

Fla-Dec

EP2.

C55

Tech.

c. 2

***FLORIDA COASTAL SEDIMENT CONTAMINANTS
ATLAS***

TECHNICAL VOLUME

DOCUMENTS DEPOSITORY

APR 16 2001

**Florida State University Library
Tallahassee, Florida**

Florida Department of Environmental Protection
3900 Commonwealth Boulevard
Mail Station 46
Tallahassee, Florida 32399-3000

1994

INTRODUCTION

This technical volume supplements the *Florida Coastal Sediment Contaminants Atlas* by providing additional information on chemical data and interpretive methods presented in the *Atlas*.

The majority of information in the *Atlas* is based on nearly ten years of work by the Florida Department of Environmental Protection (FDEP), through the Coastal Contaminants Survey. This work was undertaken to remedy a critical gap in the state's ability to identify and interpret contaminants in coastal areas. The coastal contaminants survey includes chemical information on approximately 700 sites located throughout the state, in a variety of pristine to impacted coastal areas. The survey sampling dates and areas are listed in Section One.

Section Two of this volume explains sample collection procedures, chemical analysis, and interpretation of sediment trace metal and organic contaminant data. Laboratory and field measurements in the FDEP database are summarized in Section Three. Sections Four and Five discuss metals and organic contaminants and their possible sources.

Further information regarding specific analytical methods and the statistical rationale behind the metal-to-aluminum normalization method can be found in the following FDEP documents: *Deepwater Ports Maintenance Dredging and Disposal Manual* (1984), and *A Guide to the Interpretation of Metal Concentrations in Estuarine Sediments* (1988).

TABLE OF CONTENTS

INTRODUCTION	I
TABLE OF CONTENTS	III
SECTION 1. FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION COASTAL SEDIMENT SAMPLING PROJECTS	
1.0 Introduction.	1
1.1 Selected Sediment Chemistry Research Projects	2
SECTION 2. FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION SAMPLE COLLECTION, LABORATORY ANALYSIS, AND DATA INTERPRETATION	
2.0 Introduction.	4
2.1 FDEP Sample Collection Methods	4
2.1.1 Background	4
2.1.2 Rationale for sampling design	4
2.1.3 Field Methods	5
2.1.3.1 Current Procedures.	6
2.2 Laboratory Analysis of Sediment Samples	6
2.2.1 Metals analyses	6
2.2.2 Organics analyses	7
2.3 Sediment Trace Metal Data Interpretation	7
2.4 Interpretation of Sediment Toxic Organic Contaminant Data	10
SECTION 3. SEDIMENT AND WATER COLUMN MEASUREMENTS IN THE FDEP DATABASE	
3.0 Introduction.	11
3.1 Metals and Nutrients.	11
3.2 Organic Compounds	12
3.2.1 Chlorinated Pesticides	12
3.2.2 Polynuclear Aromatic Hydrocarbons	12
3.2.3 Polychlorinated Biphenyl Compounds	12
3.2.4 Phenolic Compounds	12
3.2.5 Aliphatic Petroleum Hydrocarbons	12
SECTION 4. SOURCES AND USES OF METALS AND SEMI-METALS EXAMINED IN THE ATLAS	14
SECTION 5. SOURCES AND USES OF TOXIC ORGANIC COMPOUND CLASSES EXAMINED IN THE ATLAS	16
REFERENCES	18

LIST OF FIGURES

Figure 1. 9

Graphical example of the covariance between aluminum and lead concentrations in the Florida "clean" coastal sediment database.

Figure 2. 9

Graphical example of the covariance between aluminum and lead with the 95% prediction limits included. An example of the metal enrichment factor calculation is shown.

LIST OF TABLES

Table 1 11

Limits of detection for metals and nutrients analyzed by different laboratories.

Table 2 13

Organic Compounds in major categories.

SECTION 1. FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION COASTAL SEDIMENT SAMPLING PROJECTS.

1.0 Introduction

The Atlas includes data from many surveys conducted to address a variety of objectives. The following list depicts major projects, areas, and year(s) that sediment samples were collected.

<u>Project/Area</u>	<u>Year</u>
<u>Deep Water Ports Project</u>	1983 - 1984
Port of Jacksonville/St. Johns River	
Port Canaveral	
Port Ft. Pierce	
Port of Palm Beach	
Port of Miami/Miami River/Biscayne Bay	
Port Manatee	
Port of St. Petersburg	
Port of Tampa	
Port St. Joe	
Port of Panama City	
Port of Pensacola	
<u>Statewide Survey of Clean Reference Sites to Establish Metals Enrichment Interpretive Tool</u>	1986 - 1991
<u>Estuarine Surveys</u>	
Biscayne Bay	1985, 1989
Hillsborough Bay	1985, 1989
Pensacola Bay	1985
Lower St. Johns River	1988
Charlotte Harbor	1989
Lake Worth	1989
Perdido River and Perdido Bay	1988 - 1991
West Central Florida	1991

1.1 Selected Sediment Chemistry Research Projects

Besides Florida Department of Environmental Protection efforts reported in this atlas, other researchers have considered sediments as an important constituent to assess marine environments. Studies completed or in progress, and principle investigators, are listed.

<u>Laboratory/Source of Data</u>	<u>Project Area, Authors, and Date of publication</u>
Mote Marine Laboratory Sarasota, FL.	St. Johns River Estuary, Pierce <i>et al.</i> , 1988; Northern Sarasota Bay, Dixon, 1988; Port Manatee Project, Hofmann and Dixon, 1989; Sarasota Bay Project, Lowrey, in press.
Florida Institute of Technology, Department of Oceanography Melbourne, FL	Indian River Lagoon, Trefry <i>et al.</i> , 1983; Trefry and Stauble, 1987; Gu <i>et al.</i> , 1987; Hillsborough River, Trefry <i>et al.</i> , 1989; Manatee Pocket in the St. Lucie estuary, Trefry <i>et al.</i> 1990 & 1992.
Center for Nearshore Marine Science University of South Florida Tampa, FL	Tampa Bay, Doyle <i>et al.</i> 1989; Brooks and Doyle, 1989 & 1992.
Institute for Coastal and Estuarine Research, University of West Florida Pensacola, FL	Sediment core study from Bayou Chlco, Pensacola Bay. Stone and Morgan 1991.
National Atmospheric and Oceanic Administration (NOAA)	National Status and Trends Report, Long and Morgan 1990; Toxicants and the potential for their biological effects in Tampa Bay, Long <i>et al.</i> 1991; in preparation; Metal contaminant assessment in the southeast United States, Hanson and Evans, 1991.
South Florida Water Management District, West Palm Beach, FL	Pesticides in sediments and surface water in the South Florida Water Management District, Pfeuffer 1985; 1991.
Department of Environmental and Engineering Sciences University of Florida Gainesville, FL	Toxic pollutants in sediments and surface water at selected sites in Florida, Delfino <i>et al.</i> 1991.

United States Fish and Wildlife Service

Sediment studies in St. Andrew and St. Joseph Bay Systems, Brim *et al* (in preparation); Perdido Bay sediment study, 1993; Contaminants in the Crystal River estuary, Facemire 1991.

Collier County
Pollution Control Department

Estuarine and freshwater sediment studies, Grabe, 1991a & 1991b; Bishof, 1991.

Florida Department of Environmental
Protection, Tallahassee, FL

Sediment trace metals documents, Schropp and Windom, 1988; Schropp *et al.*, 1990; Windom *et al.* 1989; Perdido Bay study, Schropp *et al.* 1991; Laboratory Inter-comparison study, Schropp, 1992; Metal contamination assessment, Seal *et al.* 1993.

SECTION 2. FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION SAMPLE COLLECTION, LABORATORY ANALYSIS, AND DATA INTERPRETATION.

2.0 Introduction

This section explains sample collection, chemical analysis, and interpretation of sediment trace metal and organic contaminant data. More information, including the statistical rationale behind the metal-to-aluminum normalization method, can be found in the FDEP 1988 document *A Guide to the Interpretation of Metal Concentrations in Estuarine Sediments* (Schropp and Windom 1988).

2.1 FDEP Sample Collection Methods

2.1.1 Background

Most contaminants discharged into coastal waters via municipal and industrial discharges and runoff rapidly attaches to particulate matter and become incorporated in bottom sediments. Although this pathway has been known for many years, only recently has the threat of contaminated sediments to marine resources and human health received widespread public attention.

Good quality sediments are critical to ecosystem health for several reasons. Sediments are reservoirs for contaminants, and the accumulation of pollutants occurs even though the overlying water column often contains only traces of contaminants. Sediments integrate metals and organic compounds over time from discharges, and can act as long-term sources of contaminants and nutrients into the system after the original pollutant discharges have ceased. Ultimately, sediment contamination can affect the health of bottom-dwelling organisms by direct contact and ingestion, and through their effects on benthic animals, contaminants can be transferred elsewhere in the food web.

2.1.2 Rationale for sampling design

Sediment sampling sites were selected in coastal systems to test for contamination from a variety of sources. Most sites were located near point or nonpoint discharges, which were considered potentially impacted areas. This bias in the sampling design was deliberate to enable FDEP to gain an initial understanding of the severity and extent of contamination. This approach does not provide a statistically valid estimate of the aerial extent of contamination. Additionally, a number of sampling sites (clean reference sites) were selected in areas removed from potential pollution sources to develop an approach for distinguishing natural from anthropogenically enriched sediments.

Prior to field sampling, station locations were identified after study of local drainage features, land uses, water depth, potential depositional areas, navigation charts and, typically, meetings with local government staff. Station selection fell into two categories: areas where a clean reference site might be best located, or areas where contamination

was suspected. Selected stations were plotted on navigation charts, and latitude and longitude calculated for each station.

2.1.3 Field Methods

In the field, stations were located using LORAN-C by latitude and longitude, compass bearings and cross referenced to navigation charts. LORAN-C was compensated to known local reference points on most the recent edition of navigation charts.

Upon arrival at the station, the boat was anchored and engines shut off. The location, time, date, weather conditions, and compass bearings were recorded in a station log notebook. Water column physical parameters were taken at the surface, mid-depth and bottom using a calibrated YSI model 57 Dissolved oxygen meter, and YSI model 59 Salinity, Conductivity and Temperature meter. These measurements were recorded in the station log notebook. Written descriptions of the sediment sample characteristics were also recorded.

Sediments were collected from the boat, using a stainless 9X9" PONAR grab. The grab was suspended from a holst mounted on the port side of the boat. The grab was acid washed and rinsed with deionized water before use, and thoroughly rinsed with ambient water between grabs. A 10% HCl solution (prepared in the DEP Biology Lab) was used to acid rinse all utensils, the sampling device, and spatulas used to transfer samples into sampling jars.

Once the sampler was retrieved, it was swung aboard, and the sampler carefully emptied into a clean, acid washed and rinsed tub. The top two centimeters of sediment were scooped from the top of the grab. Repeated grabs were made at the same site, while the boat was at anchor, until enough material was collected for all analyses.

Samples were transferred to glass jars supplied by the laboratory, or purchased (I-chem #220 - 0250, or whirl-paks™) which have been precleaned by the manufacturer to meet EPA specifications for organic and inorganic materials. Sample containers were labeled with pertinent information, including time, station number and date. When filled with the sample, containers were immediately placed on ice. The time of collection, sample number, replicate number and location were recorded on field log sheets, and on chain of custody sheets for shipment to the lab.

Samples were sometimes collected by using sediment coring tubes. This option was reserved for waters too shallow to allow entry by the boat, or when sensitive habitats (i.e., grass beds, corals) precluded use of a large bottom sampling device. Three acid washed and rinsed clear cellulose-acetate-butyrate core tubes, 2" diameter x 12" long, with caps were used for each replicate. Three replicates were collected for each station.

Core tubes were plunged into the sediment, and the top capped. The core tube was retrieved by carefully displacing the sediment around the core to place the bottom cap on the core tube, and lifted from the sediment. These cores were taken by the diver to

the boat, where they were transferred into containers using an acid washed and rinsed extruding tool. The top 3-5 centimeters of the cores were placed in the collecting jar or whirlpak, and the remainder discarded. Each replicate sample was a composite of the three cores. Logging and chain of custody procedures were the same as described above.

2.1.3.1. Current Procedures

Since 1991, several changes have been made to the FDEP standard field protocol that may be of interest to those conducting field operations. Stations are now located using a Global Positioning System (GPS) in addition to traditional methods. A 12"x12" Kynar coated stainless steel "Young" grab is used to collect sediment, and is deployed in a similar fashion as the PONAR. In addition to acid washing, full strength acetone is used to rinse all gear prior to sampling and between all stations. This volatilizes any organic contaminants that might be resident on the sampler. The top two centimeters of sediment are scooped from the top of the sampler with an acetone rinsed sterile scoop. The sediment is then transferred to a stainless container, and homogenized using an acid washed, acetone rinsed, long handled stainless scoop. All other procedures remain as stated above.

2.2 Laboratory Analysis of Sediment Samples

From 1982 to 1990, all samples were analyzed by Savannah Laboratories and Environmental Services, Inc. in Savannah, Georgia. From 1990 to 1991, the Skidaway Institute of Oceanography in Savannah, Georgia analyzed sediments. Analyses done by both laboratories can be found in Section Three.

2.2.1 Metals analyses

All metals, except mercury, were analyzed by Savannah Laboratories and Environmental Services, Inc (SLES) using graphite-furnace or flame atomic absorption spectrometry after total digestion (dissolution) of the sediment with hydrofluoric (HF), nitric (HNO₃), and perchloric (HClO₄) acids. Mercury was analyzed by the cold vapor atomic absorption technique after a milder digestion.

From 1990 to 1991, the Skidaway Institute of Oceanography in Savannah, Georgia analyzed metals by ICP (Inductively-coupled plasma) mass spectrometry or by atomic absorption spectrometry after performing the HF-HNO₃-HClO₄ acid digestion sequence. Mercury was analyzed by a method that combines the principle of isotope dilution with ICP mass spectrometry (Windom and Smith 1992). Strict laboratory procedures concerning both accuracy and precision were followed by both the SLES facility and Skidaway Institute of Oceanography. A National Institute of Standards and Technology estuarine sediment standard (NIST SRM 1646) was employed as a quality control check by both SLES and Skidaway laboratories.

Total digestion of the sediment sample is necessary to employ the normalization method (discussed in section 2.3) to estimate metal contamination. Total digestion is also strongly

encouraged to produce comparable data in trend monitoring of contaminants. Use of hydrofluoric acid ensures dissolution of silicate minerals in the sediment, some of which may contain trace metals. Liberation of trace metals bound to organic molecules requires a strong oxidizing dissolution stage, which is accomplished through use of high quality nitric, perchloric and hydrochloric acid (FDEP, Deepwater Ports Maintenance Dredging and Disposal Manual, 1994) or aqua regia, a mixture of HNO_3 and HCl acid (NOAA method by Hanson and Evans 1991). Other acid digestion techniques, commonly referred to as "weak" or "preferential" digestion, employ various dissolution times, temperatures, and types of acidic solutions to dissolve sediments. The FDEP discourages use of techniques other than total digestion for general environmental monitoring when comparing data sets.

The FDEP conducted a laboratory intercalibration exercise that illustrated the variability of sediment data from different analytical laboratories (Schropp 1992). Four laboratories participated in the exercise, which assessed accuracy and precision of reported metals data from coastal sediments and sediment reference materials (standards). The laboratories represent facilities that typically report environmental data to state, regional, and local agencies. Results of the exercise showed that sediment trace metal data from different laboratories may not be comparable if different sample digestion techniques are used. This conclusion of the FDEP study is supported by the results of an International intercalibration exercise for trace metals analysis in marine sediments (Loring and Rantala 1988).

2.2.2. Organics analyses

Organic compounds were analyzed at Savannah Laboratories in Savannah, Georgia, by gas chromatographic techniques. No organic compounds were analyzed at the Skidaway Laboratories in 1990 or 1991. Standard EPA quality assurance procedures were followed by Savannah Labs.

2.3 Sediment Trace Metal Data Interpretation

Metals occur naturally in sediments and must be distinguished from metals concentrations contributed by human activities in order to identify contamination. To distinguish anthropogenic enrichment from natural metals concentrations in sediments, a mathematical method known as normalization was used in the *Atlas*. Normalization is simply defined as a method where constant natural chemical relationships are detected, and used as a basis for comparison.

The normalization method has been used in other parts of the country with favorable results (Goldberg *et al.* 1979; Trefry *et al.* 1985; Loring 1991). Hanson and Evans (1991) published a trace metal enrichment aluminum normalization model based on a NOAA coastal sediment database of sites in the Atlantic and Gulf of Mexico coastal areas. Similar approaches using iron as a normalizing element were developed by Trefry and Presley (1976) to evaluate metal concentrations in sediments from the Gulf of Mexico and

by Zdanowicz (1991) to evaluate anthropogenic metal enrichment by offshore dumping of contaminated dredged sediment and sewage sludge in the Atlantic Ocean.

The metal-to-aluminum normalization method developed in the 1988 FDEP publication, *A Guide to the Interpretation of Metal Concentrations in Estuarine Sediments*, was based on a "clean" sediment database. Over 100 sites were selected throughout the state for inclusion in the "clean" database, based upon their remoteness from known or suspected anthropogenic metal sources. At these sites, sediment metal concentrations are generally expected to express natural relationships with aluminum (Figure 1).

The aluminum concentration of the sediment was chosen as a normalizing factor because 1) aluminum has a high crustal abundance; 2) aluminum exhibits a highly refractory chemical behavior (e.g., aluminum is not easily separated from other metals during weathering); and 3) the relatively small amounts of aluminum produced from anthropogenic sources are overwhelmed by the abundance of naturally-occurring aluminum in coastal sediments.

Eight metals (As, Cd, Cr, Cu, Hg, Pb, Ni, and Zn) were tested to determine their relationship to aluminum. Based on the relationships between seven of the eight metals (excluding mercury) and aluminum in clean sites, the FDEP developed a set of graphical tools to assess trace metal contamination in a sediment sample. For example, Figure 1 shows that as aluminum concentrations in "clean" sediments increase, metals concentrations, in this case lead, also increase.

Least squares regression analysis, using aluminum concentration as the independent variable and the concentration of the other metal as the dependent variable, was employed to fit regression lines to the data. Using results of the regression analysis, 95 percent prediction limits were calculated, which can be seen in Figure 1. The width of the prediction limits varies depending on the magnitude of the correlation coefficients between the metal in question and aluminum (Schropp and Windom 1988).

If a trace metal concentration falls above the upper 95 percent limit, the sample is designated as "enriched" in that metal. The enrichment factor is the ratio of the measured metal concentration to its maximum expected concentration in natural sediments (Figure 2). At a given concentration of aluminum, the enrichment factor is determined using the following equation:

$$\text{Metal Enrichment Factor} = \frac{\text{Observed Metal Concentration } (\mu\text{g}\cdot\text{g}^{-1})}{\text{Maximum Expected Natural Metal Concentration } (\mu\text{g}\cdot\text{g}^{-1})} \quad (1)$$

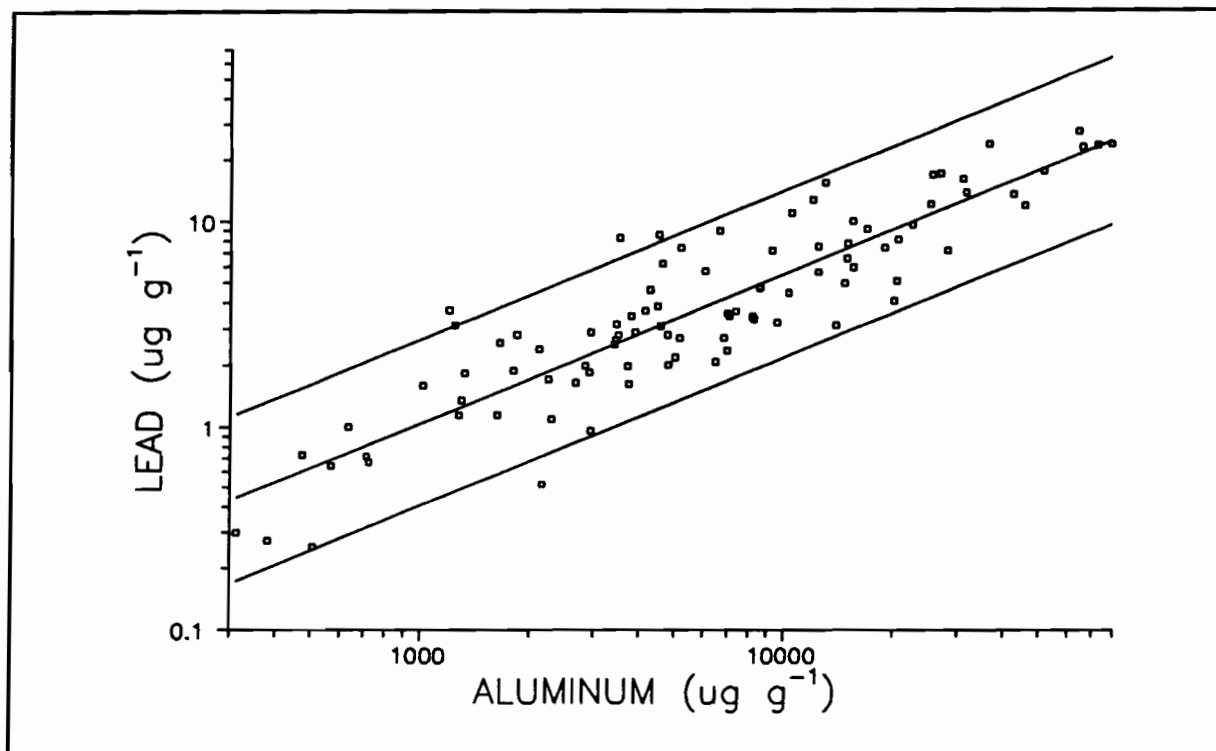


Figure 1. Lead/aluminum relationship from statewide "clean" sediments.

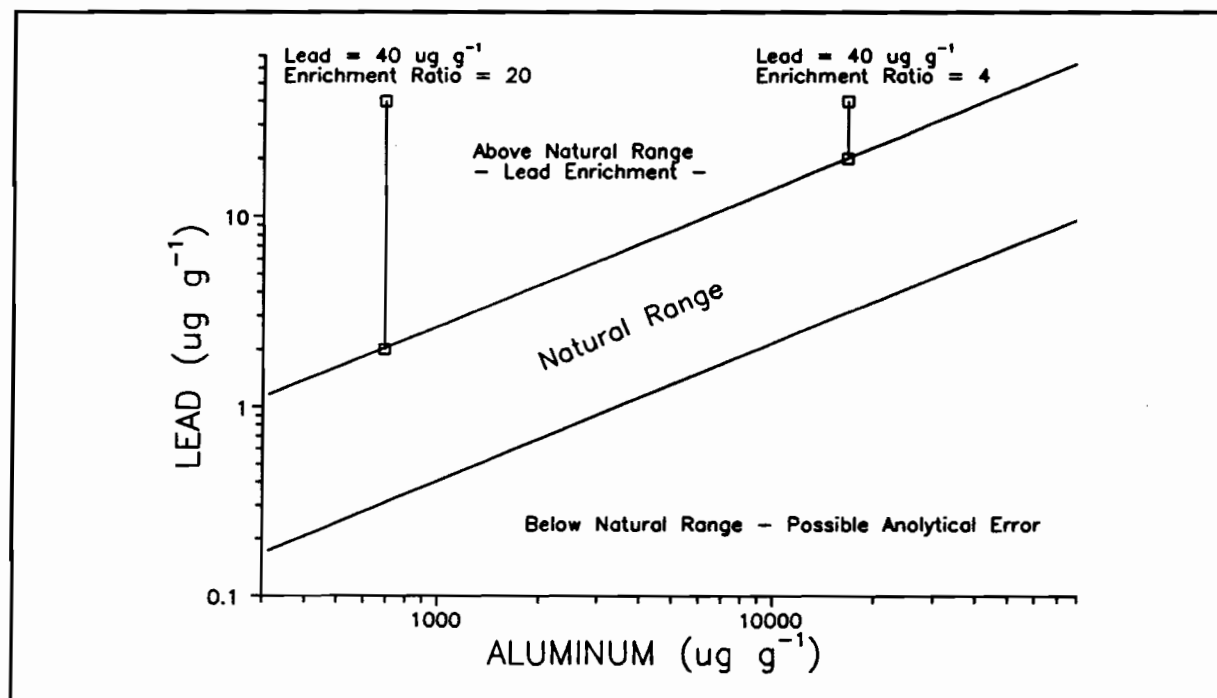


Figure 2. Interpretation of Lead data using lead/aluminum relationship.

Mercury does not significantly covary with aluminum concentrations in the "clean" data set. To graphically express mercury data in the *Atlas*, the maximum concentration of mercury observed in the clean data set ($0.21 \mu\text{g}\cdot\text{g}^{-1}$ (21 ppb)) was selected to represent the background value for natural mercury concentrations. The mercury enrichment factor used in the *Atlas* was calculated by dividing the mercury concentration at a site by the value $0.21 \mu\text{g}\cdot\text{g}^{-1}$ (21 ppb).

2.4 Interpretation of Sediment Toxic Organic Contaminant Data

Toxic organic contaminants in a sediment sample are typically reported in the $\text{ng}\cdot\text{g}^{-1}$ (ppb) range on a dry weight basis. As discussed in the *Atlas*, normalization of organic contaminants to total organic carbon is used to account for the influence of organic carbon on bioavailability, and therefore the potential for toxicity.

For plotting purposes in the *Atlas*, the concentrations of all compounds in a class of organic contaminants were summed. Then the total sum of each class was normalized to the total organic carbon (TOC) concentration of the sample. This calculation is outlined in the following equation.

$$\text{Organic Compound Class}_{(\text{normalized})} = \frac{\sum \text{Organic Compound } (\text{ng}\cdot\text{g}^{-1}) (1 \mu\text{g}\cdot 1000 \text{ ng}^{-1})}{\text{Total Organic Carbon } (\mu\text{g}\cdot\text{g}^{-1})} \cdot 10^6 \quad (2)$$

The concentration of the organic compound is converted into micrograms per gram (ppm), and multiplied by 10^6 to convert the number to a positive exponent for plotting purposes. The normalized organic concentration is indicated using barcharts that have a logarithmic scale.

SECTION 3. SEDIMENT AND WATER COLUMN MEASUREMENTS IN THE FDEP DATABASE.

3.0 Introduction

Two laboratories have been responsible for all analytical results contained in the FDEP sediment quality database, as mentioned in section 2. Variables and limits of detection are contained in Table 1.

3.1 Metals and Nutrients

The limit of detection of each variable is provided in units of $\text{mg}\cdot\text{kg}^{-1}$ (ppm) on a dryweight basis. The expression "NA" indicates the sample was not analyzed for this variable.

Table 1. Limits of detection for metals and nutrients analyzed by different laboratories.

	<u>Savannah Laboratories and Environmental Services, Inc.</u>	<u>Skidaway Institute of Oceanography.</u>
Aluminum	10.0	10.0
Arsenic	1.0	0.8
Barium	10.0	0.02
Cadmium	0.05	0.02
Chromium	1.0	0.99
Copper	1.0	0.13
Iron	1.0	10.0
Lead	1.0	0.04
Lithium	NA	0.58
Manganese	NA	1.0
Mercury	1.0	0.007
Nickel	1.0	0.25
Silver	0.05	0.001
Titanium	NA	5.0
Vanadium	NA	0.005
Zinc	1.0	0.38
Total Carbonate	100	10.0
Total Organic Carbon	100	10.0
Total Kjeldahl Nitrogen	1.0	10.0
Total Phosphorus	1.0	5.1

3.2 Organic Compounds

The following paragraphs list major groups of organic compounds referenced in the *Atlas*, and detection limits. The following compounds were not necessarily analyzed for every sample. Individual organic substances included in the following classes of contaminants are found in Table 2.

3.2.1 Chlorinated Pesticides

Chlorinated pesticides were measured as separate compounds at Savannah Laboratories. In the *Atlas*, all pesticides were grouped into one category for plotting purposes. Detection limits for chlorinated pesticides ranged from 0.001 to 0.1 mg·kg⁻¹.

3.2.2 Polynuclear Aromatic Hydrocarbons (PAHs)

PAHs are complex organic compounds that form during incomplete burning of coal, oil and gas, garbage, or other organic substances. PAHs can occur naturally, but the majority are produced by anthropogenic activity. PAH detection limits were 0.1 mg·kg⁻¹.

3.2.3 Polychlorinated Biphenyl Compounds

The compounds known as PCBs were measured as the total concentration of all PCB congeners (compounds) by Savannah Laboratory. In the *Atlas*, all PCBs are grouped into one class for plotting purposes. PCB detection limits were 0.1 mg·kg⁻¹.

3.2.4 Phenolic Compounds

These compounds are also grouped into one class in the *Atlas*. The detection limits for phenolic compounds range from 0.2 to 0.5 mg·kg⁻¹.

3.2.5 Aliphatic Petroleum Hydrocarbons

Aliphatic petroleum hydrocarbons (APH) are long-chain organic molecules that enter the environment during petroleum releases (both crude oil and refined product). In the FDEP database, these compounds are listed individually from Aliphatic C-10 through C-30. These compounds are grouped into one class in the *Atlas*. The APH limit of detection was 0.5 mg·kg⁻¹.

Table 2. Organic Compounds in major categories.

<u>Chlorinated Pesticides</u>	<u>Polynuclear Aromatic Hydrocarbons</u>	<u>Phenolic Compounds</u>
Aldrin	Acenaphthene	2-Chlorophenol
Mirex	Acenaphthylene	2,4-Dichlorophenol
pp-DDT	Anthracene	2,4-Dimethyl phenol
4,4'-DDD	Crysene	4,6-Dinitro-o-cresol
4,4'-DDE	+Benzo(a)anthracene	2-Nitrophenol
4,4'-DDT	Benzo(a)pyrene	4-Nitrophenol
Endrin	Benzo(ghi)perylene	P-Chloro-m-cresol
Chlordane	Benzo(bk)fluoranthene	Penta-Chlorophenol
Alpha-BHC(Toxaphene)	Fluorene	Phenol
Beta-BHC	Indeno(1,2,3-cd)pyrene	2,4,6 Trichlorophenol
Delta-BHC	Naphthalene	4-chloro-m-cresol
Gamma-BHC(Lindane)	Phenanthrene+Anthracene	2,4 Dinitrophenol
Dieldrin	Benzo(a)anthracene	
Endosulfan I	Benzo(b)fluoranthene	
Endosulfan II	Dibenzo(a,h)anthracene	
Endosulfan sulfate	Phenanthrene	
Endrin Aldehyde	1-methylnaphthalene	
Heptachlor	Benzonitrile	
Heptachlor epoxide	Quinoline	
Kepone	Quinaldine	
Methoxychlor	8-methylquinoline	
	7,8-Benzoquinoline	
	2,4-Dimethylquinoline	
	Acridine	
	Indeno(1,2,3)pyrene	
<u>Polychlorinated Biphenyls</u>		
Aroclor-1016		
Aroclor-1221		
Aroclor-1232		
Aroclor-1242		
Aroclor-1248		
Aroclor-1254		
Aroclor-1260		
Measured as a sum of all PCB congeners		

SECTION 4. SOURCES AND USES OF METALS AND SEMI-METALS EXAMINED IN THE ATLAS.

4.0 Introduction

Trace metals are found naturally in the environment due to weathering of minerals that contain these elements. Many trace metals in extremely low quantities are beneficial to the biological function of organisms, but some have no recognizable biological functions. All trace metals cause deleterious biological effects when present in high concentrations. Common anthropogenic trace metal sources are listed. All listed metals are released in some degree by fossil fuel combustion and waste incineration.

Metal	Sources and Uses
Arsenic (As)	The semi-metal As is the active element in some pesticides and herbicides. Arsenic is released by combustion of fossil fuels (e.g., coal). The use of As as a rodenticide is no longer practiced, but As is used as a herbicide.
Cadmium (Cd)	Natural sources of Cd include weathering of phosphate-bearing sedimentary rocks, which are common in parts of Florida. Cd sources include electroplating industries, pigment production, and manufacture of plastic stabilizers and lead-zinc batteries.
Chromium (Cr)	Cr is used in the production of chrome metal plating, dyes, paint, explosives, ceramics, and glass.
Copper (Cu)	Sources of Cu include leaching of brass and copper pipe by acidic water, aquatic weed and algae control, and marine paint, where Cu is leached into the water column. Cu is also used as a fungicide and pesticide in agriculture.
Lead (Pb)	The largest anthropogenic source of Pb is the production of lead-zinc batteries. Other sources include manufacture of alkyl-lead additives, solder, paints, glassware, ammunition, radiation shielding, and fossil fuel combustion. Much of the present Pb burden in sediment is from past combustion of leaded gasoline.

Mercury (Hg)	The major sources of mercury in Florida include: soil degassing, municipal solid waste combustion, medical waste incineration, paint application and the electric utility industry. Other sources of Hg include dental preparations, anti-mildew agents in paint and sheetrock mud, manufacture of electrical equipment, open burning, transportation (fuel) and other fuel burning (FDER 1992). Significant quantities of Hg may be bound to organic particles in sediment and soils. Upon exposure of these materials to air (e.g. by agricultural conversion of wetlands), Hg can become bioavailable.
Nickel (Ni)	Ni is used primarily in the production of stainless steel. Ni is used as a catalyst in industrial processes, and in oil refining. Sources include electroplating industries.
Zinc (Zn)	Zn is used in the production of brass, batteries, galvanized coatings to protect iron and steel, and marine paints. Submerged "sacrificial" Zn plates are used on ships to reduce oxidation (rusting) of metallic parts exposed to saltwater, leading to high Zn levels in some marina sediments.

SECTION 5. SOURCES AND USES OF TOXIC ORGANIC COMPOUND CLASSES EXAMINED IN THE ATLAS

5.0 Introduction

Natural and anthropogenic sources of major organic compound classes are listed. Except for a few aliphatic hydrocarbons and polynuclear aromatic hydrocarbons, these compounds are manmade.

Organic Compound Class	Sources and Uses
Chlorinated Pesticides	Chlorinated pesticides are complex organic compounds to which chlorine has been added. They are used to (partially) control insects. Some common pesticides include dieldrin, chlordane, lindane, and mirex. DDT and its breakdown products (DDD and DDE) have been detected as recently as 1991 in Florida sediments, although use of DDT has been halted in the U.S. However, U.S. chemical companies still manufacture DDT for use in other countries.
Polynuclear Aromatic Hydrocarbons	PAHs are complex organic compounds that form during incomplete burning of coal, oil and gas, garbage, or other organic substances. The term PAHs is applied to compounds that have two or more benzene rings. PAHs can occur naturally, but the majority are produced by anthropogenic activity. Oil and fuel spills are a source of PAHs in estuarine systems. Some PAHs are used in production of pharmaceutical products, dyes, pesticides, and plastics.
Polychlorinated Biphenyls	The term PCBs is applied to organic molecules that contain chlorine substituted into a biphenyl ring. PCBs were used in closed electric systems (transformers), and in other applications, all of which were discontinued in 1971. Introduction into the environment still occurs, for example from waste incineration. These molecules are extremely persistent stable compounds in the environment.
Phenolic Hydrocarbons	Organic solvents used in the manufacture of resins, paint, and plastics. Some are used as a disinfectant. Some phenolic compounds occur naturally in wood, petroleum, and tar, and are constituents of human and animal wastes.

Aliphatic Petroleum Hydrocarbons	Organic molecules formed by chains (polymers) of carbon atoms released in aquatic environments by petroleum spills during loading/offloading, transport and production activities. Most petroleum hydrocarbons are released into the environment during transport activity, and not by offshore petroleum or natural gas exploration and/or production.
----------------------------------	---

Florida Coastal Sediment Contaminants Atlas Technical Volume References

- Bishof, D.E., 1991. Limnological monitoring and investigations program: Sediment quality monitoring semiannual report. Collier County Pollution Control Department.
- Brim, M., 1993. Toxics characterization report for Perdido Bay, Alabama and Florida. United States Fish and Wildlife Service, publication no. PCFO-EC-93-04. Panama City, FL.
- Brim, M., (in preparation). Sediment chemistry of St. Andrew Bay, United States Fish and Wildlife Service. Panama City, FL.
- Brooks, G.R. and Doyle, L.J., 1989. Recent geological history of mud-dominated sediments in Hillsborough Bay, Florida: Final report to City of Tampa.
- Brooks, G.R. and Doyle, L.J., 1992. A characterization of Tampa Bay sediments, phase III: distribution of sediments and sedimentary contaminants. Report submitted to the Southwest Florida Water Management District by the Center for Nearshore Marine Science of the University of South Florida.
- Broward County Department of Resource Protection, 1993. New River Study: Final Report.
- Delfino, J.J., Coates, J.A., Davis, W.M., Garcia, K.L., Jacobs, M.W., Marincic, K.J., and Signorella, L.L., 1991. Toxic pollutants in discharges, ambient waters, and bottom sediments. Report to the Department of Environmental Regulation, 405 pp.
- Dixon, L.K., 1988. Non-point water quality impacts in northern west coast Inland Navigation District waters. Final report submitted to Manatee County Public Works Department. Technical Report No. 126, Mote Marine Laboratory, Sarasota, Florida.
- Doyle, L.J., Brooks, G.R., Fanning, K.A., Van Vleet, E.S., Byrne, R.H., and Blake, N.J., 1989. A characterization of Tampa Bay sediments. A report submitted to the Southwest Florida Water Management District by the Center for Nearshore Marine Science of the University of South Florida.
- Facemire, C.F., 1991. Copper and other contaminants in King's Bay and Crystal River (Florida) Sediments: Implications for impact on the West Indian manatee. Report to the U.S. Fish and Wildlife Service.
- Florida Department of Environmental Regulation, 1984. Deepwater ports maintenance dredging and disposal manual: a guide to planning, estuarine chemical data collection, analysis, and interpretation. Fourth Revision. Florida Department of Environmental Regulation. 94 pp. and 1 appendix.
- Florida Department of Environmental Regulation, 1992. Mercury emissions to the atmosphere in Florida. Report prepared by KBN Engineering and Applied Sciences, Gainesville, FL.

Goldberg, E.D., Griffin, J.J., Hodge, V., Kolde, M., and Windom, H., 1979. Pollution history of the Savannah River estuary, *Environmental Science and Technology*, v. 13, p. 588-594.

Grabe, S., 1991a, Sediment quality in estuarine waters of Collier County: April and August 1991. Collier County Pollution Control Department.

Grabe, S., 1991b. Inland sediment quality annual report, 1991. Collier County Pollution Control Department.

Gu, D., Irlcanin, N., and Trefry, J.H., 1987. The geochemistry of interstitial water for a sediment core from the Indian River Lagoon, Florida. *Florida Scientist*, v. 50, 99-110.

Hanson, P.J. and Evans, D.W., 1991. Metal contaminant assessment for the Southeast Atlantic and Gulf of Mexico Coasts: Results of the National Benthic Surveillance Project over the first four years 1984-1987. National Oceanic and Atmospheric Administration (NOAA) Technical Memorandum NMFS-SEFSC-284, 77 pp.

Haunert, D.E., 1988. Sediment characteristics and toxic substances in the St. Lucie Estuary, Florida. Technical Publication 88-10, South Florida Water Management District.

Hofmann, S. and Dixon, L.K., 1989. Metals characterization of sediments at Port Manatee. Final report submitted to Manatee Port Authority. Technical Report No. 135, Mote Marine Laboratory, Sarasota, Florida.

Long, E.R. and Morgan, L.G., 1990. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. National Oceanic and Atmospheric Administration (NOAA) Technical Memorandum NOS OMA 52, 223 pp.

Long, E.R., MacDonald, D. and Cairncross, C., 1991. Status and trends in toxicants and the potential for their biological effects in Tampa Bay, Florida. National Oceanic and Atmospheric Administration (NOAA) Technical Memorandum NOS OMA 58, 77 pp.

Long, E.R. et al., in preparation. Magnitude and extent of sediment toxicity in Tampa Bay, Florida. National Status and Trends Program, Bioeffects Assessment Program.

Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES (International Council for the Exploration of the Sea) Journal of Marine Science*, v. 48, 101-115.

Loring, D.H. and Rantala, R.T.T., 1988. An intercalibration exercise for trace metals in marine sediments. *Marine Chemistry*, v. 24, 13-28.

Lowrey, S., Dixon, L.K., and Sherbloom, P., in press. Water quality trends and baywide monitoring results for Sarasota Bay. Final report submitted to Sarasota Bay National Estuary Program. Technical Report No. 253, Mote Marine Laboratory, Sarasota, Florida.

Pierce, R.H., Dixon, L.K., Brown, L.C., and Rodrick, G., 1988. Characterization of baseline conditions of the physical, chemical, and microbiological environments in the St. Johns River Estuary. Final report submitted to the Florida Department of Environmental Regulation, Technical Report No. 128, Mote Marine Laboratory, Sarasota, Florida.

Pfeuffer, R.J., 1985. Pesticide residue monitoring in sediment and surface water within the South Florida Water Management District, volume 1. Technical Publication 91-01. South Florida Water Management District.

Pfeuffer, R.J., 1991. Pesticide residue monitoring in sediment and surface water within the South Florida Water Management District, volume 2. Technical Publication 91-01. South Florida Water Management District.

Seal, T.L., Calder, F.D., Sloane, G.M., Schropp, S.J., and Windom, H.L., 1992. Assessment of trace metal contamination of estuarine and marine sediments from Florida. Geological Society of America Abstracts with Programs, Volume 25, p.68.

Schropp, S.J., 1992. An laboratory intercomparison exercise for sediment metal analyses. Florida Department of Environmental Regulation Open-file Report.

Schropp, S.J. and Windom, H.L., 1988. A guide to the interpretation of metal concentration in estuarine sediments. Coastal Zone Management Section, Florida Department of Environmental Regulation, 44 pp.

Schropp, S. J., Calder, F.D., Sloane, G.M. and Windom, H.L., 1990. Interpretation of metal concentration in estuarine sediments of Florida using aluminum as a reference element. *Estuaries*, v. 13, 227-235.

Schropp, S.J., Calder, F.D., Sloane, G.M., Swanson, K.O., Carlton, J.C., Halcomb, G.L., Windom, H.L., Huan, F., Taylor, R.B., and Hull, T., 1991. A report on physical and chemical processes affecting the management of Perdido Bay: Results of the Perdido Bay Interstate Project. Florida Department of Environmental Regulation, Tallahassee, FL.

Stone, G.W. and Morgan, J.P., 1991. Heavy metal concentrations in subsurface sediments, Bayou Chico, Pensacola, Florida. Report prepared for the Florida Department of Environmental Regulation by the Institute for Coastal and Estuarine Research, The University of West Florida, Pensacola.

Trefry, J.H., Metz, S., and Trocine, R.P., 1985. The decline in lead transport by the Mississippi River. *Science*, v. 230, 439-441.

Trefry, J.H. and Presley, B.J., 1976. Heavy metals in sediments from the San Antonio Bay and the northwest Gulf of Mexico. *Environmental Geology*, v. 1, p. 283-294.

Trefry, J.H. and Stauble, D.K., 1987. Origin, composition and fate of organic-rich sediments in coastal estuaries. Report to The Florida Sea Grant College and the Florida Department of Environmental Regulation.

Trefry, J.H., Trocine, R.P. and Metz, S., 1989. Quantifying sedimentation and pollution in the Lower Hillsborough River. Report to the City of Tampa.

Trefry, J.H., Sathoughi, M., Sullivan, M.D., Steward, J.S., and Barber, S., 1983. Trace metals in the Indian River Lagoon, Florida: The copper story. *Florida Scientist*, v. 46, 415-428.

Trefry, J.H., Chen, N., Trocine, R. and Metz, S., 1990. Manatee Pocket sediment analysis. Report to the South Florida Water Management District. 43 pp. and two appendices.

Trefry, J.H., Chen, N., Trocine, R. and Metz, S., 1992. Impingement of organic-rich, contaminated sediments on Manatee Pocket, Florida. *Florida Scientist*, v. 55.

Windom, H.L., Schropp, S.J., Calder, F.D., Ryan, J.D., Smith, R.G., Jr., Burney, L.C., Lewis, F.G., and Rawlinson, C.H., 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. *Environmental Science and Technology*, v. 23, 314-320.

Windom, H.L. and Smith, R.G., 1992. Analysis of mercury species in groundwater using inductively coupled plasma-mass spectrometry and gas chromatography. Report submitted to the State of New Jersey, Department of Environmental Protection and Energy.

Zdanowicz, V.S., 1991. Determining the fates of contaminated wastes dumped in the New York Apex by use of metal enrichment factors. *Environmental Science and Technology*, v. 25, 1760-1766.