boat operations.

(Continued)

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* After USEPA/COE (1981)

Sampler	Characteristics
Petersen Grab	This sampler, like the Franklin-Anderson, is suitable for taking bulk sample material in most types of sediment. It is quite unsuited for studies of detailed and specific sediment properties, though it is perhaps a little more successful in taking gravel samples. Either of these two samplers (Petersen or Franklin-Andersen) will do well as a general purpose bulk sampler.
Ponar Grab	An excellent general purpose bottom sampler. In practice it operates better than either the Petersen or Franklin-Anderson over the full range of bottom types. It can also obtain bottom samples with little or no disturbance and with the protecting screens removed or folded back, direct access can be had to the sediment surface of the sample. Such access to an undisturbed sample makes it suitable for geochemical, sedimentological, biological, and structural studies. Because of the large sample volume and its relatively undisturbed state, this sampler is very suitable for population studies of the bottom sediment fauna.
Shipek Bucket Sampler	An excellent general purpose sampler, though perhaps a little heavy for small boat operation. This sampler is capable of working with almost equal success on all types of bottom material. It provides a sample even less disturbed than the Ponar, making it the most suitable sampler (under test) for detailed geological studies of the sediment surface. The sampler volume is significantly less than that of the Ponar, and the quantity of material sampled at maximum cutting depth is also less than the Ponar. These two points may, therefore, favor the Ponar for certain biological (population) studies. On the other hand, the rapid rotation of the Shipek bucket, as opposed to the much slower closure of the Ponar's jaws, may make it more suitable for sampling sediment containing a significant population of nonsessile forms.

APPENDIX 9: Typical data sheets employed during DER's Deepwater Port studies.

METEOROLOGICAL AND GENERAL FIELD CONDITIONS

1. Location (Port/Harbor) & Station Number ______________________

2. Station Description ______________________

3. Date (mo/day/yr) ______________________

4. Observation By ______________________

5. Previous Night's Weather (include rainfall, wind conds., cloud cover, drops in ambient air temp) ______________________

6. Meteorological Conditions on Station (include cloud cover, rainfall, etc.) ______________________

   Air Temp ________ Wind Direction ____________ Wind Speed ________

7. Water Conditions (include observations of wave conditions, algal blooms, turbidity plumes, foaming, surface slicks, tidal phase and velocity, currents, etc) ______________________

8. General Conditions and Additional Comments (include vessel traffic, outfalls, dredging operations, biota observed, etc.) ______________________

IN SITU DATA SHEET

Recorded By______________ Observations by __________ Time of Day_______ (start)

Water Depth________ Time of Day_______ (end)

METHOD	PARAMETER	TOP READING	MID READING	BOTTOM READING
SCT METER	Temperature (°C)			
	Salinity (o/oo)			
	Conductivity (µmhos)			
D.O. METER	Temperature			
	D.O. (mg/l)			

Peristalitic Pump Data (Collected @ Mid-depth)

METHOD	PARAMETER	INITIAL VALUE	FINAL VALUE
HACH Turbidi-meter	Turbidity (NTU)		
Thermom.	Temperature (°C)		
Meter Corning	pH		
Secchi disk	Secchi (ft.)		

Secchi collected prior to and following remote & peristaltic sampling.

APPENDIX 9 (continued)

WATER AND SEDIMENT SAMPLE FIELD RECORD

Port and Station ____________________

Date ____________________

Collected by ____________________

I. Water Samples:

Check when collected:

	REP#1	REP#2	REP#3
Metals			
Hg			
Nutrients			

II. SEDIMENTOLOGY:

Check when collected:

	REP#1	REP#2	REP#3
Metals			
Hydrocarbons			

A. PONAR SEDIMENT QUALITY (note texture, smell, presence of oxidized layer, color, etc.) ____________________

B. CORER SEDIMENT QUALTITY (note texture, smell, color, zonation, etc.) ____________________

C. Additional Comments ____________________

APPENDIX 10

CHAIN OF CUSTODY & CHECKOFF LIST

Station	Sediment 1 liter glass	Water - Metals 500ml plastic (red) HNO3		Water 500ml plastic (green) H2SO4	Water 500ml plastic (purple) no pres.	Water 1 gallon plastic no pres.
MIA-1	3	3	3	3	3	*
MIA-2	3	3	3	3	3	*
MIA-3	3	3	3	3	3	1
MIA-4	3	3	3	3	3	*
MIA-7	0	3	3	3	3	*

Samples taken by: ______________________________ Date: ______________

Delivered to bus station by: ______________________ Date: ______________

Received by: __________________________________ Date: ___________

Smith Brothers Chemical Laboratories

Instructions:
1. Field personnel, please circle numbers above when bottles are filled.
2. Sample custodian, please "X" circled numbers when samples are checked in. Please note any broken or missing samples.

APPENDIX 11: SAMPLE SUMMARY TABLES OF PHYSICAL AND CHEMICAL RESULTS.

GENERAL PHYSICAL AND CHEMICAL WATER QUALITY CHARACTERISTICS

SPRING/DRY SEASON

STATION PARAMETER											STANDARD
TEMPERATURE (°C)											
SALINITY (ppt)											
pH											
DISSOLVED OXYGEN mg/l											
DISSOLVED OXYGEN % SATURATION											
TURBIDITY (NTU)											
CONDUCTIVITY (µmhos)											
TOTAL KJELDAHL NITROGEN (mg/l)											
AMMONIA - N											
PHOSPHATE - P											
NITRATE - N											
TOTAL ORGANIC CARBON											
TOTAL SUSPENDED SOLIDS mg/l											

APPENDIX 11 (continued)

INORGANIC WATER QUALITY

SPRING/DRY SEASON

STATION PARAMETER mg/liter																	STANDARD
	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	
CADMIUM																	
COPPER																	
IRON																	
LEAD																	
MERCURY																	
NICKEL																	
SILVER																	
ZINC																	

APPENDIX 11 (continued)

GENERAL PHYSICAL AND CHEMICAL SEDIMENT CHARACTERISTICS

SPRING/DRY SEASON

STATION PARAMETER ppm {dry basis}												
	MEAN	σ	MEAN	σ	MEAN	O	MEAN	σ	MEAN	σ	MEAN	σ
SPECIFIC GRAVITY[1]												
TOTAL KJELDAHL NITROGEN												
TOTAL ORGANIC CARBON												
AMMONIA -N												
TOTAL PHOSPHORUS - P												
NITRATE - N												
OIL AND GREASE												
BIOCHEMICAL OXYGEN DEMAND {mg O_2/kg}												
TOTAL SOLIDS {%}												
SULFATE												

APPENDIX 11 (continued)

INORGANIC SEDIMENT QUALITY

SPRING/DRY SEASON

STATION PARAMETER ppm {dry basis}														
	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ
ALUMINUM														
CADMIUM														
CHROMIUM														
COPPER														
IRON														
LEAD														
MERCURY														
NICKEL														
SILVER														
ZINC														
MANGANESE														

APPENDIX 11 (continued)

ORGANIC SEDIMENT QUALITY

SPRING/DRY SEASON

STATION PARAMETER ppm {dry basis}																						
PESTICIDES	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ	MEAN	σ
MIREX																						
TOXAPHENE																						
DDT																						
ALDRIN																						
CHLORDANE																						
OTHER CHLORINATED {DDE}																						
PCB's																						
OIL AND GREASE																						
PHENOLS																						
PHENOL																						
2-CHLOROPHENOL																						
2,4-DICHLOROPHENOL																						
2,4,6-TRICHLOROPHENOL																						
4-CHLORO M CRESOL																						
2,4 DINITROPHENOL																						
PENTACHLOROPHENOL																						

MERCURY INTERCALIBRATION FOR DEEPWATER PORTS MAINTENANCE DREDGING STUDY

INTRODUCTION

During the first year of the Deepwater Ports Maintenance Dredging Study, results of mercury analyses of estuarine water samples indicated that waters in several ports did not meet the State Water Quality Standard of 0.1 µg/l (parts per billion). The analyses were performed in a commercial laboratory using the EPA standard method for mercury analyses of wastewater. This method has a specified detection limit of 0.2 µg/l and is primarily designed for studying polluted freshwaters.

The high mercury results were considered to be possibly unreliable for the following reasons:

1. The EPA standard method employs large amounts of oxidizing agents for treating samples.

   Additions of excessive amounts of oxidizing agents, such as potassium permanganate and persulfate, to brackish or saline waters may oxidize the halogens (present as anions), to their gaseous form. If these gases are not efficiently removed from the sample, positive interferences may occur due to the absorption of light in the UV range during analysis.

2. Contamination may occur in commercial laboratories routinely processing samples from highy polluted areas. Glassware and labware maybe contaminated to an extent that a relatively high systematic analytical blank for mercury analysis may result. Additionally, some analytical procedures used in commercial labs require mercury reagents (e.g., COD and TKN analyses) which may also lead to spuriously high blank levels.

3. Research findings do not support mercury values obtained in the ports study.

A. A paper by Windom and Taylor (1979) reports average levels of mercury for southeastern U.S. rivers of from 18 to 37 ng/l (parts per trillion). The St. Johns River was one of those areas studied. Mercury concentrations in shelf waters adjacent to these rivers varied from 8 to 46 ng/l.

B. An international intercalibration exercise for mercury analysis of North Atlantic seawater (Olafsson, 1982) involving 36 recognized marine chemistry laboratories reported a mean value of 9 ng/l. All laboratories analyzed samples blindly and independently. None of the laboratories recognized as competent in analytical chemistry of mercury in marine waters use large amounts of oxidizing agents.

Because of the suspected unreliability of the mercury results in the first year of study, the following exercise was conducted to evaluate analytical techniques prior to carrying out further mercury analyses during the second year of the project.

DESCRIPTION OF THE EXERCISE

The purpose of this exercise was to compare the results of mercury analyses of natural and spiked water samples by several laboratories using different methods. By using water samples from one of the ports for which high mercury concentrations were previously reported, the exercise could also serve as a check on first year project results.

The Port of Jacksonville was chosen as the site to collect the water for the experiment since the results of the first year's study indicated high levels of mercury at 9 stations in the St. Johns River. Large volume water samples were collected from three stations where high levels were previously reported (FDER, 1983) and from a fourth station just offshore which should have low mercury concentrations. The water was collected in the same manner (i.e., peristaltic pump) as during the original study.

Once the samples were collected, they were preserved with Ultrex nitric acid (HNO_3) and then were returned to the Skidaway Institute of Oceanography. The samples from the suspected contamination sites (JAX-5A, 5B and 6A) were divided into four, approximately one liter aliquots in a Class 100 cleanroom. Four - 4 liter samples were collected at the offshore station (JAX-9C). One of the samples was treated only with preserving nitric acid and the other three were spiked as follows:

1. spiked with inorganic mercury standard to contain the ambient concentration plus 100 ng/l.
2. spiked with EPA organomercury standard to a level 100 ng/l above ambient.

3. spiked with 1 ml of PAH per liter.

All four or these samples (blank and spiked) were then divided into four aliquots.

One aliquot of each of the seven samples (three samples and the blank, and spiked JAX-9C samples) were shipped to four laboratories to be analyzed for total mercury. All samples, were labeled X-Y where X was the lab number (1 to 4) and Y was the sample number (1 to 7). The ordering of the sample number was arbitrary so that no analyst would know the nature of the sample. Unfortunately, one set of samples was broken during shipping so only the remaining three laboratories analyzed the samples.

All labs analyzed the samples in at least duplicate. The analytical techniques used are as follows:

Lab 1: Samples were placed in bulb stoppered silica flasks, 1% $K_2Cr_2O_7$ solution added (1 ml/100g) and set aside for 24 hrs. Samples were then U.V. irradiated for 4 hours under a1 KW Hanovia lamp. Mercury determination was by cold vapor atomic absorption after $SnCl_2$ reduction and preconcentration by amalgamation on gold (In K. Grasshoff [ed]: Methods of Seawater Analysis, 2nd ed.). A procedural blank of 0.6 ngHg kg^{-1} was subtracted.

Lab 2: Two procedures were used. The first was the cold vapor technique described in the EPA "Methods for Chemical Analysis of Water and Wastes" (1979) section 245.2. The second technique was that used by Windom and Taylor (1979). This technique employed cold vapor atomic absorption. The instrument used for the analyses was a Laboratory Data Control mercury monitor having a 30-cm optical cell and stable light source and detector. The analysis required 200-ml. Sufficient 5% (w/v) potassium permanganate was added until the sample maintained the permanganate color for 15 minutes. Further oxidation was accomplished using 2 ml of 5% (w/v) potassium disulfate. This was allowed to stand 30 min and then 2 ml of 12% (w/v) NaCl-hydroxylamine hydrogen sulfate was added to eliminate excess oxidizing materials. Finally, 10 ml of 10% (w/v) $SnCl_2$ in 3.N H_2OSO_4 was added and the sample bottle was fitted to a closed aeration apparatus for analysis.

Lab 3: The EPA method in section 245.5 of "Methods for Chemical Analysis of Water and Wastes". No other method was used.

RESULTS

The results of analyses of water samples collected at the four stations (Table 1) show considerable variation among the three laboratories (Lab No. 2, did not report results using the EPA method since it gave spurriously high values). The highest values reported were for aliquots analyzed using the EPA method (Lab No.3) while lowest values were obtained using the techniques described by Lab 1, which were designed for low ambient concentrations. It is interesting to note that Lab 3 found the highest concentration at the offshore station, JAX-9C, is the station having the highest salinity. This suggests a chloride interference.

Inorganic spikes of aliquots from JAX-9C were quantitatively recovered by Laboratories 1 and 2 but Lab 3 reported an excessive recovery of the spike, again suggesting interference (Table 2). The organic mercury spike was recovered well by Laboratory 1, but does not appear to recover strongly-bound organic mercury. Again, Laboratory 3, using the EPA method, reported excess recovery of the spike.

Addition of PAH appears to positively interfere with the analytical technique used by Lab No. 1. Laboratory 2 reported mercury concentrations in the PAH spiked aliquot lower than the unspiked sample. Laboratory 3 reported about the same value for unspiked and PAH spiked samples.

DISCUSSION

Laboratory 1 is internationally recognized as an expert laboratory in the analysis of mercury in seawater. The techniques it uses are geared to analyzing mercury at very low, ambient oceanic concentrations and therefore has low detection limits. Also this laboratory operates in a very clean manner since ambient trace element analysis of seawater is its main function. The analytical technique used by this lab thus has low procedural blanks (i.e., 0.6 ng/l). The techinque used by this laboratory, however, does not appear to recover strongly bound organomercury compounds. This technique, therefore, is probably unsuitable for water containing high concentrations of organomercury compounds (i.e., heavily polluted waters).

The EPA technique used by Laboratory 3 (and Laboratory 2, but values not reported) appears to be completely unsuitable for estuarine waters probably due to chloride interferences. The detection limit of 200 ng/l also limits the usefulness of this method.

The techinque used by Laboratory 2 (a commercial laboratory) appears to recover inorganic and organic mercury spikes adequately. Ambient mercury concentrations reported by this lab, however, appear to be considerably higher than expected based on past studies using the same technique (Windom and Taylor, 1979) and given the results of Laboratory 1. Laboratory 2, like all commercial laboratories, routinely analyzes water and wastewater samples containing a wide range of mercury concentrations. It also conducts other chemical analyses that may lead to a high potential for mercury contamination during sample handling. Thus, it is not surprising that unspiked samples yield high reported mercury concentrations. It would appear that this laboratory is probably not capable of analyzing mercury at concentrations below approximately 40 to 50 ng/l (.04 to .05 parts per billion).

CONCLUSIONS

From the results of this intercalibration exercise it appears that results of mercury analyses particularly under marine and estuarine conditions, should be viewed with reservation. Attention must be paid to the analytical techniques used to determine whether it was designed for examining polluted or ambient conditions. It appears that the EPA method is of little use in establishing ambient conditions in estuarine waters,and other techniques that appear to be useful for this purpose should be employed. It is likely that commercial laboratories will have real mercury detection limits (because of large blanks) on the order of several tens of nanograms per liter which is near the State Water Quality Standard, although recoveries may be fairly precise. It would, therefore, appear that mercury concentrations near or slightly above state standards reported by such labs, even when they use appropriate techniques, should not be interpreted as a clear indication that the standard is, indeed, exceeded. If, however, there is a good reason to suspect an area of being contaminated with mercury, more detailed and carefully conducted studies will be required to established the actual level of mercury in the water column.

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REFERENCES

Florida Department of Environmental Regulation (1983). Deepwater Ports Maintenance Dredging Study: Ports of Jacksonville, Tampa, Manatee and Pensacola.

Oalfsson, J. (1982). An intercalibration for mercury in seawater. Marine Chemistry 11: 129-142.

Windom, H.L. and F.E. Taylor (1979). The flux of mercury in the South Atlantic Bight. Deep-Sea Res. 26A: 283-292.

TABLE 1

RESULTS OF ANALYSES OF WATER SAMPLES COLLECTED IN JACKSONVILLE HARBOR

LAB NUMBER	1	2	3
JAX-5A	12	40	300
JAX-5B	5.5	70	220
JAX-6A	7.9	110	220
JAX-9C	2.7	75	590

TABLE 2

RESULTS OF HG ANALYSES OF SPIKED SEAWATER SAMPLES
(all concentrations are in ng/l)

LAB NUMBER	1	2	3
BLANK (JAX-9C)	2.7	75	590
BLANK + 100 ng/l (inorganic)	102	175	710
PERCENT RECOVERY	99	100	120
BLANK + 100 ng/l EPA STD*	16	170	1270
PERCENT RECOVERY	14	95	680
BLANK + PAH	7.9	50	630
PERCENT RECOVERY	290	66	107

*Includes organomercury compounds.