HEAVY METAL ACCUMULATION IN MID-BISCAYNE BAY, DADE COUNTY, FLORIDA

Final Report

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[NOTE: PAGE ONE OF THE DOCUMENT IS MISSING. AUTHORS ARE NO LONGER AT FLORIDA INTERNATIONAL UNIVERSITY.]

give the bay an important role in the social, cultural and economic life of Dade County. The continued pollution of the bay, particularly that area north of the Rickenbacker Causeway, has threatened to destroy many of those qualities that have attracted people to the area.

One aspect of the Biscayne Bay management problem is predicting the effect of development on water quality. The urban development of Dade County has increased both the point and non-point pollution load to the bay. To properly evaluate future development information is needed on current conditions. Also, the effectiveness of pollution control strategies should be evaluated with a reference for environmental changes. This study is a start in developing the necessary baseline data.

Finally, a unique opportunity exists to study the effect of development on the Bay. A residential and commercial complex has been proposed for Fisher Island (see Figure 1). An alternative proposal has been to use the area for a park, either as a high use "theme" park or a lower use "Elliott Key" area. While the current proposals would result in a range of development the opportunity exists to study changes in the surrounding marine environment during the construction, operation and continued use of the area. Again, this study will provide baseline data to assist in such a monitoring operation.

The area of mid-Biscayne Bay was chosen because it reflects a critical juncture between the North Bay, generally acknowledged as polluted, and the South Bay, generally thought of as unpolluted. The Rickenbacker Causeway forms a barrier to free flow between the north and south sections of the study area and thus appears as a natural dividing-line. The study area was defined as that area bounded approximately by Government Cut (Dodge and Lummus Islands) on the North and a line from the Southern tip of Key Biscayne (Cape Florida) to the outlet of the Coral Gables Waterway (see Figure 1). The study area includes the mouth of the Miami River, a suspected source of pollutants, Fisher Island (Figure 2), proposed for major urban development, the Coral Gables Waterway, a possible source of urban runoff and associated pollutants, and the Key Biscayne Municipal Dump and sewage treatment plant.

Generally speaking, the heavy industrialization along the Miami River, the restricted circulation, the port activity and the bulkheading of the north study area would tend to indicate greater pollution. The south study area has more circulation, less urbanized development and few major sources of pollution, (the Coral Gables Waterway being the one major exception). These characteristics make the mid-bay area attractive as a first attempt to gather baseline data on environmental conditions.

Methodology

The study proceeded in three basic phases: 1) a survey of the study area to define conditions and determine areas of special interest; 2) detailed samplings of the north and south study areas; and, 3) samples around Fisher Island. The collection and analysis methodology is discussed next.

Sediment was collected from a boat at locations in the study area (Figure 3-5). The sampling sites were chosen to provide baseline conditions in the bay. Annex A provides a detailed description of the initial sampling sites, while Annexes B and C describe the sampling sites in the north and south study areas, respectively. Table 1 lists the parameters measured at each site and the type of measuring device used.

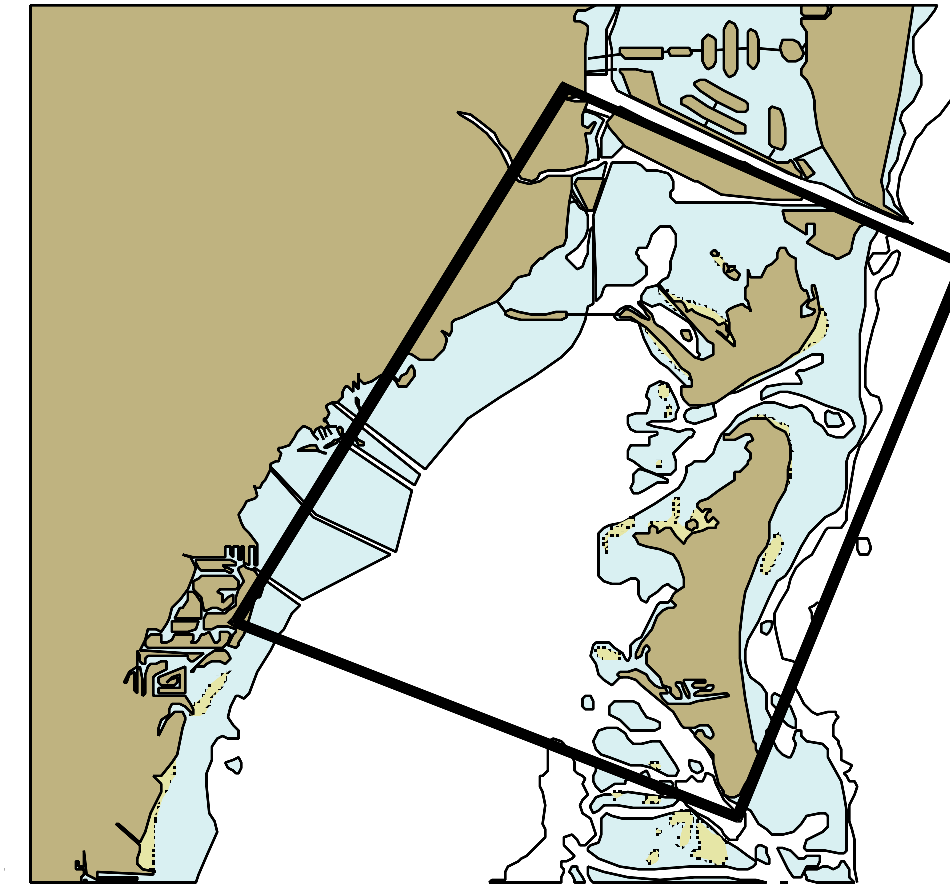

Figure 1. Study area (from Michel, 1965). [NOTE: CHART IN ARCHIVE COPY WAS NOT CLEAR. THE STUDY AREA WAS MARKED IN A CURRENT NOAA CHART.]

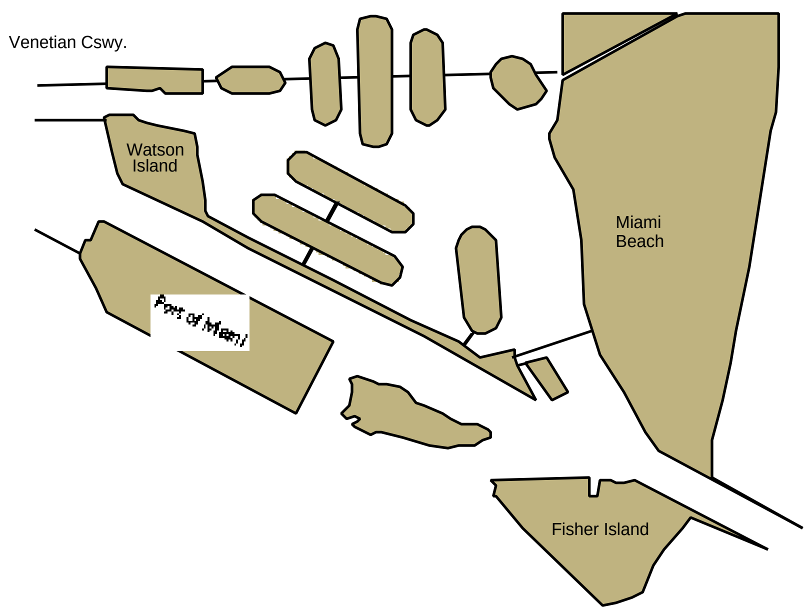

Figure 2. Location of Fisher Island.

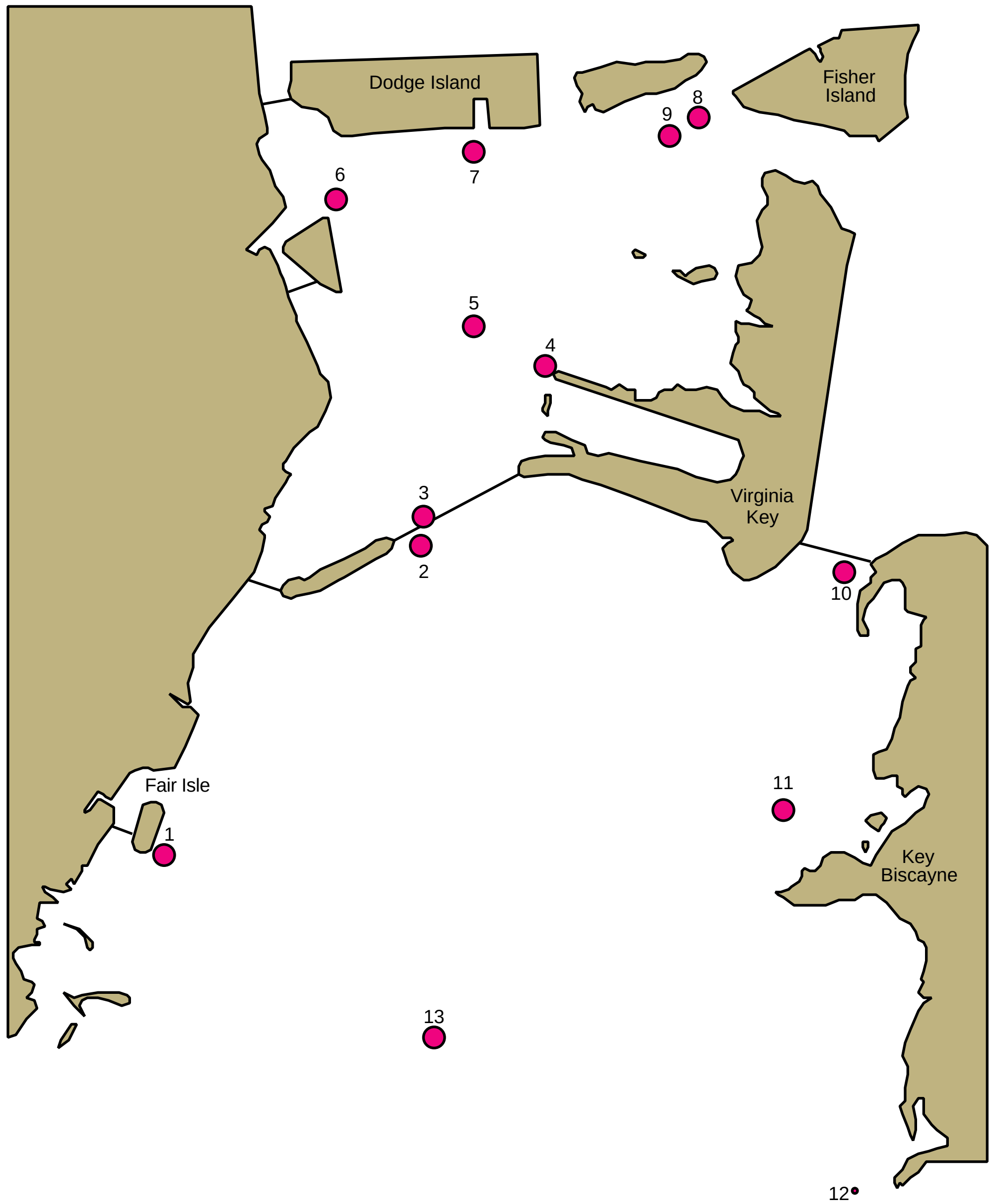

Figure 3. Study area and sampling points.

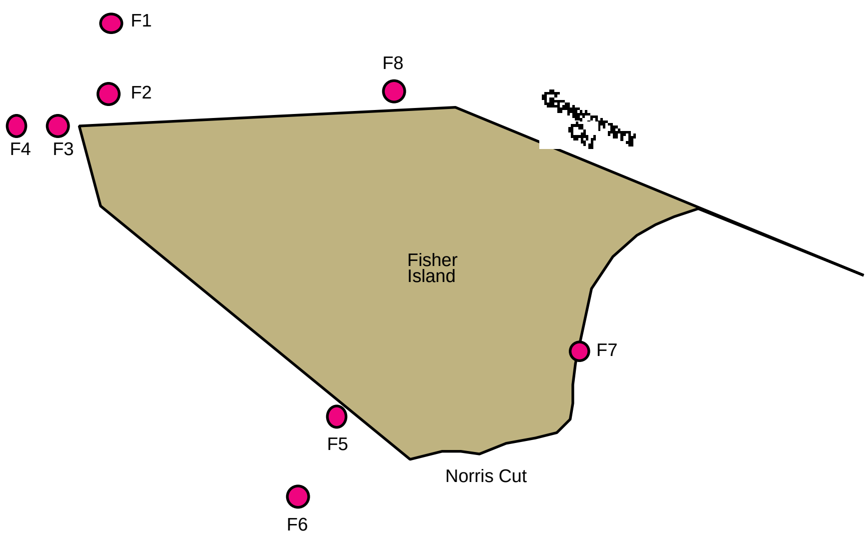

Figure 4. Fisher Island sampling sites.

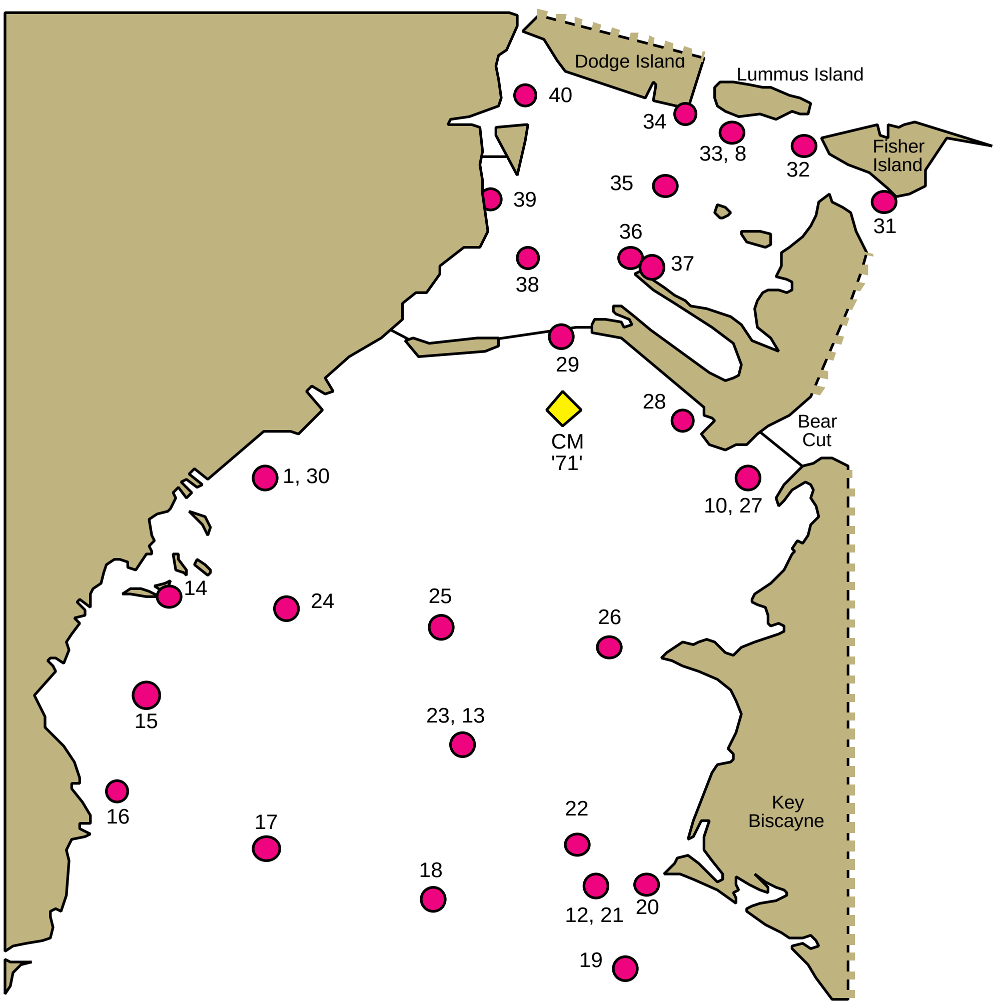

Figure 5. Sample points for second phase testing. (Channel marker is noted with a yellow diamond.) [DASHED LINE INDICATES INCOMPLETE LAND MASS.]

Table 1. Parameters and measuring devices

Heavy metals (cadmium, lead, mercury, zinc)	Perkin-Elmer 503 Atomic Absorption Spectrophotometer
Temperature, Conductivity Salinity	YSI Model 33 S-C-T Meter
Depth	Sounding line

Sediment samples were collected using a Ponar Dredge. Since the bay bottom is mostly covered with fine sediment and sand few problems were experienced. In areas with heavy vegetation or gravel bottom the dredge was used several times to obtain enough material for analysis. This procedure would disturb the bottom and may have lost the fine particles. The effect of this on sample analysis cannot be evaluated at this time. The top two to three centimeters of sediment collected in the dredge was placed into sterilized, pre-sealed plastic bags. The samples were brought to the laboratory, placed in separate porcelain crucibles, air-dried at 60 °C for 12 hours, then ground with a mortar and pestle and placed into glass jars until pre-analysis chemical treatment. All blanks and standards were processed in precisely the same manner mentioned below.

Zinc

Subsamples of 5 g ± 0.001 g were weighed on a Mettler analytical balance and placed in 250 mL Erlenmeyer flasks. To the flasks were then added 10 mL of concentrated HCl, and 10 mL of concentrated HNO_3. The samples were placed on a hot plate, heated slowly to a boil, and then allowed to boil for at least 15 minutes. After being allowed to cool to room temperature, the sample mixtures were filtered, washed, and brought up to 100 mL in 250 mL polypropylene bottles. All solutions were aspirated directly from the plastic bottles.

Lead and Cadmium

A second subsample of 5 g is weighed out as above and digested and filtered in the same manner. After the filtered solution is placed in the polypropylene bottle, the pH is adjusted to 2.8 and poured into a 250 mL separatory funnel. To this is added 5 mL of 1% ammonium pyrollidine dithiocarbonate [DITHIOCARBAMATE?] and the funnel shaken for one minute. The lead and cadmium is extracted by the addition of 10 mL of methyl isobutyl ketone, shaken for one minute, and the solution is allowed to equilibrate for five minutes. The lower aqueous layer, was drawn off and the organic layer drained into a test tube and aspirated directly.

Mercury

A 5 gram subsample was weighed and placed into a 250 mL Erlenmeyer flask along with one gram of potassium permanganate ($KMnO_4$). Ten mL of water were added to dissolve the $KMnO_4$ and 20 mL of concentrated nitric acid were added for digestion of the sample. The flasks were then placed in a water bath at 60° C for two hours, cooled at room temperature, and filtered. The sample was made up to 100 mL with deionized water, placed into 300 mL BOD bottles, and analyzed directly.

Table 2. Heavy metal concentration for first phase. (All values in ppm.)

Heavy Metal	North Area		South Area	
	Mean	Variance	Mean	Variance
Cadmium	0.022	0.00065	0.042	0.0009
Lead	4.3	7.7	3.4	4.3
Mercury	0.159	0.005	0.238	0.075
Zinc	7.2	20.3	4.92	0.84

All analyses were performed on a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer and Model 56 Strip Chart Recorder. Lead, cadmium and zinc were measured according to the Perkin-Elmer instruction manual, while mercury was determined by the cold vapor apparatus supplied by Perkin-Elmer.

All glassware used was washed in hot, soapy water, rinsed in tap water, washed with dichromic acid and rinsed in deionized water. All chemicals used were analytical reagent grade, and standards were Fisher Certified Atomic Absorption grade.

Results and Analysis

The mean value and variance for the first phase sampling are presented in Table 2. More detailed information on the location of the sampling sites and the concentrations of each heavy metal for each site are contained in Annex D. In general, the results are as expected for an estuary that has been affected by development but not the receptor of industrial waste. The reading for zinc at sample site 12 was determined erroneous and not included in the subsequent analysis.

For phases 2 and 3, samples were collected from the study area north and south of the Rickenbacker Causeway, respectively. This causeway was chosen as the dividing line for this study since it is generally accepted as the boundary between the north and south bay. The mean and variance of the samples are presented in Table 3. From the north area, 10 samples were collected and 17 samples taken from the south area. The results indicate that the north and south areas do not differ in the level of heavy metal in the sediment. The statistical analysis is described in later sections of this report. The sections immediately following describe the results of testing samples from areas adjacent to the primary study area and from points removed from the study area.

The mean and variance for the second and third phase samples is provided in Table 3

Samples around Fisher Island were taken to determine baseline conditions for future studies to determine the effect of any development of the island. Table 4 provides the mean values for the samples taken around the island. it is difficult to make definitive statements about the relative magnitude of heavy metals between the island and the remainder of the study area because of the low number of samples taken. However, some comparison can be made with the readings from areas outside of the study area in the northern areas and from some south bay samples. These are reported next.

Table 3. Average and variance of heavy metal concentrations for phase 2 and 3. (All values in ppm)

Heavy Metal	Mean	Variance
PHASE 2 NORTH (10 samples)		
Cadmium	0.04	0.0016
Lead	2.43	8.85
Mercury	0.077	0.013
Zinc	28.59	1553.4
PHASE 3 SOUTH (17 samples)		
Cadmium	0.03	0.0003
Lead	1.6	1.45
Mercury	0.102	0.0038
Zinc	8.39	40.96

A partial evaluation of the conditions between the South Bay area, North Bay area and Fisher Island in comparison to the study area, can be made from samples taken at Elliott Key, Snapper Creek, and north of the study area. Personnel of the Dade County Environmental Resources Management Department collected a sample approximately 100 meters from the mouth of Snapper Creek. An additional sample from Elliott Key and the north bay was collected for comparison. The results of analysis of these samples is presented in Table 5. Since these are onetime samples, and not repeated, the comparison should not be considered a firm finding, but for illustrative purposes only.

A preliminary analysis of the data collected during the first phase indicated higher concentrations of cadmium and mercury in the south study area and lead and zinc in the north study area. The differences are not significant at a 5% level. In addition, a large concentration of zinc was found in the sample from point 12. One goal of the second phase was to confirm these findings. Since the additional sampling could not confirm the high reading at point 12, it was deleted. A statistical analysis of the other data is included in the following sections.

The data was tested for significant difference in means for the north and south study area samples. The test of hypothesis for the difference of two expected values, variances unknown and possibly unequal, as contained in the STAT03 program in the Florida International University UNIVAC 1106 computer was used. In no case was there a statistically significant difference in the means and the hypothesis that the concentrations of cadmium, lead, mercury and zinc in the north and south study areas are equal was not rejected.

Table 4. Mean values of heavy metals in sediments around Fisher Island (all values in ppm.)

Heavy Metal	Mean	Variance
Cadmium	0.018	0.00013
Lead	1.02	0.71
Mercury	0.031	0.00053
Zinc	11.46	36.35

Comparison between average values is always fraught with dangers and should be used with caution. This is especially true when some of the values are the result of single readings and have not been repeated. Nonetheless, some observations would seem appropriate from the data presented earlier. In general, the heavy metal values seem to be within the same range for the samples within and without the study area. On the other hand, Fisher Island seems to exhibit concentrations slightly below those for the remainder of the study area. This may be the result of being closer to the ocean and having better mixing. While it is not too surprising that Snapper Creek is approximately the same as the study area, it receives runoff from several heavily urbanized areas, the reading from Elliott Key was greater than the investigators had expected. One possible explanation is the heavy power boat use in the area, but this is at best a partial explanation. The scope of the study did not permit further investigation into these areas.

Conclusions

The samples taken do not provide any final answers to the condition of the mid-bay area but do provide valuable baseline data for future studies. In brief, four conclusions can be drawn: 1) the heavy metal concentration for cadmium, lead, mercury and zinc in the north and south study areas are the same; 2) Fisher Island appears slightly lower in the concentrations of these heavy metals; 3) the area south of the mouth of the Miami River and north of the Rickenbacker Causeway may be a trap for heavy metals; and, 4) south bay areas may be as high in the studied metals as north bay areas. These conclusions are discussed in more detail in the following paragraphs.

Statistical analysis of the results presented in Tables 3 and 4 indicate the levels of cadmium, lead, mercury and zinc are not significantly different north and south of the Rickenbacker Causeway. Since this causeway has been generally accepted as a dividing line between the polluted north bay and the relatively clean south bay, this conclusion should be investigated to provide verification. While the deep south bay, the Card Sound area, was not investigated, the southernmost samples from the study do not show any significantly lower readings. This conclusion must be verified before any ma]or action can be recommended.

In general, the readings from Table 4 for Fisher Island do show somewhat lower values than the remainder of the study area.

As mentioned earlier, this could be due to greater flushing action. It does indicate that the island is in a better environmental state than has been presented in some arguments concerning development but must also be verified before major recommendations can be made on the future of the island.

Table 5. Heavy metal concentration from samples out of study area (all values in ppm).

Location			
Heavy Metal	Snapper Creek	Elliott Key	North Bay
Cadmium	0.011	0.017	0.028
Lead	3.0	2.21	1.62
Mercury	0.045	0.240	0.064
Zinc	5.53	0.66	13.44

As is noted in the text, the average values for the north and south study areas are not significantly different. However, as noted in Annex C. 38, 39 and 40 do show concentrations much higher than other north bay samples for zinc. Since zinc may move in somewhat strange ways through the environment, and only lead was noted in significantly higher concentrations in this area, this conclusion is also subject to further verification.

The study resources did not allow a detailed analysis of the entire bay and concentrated on the mid-bay area. Nonetheless, some samples were collected from south bay areas, Elliott Key and Snapper Creek. Since the readings at Elliott Key were unexpectedly high, some question must be raised about the condition of the south bay. It is possible that pollution from the northern areas has been carried to the south. it is also likely that development in the southern areas of the county is contributing heavy metals directly to the south bay. A proposal to sample from north bay to south bay along the Intracoastal Waterway has been submitted and an addendum to this report will attempt to provide additional information on this point.

In conclusion, the study has provided initial baseline data on the distribution of the heavy metals cadmium, lead, mercury and zinc in the mid-Biscayne Bay region. The prime conclusion of the study is that the concentration of these metals in the study area north of the Rickenbacker Causeway is not significantly different than the concentration south of the causeway. This finding, while subject to verification, is disturbing in that the south bay area has always been considered relatively unpolluted. Samples from further south have tended to support the finding that the south bay may be in worse shape than generally thought. It is only prudent to intensify the management procedures for the bay to insure that this valuable resource does not degrade further and to preserve and protect this valuable resource.

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ANNEX A - Location of Sites for First Sampling

Site No.	Name	Description	Time of Sample	Water Temp. (°F)	Depth (m)
I	Fair Isle	Approx. 100 meters east of south corner of island	1025	81	2.5
2	Rickenbacker #1	Approx. 100 meters south of the west end of the second bridge	1045	81	2.0
3	Rickenbacker #2	Approx. 100 meters north of the west end of the second bridge	1055	81	1.75
4	Marine Stadium	Approx. 100 meters off the NW corner of Marine Stadium	1110	81	2.0
5	Mid-North Bay	Approx. 1/2 mile NW of Site 4	1125	81	2.3
6	Miami River	Channel marker '59' at the mouth of the Miami River	1135	81	4.5
7	Marker 9	Channel marker '9' east of the mouth of the Miami River	1150	82	2.75
8	Marker 3	Channel Marker '3' west of Fisher Island	1200	82	1.75
9	Mud Flats	Approx. 300 m SSE of Fisher Island and 100 m S of Pt. 8	1225	82	0.3
10	Bear Cut	Approx. 200 m south of east end of bridge	1255	81	4.0
11	Marker G '1'	North of West Point	1315	81	3.0
12	Marker R '26'	W of Southwest Point	1345	82	4.0
13	Mid-South Bay	Approx. 1/2 distance from Site 12 to Marker '1' Dinner Key Channel	1400	82	4.0

ANNEX B - Location of Sampling Sites for South Study Area (15 December 1976)

Site No.	Name	Description	Time of Sample	Water Temp. (°F)	Depth (m)
14	Dinner Key	Channel Marker G '1' at mouth of channel	1100	36	2.2
15	Coral Gables	Channel Marker B '1' privately maintained channel north of Coral Gables Waterway	1112	36	2.0
16	Gables Waterway	Channel Marker G '1' at end of Coral Gables Waterway dredged channel	1125	37	2.3
17	Mid Bay	Approx. 1.1 miles, bearing 115* from Pt. 16	1135	36.5	3.2
18	Mid Bay	Approx. 2.5 miles, bearing 115* from Pt. 16	1155	37	4.0
19	Marker R '24'	Approx. 100 m north of Channel Marker '24'	1225	36.5	2.0
20	Marker R '2'	East of Channel Marker R '26'	1234	36.5	2.5
21	Marker R '26'	Southwest of Southwest Point, same as Pt.12	1239	36.5	4.0
22	Marker R '28'	North of Channel Marker R '26'	1245	37	2.5
23	Mid Bay	Approx. 1.3 miles, bearing 320° from Pt. 22	1307	36	4.5
24	Dinner Key Channel	Channel Marker G '1' at mouth of Dinner Key Channel	1325	36	3.8
25	Mid Bay	Approx. 0.9 miles, bearing 100* from Pt. 24	1335	36.5	4.3
26	Marker R '30'	East of West Point	1350	36.5	3.5
27	Bear Cut	Approx. 200 m southeast of Rickenbacker Causeway and 100 m west of shore. Same as Sample Pt. 10	1410	36	4.0
28	Seaquarium	South of Causeway, west of Seaquarium, approx. 100 m off shore	1420	36	3.5
29	Bridge	Bascule Bridge on Rickenbacker Causeway	1435	36	3.5
30	Fair Isle	Approx. 100ni east of south corner of island	1500	36	3.5

ANNEX C - Location of Sampling Sites for North Study Area (18 February 1977)

Site No.	Name	Description	Time of Sample	Water Temp. (°F)	Depth (m)
31	Garwood Estate	Approx. 20 m off shore, west of Garwood Estate, Fisher Island	1230	21	4.0
32		Approx. 20 m off west end of Fisher Island	1240	19	4.0
33	Marker G '3'	South of Lummus Island, same as Pt. 8	1247	19	4.0
34	Marker R '8'	Southeast end of Dodge Island	1300	19	3.0
35	Mid Bay	Halfway between Pt. 34 and Marine Stadium	1310	17	2.5
36	Marine Stadium	Approx. 100 m off northwest corner of Marine Stadium, same as Sample Pt. 4	1317	17	3.3
37		Approx. 300 m toward stack from 37	1319	16	0.5
38	ICC Marker G '67'	Intra-Coastal Waterway north of Bascule Bridge	1335	18	2.0
39	Point View	West of ICC Marker R '64', 25 m off shore	1344	18	1.5
40	Miami River	Marker M '1' At mouth of Miami River	1355	19	6.0

ANNEX D - Analysis Results by Sample Point (All values in ppm)

Sample Point	Cadmium	Lead	Mercury	Zinc
1	0.015	1.2	0.18	5.73
2	0.046	4.0	0.256	4.73
3	0.042	8.8	0.08	12.7
4	0.008	3.0	0.25	4.5
5	0.004	1.4	0.26	4.2
6	0.011	7.4	0.113	12.3
7	0.004	4.0	0.094	10.8
8	0.015	2.8	0.20	3.4
9	0.072	2.4	0.12	2.53
10	0.038	6.6	0.13	3.5
11	0.076	4.4	0.08	5.0
12	0.072	3.0	0.77	* 200.
13	0.004	1.2	0.01	5.67
14	0.021	3.3	0.097	11.3
15	0.047	0.7	0.045	2.63
16	0.026	1.7	0.122	8.6
17	0.031	1.2	0.07	1.64
18	0.059	0.4	0.107	5.56
19	0.018	2.9	0.085	6.37
20	0.024	2.9	0.055	6.26
21	0.026	0.2	0.208	7.43
22	0.03	2.3	0.075	4.04
23	0.026	1.3	0.035	12.34
24	0.025	1.6	0.042	3.57
25	0.021	0.8	0.170	12.22
26	0.088	0.2	0.070	4.27
27	0.021	2.8	0.038	3.57
28	0.02	3.9	0.235	16.55
29	0.014	0.3	0.113	8.6
30	0.016	0.5	0.177	27.66
31	0.014	0.51	0.04	1.97
32	0.008	0.67	0.005	1.97
33	0.012	0.43	0.020	1.64
34	0.006	0.91	0.120	11.15
35	0.069	2.21	0.067	10.16
36	0.025	0.55	0.010	5.57
37	0.032	0.71	0.005	2.62
38	0.041	2.94	0.380	70.49
39	0.051	6.16	0.030	72.13
40	0.138	9.20	0.070	108.2
Elliott Key	0.017	2.21	0.240	0.66
Snapper Creek	11.4	3.0	0.045	5.53
North Bay	0.028	1.62	0.064	13.44

*Sample eliminated as erroneous

Sample Point	Cadmium	Lead	Mercury	Zinc
Fisher island Samples				
Fl	0.024	2.13	0.076	12.46
F2	0.014	1.32	0.014	6.89
F3	0.010	0.49	0.023	4.43
F4	0.013	0.75	0.021	9.03
FS	0.016	0.39	0.025	15.91
F6	0.011	0.21	0.016	5.74
F7	0.015	0.49	0.016	20.16