

## **EVALUATION OF SHELF, HARBOR AND DISPOSED DREDGED SEDIMENTS AS POTENTIAL SOURCES OF DEPOSITED MUDS ON SOUTH FLORIDA REEFS**

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**Abstract:** In 1995, three quarters of a million cubic yards of material was dredged from Fort Pierce Harbor (Florida) and disposed in the Fort Pierce, Florida Ocean Dredged Material Disposal Site (ODMDS). By 1996, reports of thick mud deposits (muck) discovered on shelf hard-bottom resources raised concerns of potential adverse impacts of offshore dredged material disposal. Sediment samples were collected from hard-bottom muck deposits, the Fort Pierce ODMDS, harbor, and shelf off of St. Lucie County, Florida. Fifteen trace elements and three naturally occurring radioelements were analyzed in the silt and clay (fine) particle size fraction. Numerical classification (clustering) analysis and multidimensional scaling (ordination) of the trace element and radiometric data failed to show any strong degree of similarity between hard-bottom muck and fine sediments collected from the ODMDS or harbor locations. Hard-bottom muck tended to form unique clusters and groupings in ordination space. These data show that hard-bottom muck was unique in elemental composition and their dissimilarity to sediments taken from the dredged material disposal site and the harbor locations suggest that the muck was comprised mainly of non-dredged sediments of indeterminate origin.

### **INTRODUCTION**

The U.S. Environmental Protection Agency (EPA) Region 4 manages an active ocean dredged material disposal site (ODMDS) off of Fort Pierce, Florida (St. Lucie County). From mid-June to mid-September, 1995 an estimated 724,000 cubic yards of sediments, mainly silt and clay, were disposed in the Fort Pierce ODMDS from the Fort Pierce Harbor deepening project. This project was a substantial increase in the amount of dredged material disposed at the site.

During the summer of 1996 scientific and recreational divers reported thick deposits of fine sediments (muck) widely distributed on hard-bottom habitats near the ODMDS, which were not observed prior to the dredging project. It was suggested that a possible source of the hard-bottom sediment deposits was dredged sediments disposed at the Ft. Pierce ODMDS. Due to concerns that mud deposits on reef habitats may have originated from the Fort Pierce ODMDS, EPA Region 4, conducted an exploratory investigation of the marine sediments in the Ft. Pierce area to attempt to characterize hard-bottom muck deposits and potential sources.

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The principle objective of this investigation was to conduct a rapid screening to determine whether the chemical composition of hard-bottom sediment deposits was similar to disposed dredged sediments. A secondary objective was to provide evidence for other potential sources of hard-bottom muck deposits. To accomplish these objectives a study plan was developed that called for the collection of samples of benthic sediments from hard-bottom locations, the Fort Pierce harbor, the ODMDS and other shelf locations to provide characteristic trace element and radioactive element abundances to determine potential sources of hard-bottom muck deposits.

The selected approach compared each sediment type using elemental characteristics determined by a combination of X-ray fluorescence spectrometry (XRF) for trace elements and gamma radiation detection for naturally occurring radioelements. These techniques have been used by EPA Region 4 in the detection of disposed dredged sediments on the seafloor (CAIS, 1997, Ferry, 2002). X-ray fluorescence measures the emission of characteristic X-rays that occur when atoms are excited by an external source of radiation (Stallard et.al., 1995). X-ray fluorescence provides a rapid, simultaneous analysis of a wide range of elements. Several studies have been done using XRF techniques to analyze marine sediments (Skei et.al., 1972; Vanderstappen and Van Grieken, 1976; Dooley and Stallard, 1994; Stallard et al., 1995). The rapid, non-destructive analysis of a wide variety of elements measured over a wide range of concentrations make this technique useful for screening marine sediments.

Measurements of naturally occurring gamma radiation are commonly used in offshore mineral exploration (Noakes, *et al.*, 1974; Grosz, 1992; de Meijer et al., 2000). Emery and Uchupi (1972) found that specific heavy mineral deposits on the seafloor are significantly higher in uranium and thorium content, and in the content of their decay daughter radioisotopes, than in the surrounding natural seafloor sediments. The most common radioelements found in marine mineral deposits are potassium-40, thorium-232 and uranium-238 found in clayey sediments, placer minerals, and phosphorite minerals respectively (Emery and Uchupi, 1972; Grosz, 1992; Kunzendorf, 1992). Sediments of recent terrestrial origin (i.e., dredged sediments) tend to contain higher radioelement concentrations than native seafloor sediments resulting in unique radiometric fingerprints (de Meijer, 2000).

## **METHODS AND MATERIALS**

### **Study Area**

The Fort Pierce ODMDS lies approximately 4 miles southeast of the Fort Pierce Inlet (Figure 1). The shelf off of St. Lucie County, Florida has extensive areas of low and high relief reefs or hard-bottoms communities with characteristic assemblages of commercially important fishes and invertebrates. The hard-bottom habitats are arranged in three terraces that run approximately parallel to shore at depths of 10 - 25 feet, 55 -90 feet, and 240 - 300 feet. The dominant components of the hard-bottom communities are stony corals, gorgonians and sponges (Avent et al., 1977; Reed, 1980; Jaap, 1984).

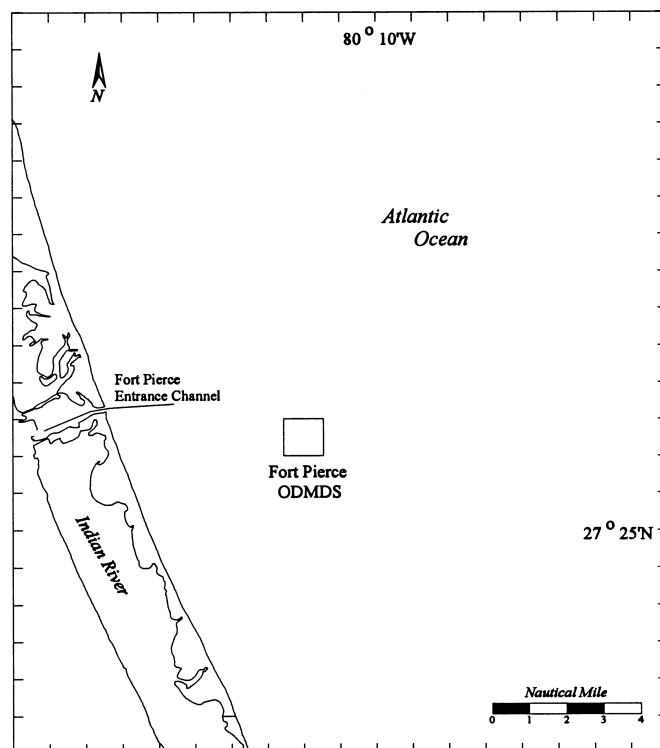


Figure 1. Fort Pierce ODMDS.

### Sample Collection

Sediment samples were collected at locations within the ODMDS, two reference areas approximately 11 km south (6 nmi) of the ODMDS, several deep (150 ft.) shelf stations approximately 13 km (7 nmi) to the northeast of the ODMDS (Figure 1), and a number of hard-bottom locations to the north, east and west of the disposal site. Sediments were also collected from the deepening project area within the Ft. Pierce harbor.

Sediment samples for trace elements and radioelement analysis were collected by divers at hard-bottom and harbor locations by scooping the upper 8 to 10 centimeters into a 1-liter nalgene jar. Nine samples were collected to represent hard-bottom muck. Four samples were taken from the harbor area. Sediment samples were collected at the deep shelf, reference areas and the ODMDS stations with a 1.0 m<sup>3</sup> Young (modified Van Veen) grab. One sample was taken from each successful grab for a total of four samples for both the ODMDS and deep shelf locations and two samples for the reference. Samples were stored at 4°C. Analyses were conducted by the Center for Applied Isotope Studies (CAIS), University of Georgia.

### Sample Analysis

All samples were standardized by sieving to a particle size less than 0.02 mm to retain only the silt and clay fractions for analysis. Six grams of sediment taken from each trace element sample

was dried and mixed with a cellulose binder and pressed into a pellet. Sediment element content was analyzed using XRF. Table 1 shows the 15 trace elements used in the characterization.

The radioelement sample was placed in a 0.5 -L Marinelli beaker, weighed and stored for 14 days to allow for the growth of gamma emitting U and Th daughter products. Gamma activity of sediment radioelements was analyzed by placing the sample in a lithium drifted germanium HPGe gamma radiation detector and pulse height analyzer for a counting time of 12,000 seconds. The results are converted to picocuries per kilogram (pCi/kg). Radioelements used in this analysis are listed in Table 1.

**Table 1. Trace elements and radioelements used in the analysis of Fort Pierce sediments.**

Analytes	Reporting Units
Magnesium (Mg), Aluminum (Al), Silicon (Si), Tin (Ti), Sulfur (S), Iron (Fe), Calcium (Ca)	Weight Percent
Chromium (Cr), Manganese (Mn), Nickel (Ni), Copper (Cu), Zinc (Zn), Strontium (Sr), Zirconium (Zr), Barium (Ba)	Parts per million (ppm)
Uranium-238 ( $^{238}\text{U}$ ), Thorium-232 ( $^{232}\text{Th}$ ), Potassium-40 ( $^{40}\text{K}$ )	Picocuries per kilogram

### Data Analysis

Sediment trace element content and radioelement data were analyzed by numerical classification (clustering) analysis and ordination analysis using non-metric multidimensional scaling (n-MDS). A logarithmic transformation of the type  $\log(x+1)$  was applied to the data in order to reduce the weighting of high radioelement count data. A triangular resemblance matrix was created from the transformed data using the normalized-Euclidean distance coefficient prior to classification and ordination (Orloci, 1973; Boesch, 1977).

Classification analysis arranges individuals (sample sites) into discrete groups (clusters) based on a resemblance function of the attribute data (Williams, 1971; Goodall, 1973; Van Tongeren, 1987). The classification method used was an agglomerative, hierarchical classification of stations as individuals using normalized Euclidean distance as the resemblance coefficient on the original data (Orloci, 1966; 1973). The results are expressed graphically as a dendrogram that displays the progressive fusion from individual sample sites to the complete population.

The purpose of ordination is to reduce the dimensionality of complex multivariate data sets to a configuration in two or three dimensions in which the placement of sample sites reflects the similarity of their composition (Goodall, 1954; Jongman, 1987). The result is a graphical representation or “map” where sites placed closer together are more similar in composition and those farther apart are less similar. The non-metric MDS method used here works on the Euclidean distance resemblance matrix used for the classification analysis and provides a

measure (stress function) of how well the site distances in the ordination map correspond to the distances or dissimilarity values in the resemblance matrix (Shepard, 1962; Kruskal, 1964).

Similarities between groups of samples based on clusters (determined by classification analysis) were tested with a non-parametric permutation procedure on the rank similarities between samples, and therefore can be termed an analysis of similarities (Primer, 2001; ANOSIM procedure). The analysis of similarities procedure works on the Euclidean distance matrix used for classification and ordination analysis and is combined with a Monte Carlo procedure for the generation of significance levels (Mantel, 1967, Hope, 1968; Sokal and Rohlf, 1981). The analysis of similarities procedure tests the null hypothesis that there is no difference in elemental composition between observed groups of samples.

The trace elements and radioelements primarily responsible for the observed differences between groups of samples was done by determining the overall percentage contribution each element makes to the average dissimilarity between each pair of groups.

## RESULTS

Figure 2 shows the dendrogram resulting from the classification of the trace element and radioelement data from Ft. Pierce sediments. Four main site groupings are distinguished at a distance of about 6.1. The first main grouping (G1) places the western (shoreward) reference sample site in its own cluster at a distance from all other samples of about 8.5. Group 2 is comprised of all nine hard-bottom muck samples that split from remaining samples at a distance of about 6.5. Group 3 clusters one replicate harbor sample with an ODMDS sample and is separated from Group 4 at a distance of about 6.0. Group 4 contains all remaining samples.

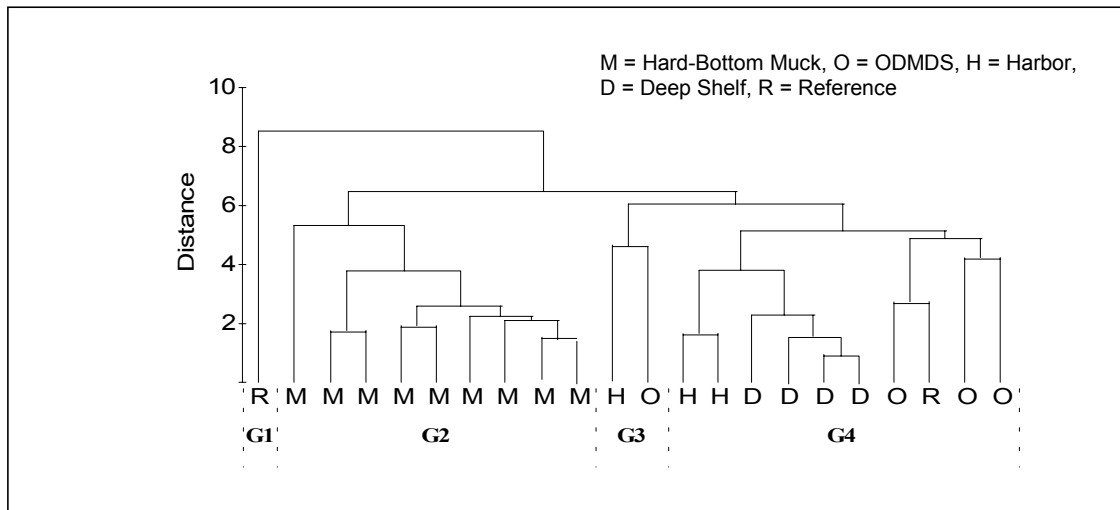


Figure 2. Cluster Dendrogram of Fort Pierce samples by trace element and radioelement composition.

The MDS ordination of the trace element and radioelement data is shown in Figure 3. The relatively low value of the stress function (0.12) indicates that the distances between samples in the ordination diagram have good correspondence to the calculated distance values. Figure 4

shows groups or clusters formed by the classification analysis superimposed on the MDS ordination plot. The major groupings formed by classification analysis, as well as some minor groupings (i.e., deep shelf samples) are well represented by the MDS ordination. It can be seen from the ordination that the hard-bottom muck samples show a high degree of dissimilarity from the other sample groupings.

The analysis of similarities between sample groups based on clusters (Figure 3) show that significant differences exist between groups (Global  $R = 0.918$ ,  $p = 0.001$ ). Paired comparisons showed that the G2 group (hard-bottom muck samples) was significantly different from the G1 reference sample ( $R = 1.0$ ,  $p = .001$ ), G3 harbor and ODMDS cluster ( $R = 0.952$ ,  $p = 0.018$ ), and G4 cluster ( $R = 0.932$ ,  $p = 0.001$ ).

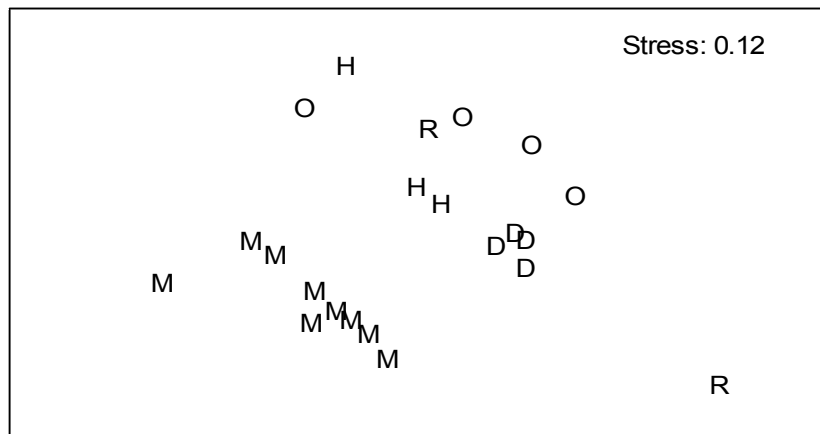


Figure 3. MDS ordination of Fort Pierce trace element and radioelement data.

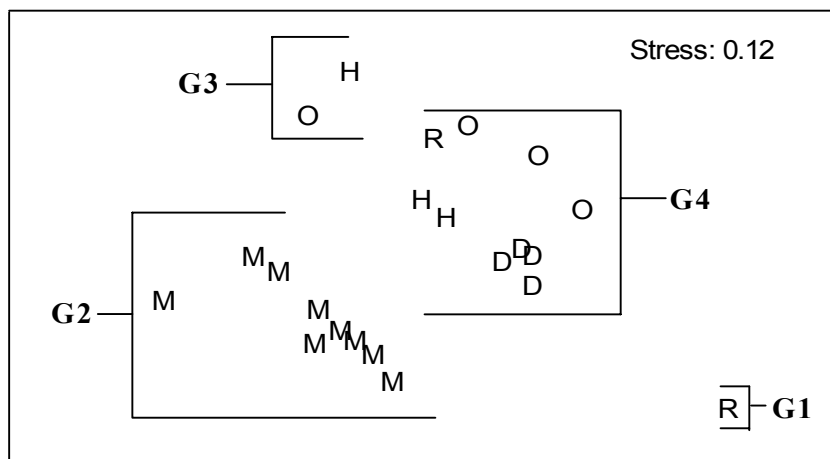


Figure 4. MDS ordination of Fort Pierce trace element and radioelement data with cluster groups separated at a distance of 6.1.

Tables 2-4 show the paired comparisons of elemental contributions to dissimilarities between hard-bottom muck samples and other sample groups formed by cluster analysis. Dissimilarity contributions between sample clusters required an average of 7 of the 18 elements (39%) used in the analysis to reach a 70% cumulative contribution and 12 of the 18 elements (67%) used were needed to reach a 90% cumulative contribution. The main contributors to differences between G2 hard-bottom muck samples and other cluster groups were tin, copper, chromium and manganese, which together accounted for an average of 61.9% of the observed dissimilarity in each case. Two radioelements, thorium-232 and potassium-40 played a role in the dissimilarity between the G2 and G1 reference sample cluster accounting for 16.1% of the observed dissimilarity (Table 2).

**Table 2. Trace elements and radioelements providing a 70% cumulative contribution to dissimilarity between hard-bottom muck cluster (G2) and sample cluster G1.**

Element	Average Abundance in Muck Cluster (G2)	Average Abundance in G1	Contribution %	Cumulative Contribution%
Cu	6.73	1.10	25.43	25.43
Ti	3.82	0.13	16.62	42.06
Cr	0.97	3.37	10.81	52.87
<sup>232</sup> Th	5.79	3.81	8.93	61.81
<sup>40</sup> K	8.22	6.62	7.21	69.01
Mn	2.55	4.13	7.13	76.14

**Table 3. Trace elements and radioelements providing a 70% cumulative contribution to dissimilarity between hard-bottom muck cluster G2 and sample cluster G3.**

Element	Average Abundance in Muck Cluster (G2)	Average Abundance in G3	Contribution %	Cumulative Contribution%
Ti	3.82	0.34	18.35	18.35
Cr	0.97	4.03	16.15	34.50
Mn	2.55	5.34	14.71	49.21
Cu	6.73	3.97	14.57	63.78
Zr	5.36	6.99	8.63	72.41

**Table 4. Trace elements and radioelements providing a 70% cumulative contribution to dissimilarity between hard-bottom muck cluster G2 and sample cluster G4.**

Element	Average Abundance in Muck Cluster (G2)	Average Abundance in G4	Contribution %	Cumulative Contribution%
Cu	6.73	3.26	17.38	17.38
Mn	2.55	5.72	15.90	33.28
Ti	3.82	0.66	15.79	49.08
Zr	5.36	8.07	13.53	62.61
Cr	0.97	3.56	12.95	75.55

## **DISCUSSION**

The results of the exploratory analyses (classification and ordination) and hypothesis testing of sediments collected from various locations around the Fort Pierce ODMDS provide strong evidence that hard-bottom muck does not resemble sediments occurring on the ODMDS in terms of its trace element and radioelement composition. Hard-bottom muck sediments also appear to be dissimilar from the Fort Pierce harbor areas from where dredged sediments disposed on the ODMDS were taken. Statistical comparisons confirm this by showing significant differences between the hard-bottom muck sample cluster and the sample clusters containing ODMDS and harbor samples (G3 and G4). Based on this evidence it appears unlikely that disposed dredged sediments contributed significantly to the muck deposits observed on hard-bottom habitats around the Fort Pierce ODMDS. Hard-bottom muck sediments also differed significantly from other surrounding seafloor sediments. These results fail to suggest a good potential candidate as a source for reef muck sediments among the various sediment types sampled.

The observed dispersion among sample types (Figure 4), particularly the reference, ODMDS and harbor samples, indicate a high degree of variability with regard to elemental abundances. The elemental differences between widely dispersed samples of the same type cannot be explained beyond natural spatial variability in sediment composition due to mixing of sediments from various sources. Additional replication of these sample types over a wider geographic area would better integrate site conditions and provide improved representation of each sediment type. It is not expected, however, that additional replication would significantly reduce the observed distances between hard-bottom muck samples and other sample types.

The intention of the study was to determine the likelihood that disposed dredged sediments contributed to the observed muck on surrounding hard-bottom habitats. The goal of the study was not to fully characterize the muck physically or chemically or provide an exhaustive determination of the contributors to the hard-bottom muck. To accomplish these goals a much broader suite of physical, chemical and biological factors would be required. In addition, consideration of other possible sediment sources and more in depth sampling of all potential sediment sources would be needed.

## **CONCLUSION**

The results of this study show that the use of X-ray fluorescence spectrometry (XRF) for trace elements and gamma radiation detection for naturally occurring radioelements provide a low cost and reliable method for characterizing marine sediments of various origins. The use of both exploratory (classification and ordination) and non-parametric statistical analyses reduces the complexity of multivariate chemical data sets in an accurate and reliable way that allow straightforward interpretation of results, without the loss of information.

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