

THE STUDY OF TRACE METALS, CHLORINATED PESTICIDES, POLYCHLORINATED
BIPHENYLS AND PHTHALIC ACID ESTERS IN SEDIMENTS OF BISCAYNE BAY

by

Eugene F. Corcoran
Melvin S. Brown
Ana D. Freay

Rosenstiel School of Marine and Atmospheric Science
university of Miami
4600 Rickenbacker Cswy.
Miami, FL 33149

Prepared for
Metropolitan Dade County
Environmental Resources Management
909 S. E. First Ave.
Miami, FL 33131

June 1984

[Restored and transferred to electronic form by A. Y. Cantillo (NOAA) in 1999. Original stored at the Library, Rosenstiel School of Marine and Atmospheric Science, University of Miami. Minor editorial changes were made.]

TABLE OF CONTENTS

INTRODUCTION.....	1
STUDY LOCATION.....	1
MATERIALS AND METHODS.....	2
COLLECTION METHODOLOGY.....	2
SUBSAMPLING.....	8
CHEMICAL ANALYSES.....	9
Synthetic Organics.....	9
Insecticides and polychlorinated biphenyls.....	9
Gas Chromatography Analysis.....	10
Metal Analyses.....	11
RESULTS AND DISCUSSION.....	12
PHTHALIC ACID ESTERS.....	12
INSECTICIDES.....	15
HERBICIDES.....	21
POLYCHLORINATED BIPHENYLS.....	21
METALS.....	21
SUMMARY AND CONCLUSIONS.....	31
LITERATURE CITED.....	32

INTRODUCTION

The purpose of this study was to establish baseline data regarding the concentration synthetic organic and metal contaminants in Biscayne Bay sediments. Wurster (1969) and Duke *et al.* (1966) have shown marine sediments can concentrate synthetic organic compounds and metals from the water column. The water solubility of these compounds is low and consequently they adhere to particulate matter which settles to the bottom (Wurster, 1969; and Edwards, 1966). Thus the sediments are a sink for these compounds and their analysis provides an integrated long term record of their introduction to the environment

A total of 45 sediments were analyzed for 7 metals, 9 insecticides, 3 herbicides, 3 polychlorinated biphenyls and 7 phthalic acid esters. The sediments had previously been collected in conjunction with "The Biscayne Bay Hydrocarbon Study" funded by the State of Florida Department of Natural Resources (Corcoran *et al.*, 1983). The 45 samples analyzed were chosen by Metropolitan Dade County Department of Environmental Resources Management (DERM) from approximately one hundred samples collected during this two year project. The sediments analyzed were all surface samples collected to a depth of 5 cm. Representative samples were selected from the different bay environments, different geographical areas, possible sources of pollutants and areas which corresponded to previously established DERM water quality stations.

The suite of contaminants which were determined are listed in Table 1. The list for both metals and synthetic organic compounds was expanded from the original target compounds. Any synthetic organic compounds which were detected in high concentrations and quantifiable with the extraction methodology employed were reported. This included aldrin, heptachlor epoxide, dieldrin, di-ethyl phthalate, di-methyl phthalate, and aroclors 1016 and 1260. In addition arsenic was included in the metal analyses. The occurrence of this element would not be expected but because of its extreme toxicity and its prior use in it was felt that it should be included.

STUDY LOCATION

Biscayne Bay is located along the southeast coast of Florida (lat. 25° 24' N, long. 80° 17' W). The bay is bounded in the north by Dumfoundling Bay and in the south by Card Sound and is contained almost entirely within Dade County, only its most northerly and southern extremities extend into Broward and Monroe Counties, respectively.

The bay is classified as a shallow, semi-tropical saline lagoon (Roessler and Beardsley, 1975). It covers approximately 573 km² (per. com., G. Milano), is north-south tending, approximately 56 km in length and averages 8 km in width, with a maximum width of 16 km. The average depth is approximately 1.8 m with a maximum depth of 4 m (Roessler and Beardsley, 1975), except in dredged areas where depths are reported to exceed 12 m.

Biscayne Bay, historically, has been divided into three regions separated by both natural and man-made structures. North bay extends from Dumfoundling Bay south to Rickenbacker Causeway; Central bay from Rickenbacker Causeway south to Featherbed Bank; South bay extends from Featherbed bank to the Arsenicker Keys. For this study South bay also includes those samples collected in the northern portions of Card Sound.

North bay has been totally developed. In excess of 40% has been either dredged or filled (Biscayne Bay Management Plan, 1981) and the entire shoreline is almost completely seawalled (Roessler and Beardsley, 1975). The area is heavily urbanized, and incorporates industrial complexes, the Port of Miami and the Miami River.

TABLE 1. Metals and synthetic organic compounds analyzed for in Biscayne Bay surface sediments.

<u>Pesticides</u>	<u>Herbicides</u>
Aldrin	2,4-D
DDE	2,4,5-T
DDD	Silvex
DDT	
Dieldrin	<u>Polychlorinated biphenyls</u>
Methoxychlor	
Endosulfan	Aroclor 1016
Heptachlor epoxide	Aroclor 1254
Toxaphene	Aroclor 1260
<u>Metals</u>	<u>Phthalic acid esters</u>
Arsenic	Butylbenzyl
Chromium	Butylglycolbutyl
Cadmium	Di-butyl
Copper	Di-ethylhexyl
Mercury	Di-isobutyl
Lead	Di-methyl
Zinc	

The Central bay is considered a transition zone between the urbanized area to the north and the lesser developed area to the south. The area is characterized by residential sections and marinas.

South bay is relatively pristine although several canal systems draining urban and agricultural areas empty into it. The area contains the 390 km² Biscayne National Park and much of the mangrove shoreline is still relatively intact. The two most prominent man-made structures in this area are the Cutler and Turkey Point power generating facilities.

Figures 1a and 1b shows the location and station numbers for the 45 elected samples. Table 2 lists the location (latitude and longitude), collection date, and coring method employed for sample collection. Table 3 presents a description of the collection sites, their regional location (north, central and south bay) and their proximity to DERM water quality stations.

MATERIALS AND METHODS

COLLECTION METHODOLOGY

The sediments samples were collected by coring. The core tube assembly consisted of 7.6-cm diameter aluminum irrigation tubing, 7.8-cm diameter circular aluminum liner plates, and 7.5-cm plastic core caps. The tubing, after being cleaned, was sealed by securing clean aluminum

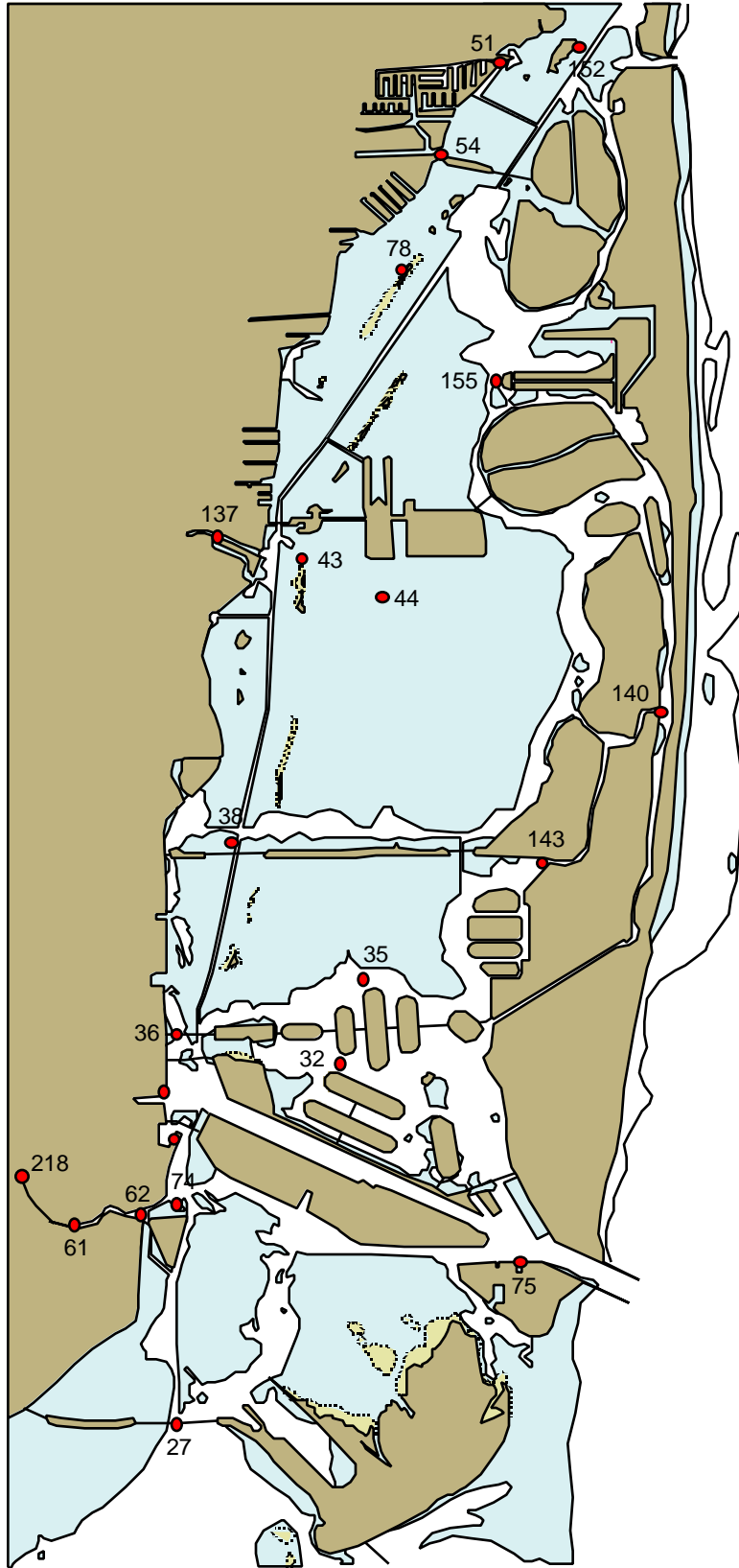


Figure 1a. Sample station locations for northern Biscayne Bay surface sediment samples.

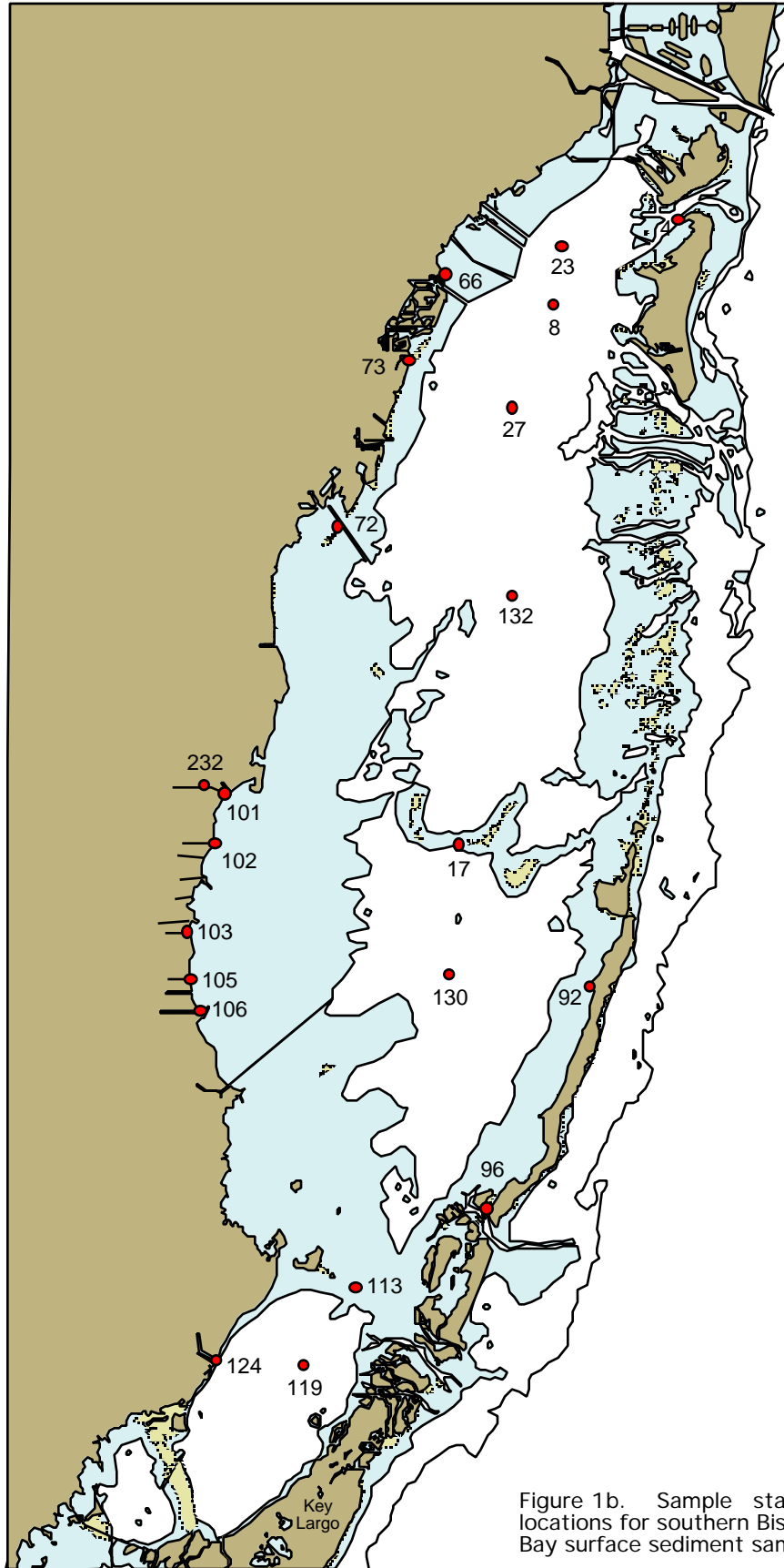


Figure 1b. Sample station locations for southern Biscayne Bay surface sediment samples.

TABLE 2. Sampling date, location, and sampling method used for collection of sediment samples. Sampling method is as follows: L = long core, S = short core, R = remote core. These methods are detailed in text.

Station Number	Sampling Date	Latitude			Longitude			Sampling Method		
		Degs.	Mins.	Sec.	Degs.	Mins.	Sec.	L	S	R
4	02/12/82	25	43	28.0	80	9	25.8	x		
8	02/12/82	25	40	52.0	80	12	29.8	x		
17	02/19/82	25	31	10.0	80	14	10.9	x		
23	02/26/82	25	42	27.9	80	12	22.8	x		
27	02/26/82	25	44	36.9	80	10	58.8	x		
32	02/12/82	25	47	11.5	80	9	48.4	x		
35	03/12/82	25	47	49.2	80	9	42.7	x		
36	03/12/82	25	47	19.3	80	10	51.8	x		
38	03/12/82	25	48	49.4	80	10	32.2	x		
43	03/12/82	25	50	5.2	80	9	26.8	x		
44	03/12/82	25	50	23.4	80	10	5.6		x	
46	03/19/82	25	55	45.3	80	7	47.8	x		
47	03/19/82	25	55	1.1	80	7	32.8	x		
51	03/19/82	25	54	0.0	80	8	34.6	x		
54	03/19/82	25	53	21.9	80	9	1.6	x		
61	04/16/82	25	46	10.3	80	11	56.6		x	
62	04/16/82	25	46	11.8	80	11	17.4		x	
66	04/21/82	25	42	21.4	80	14	45.7			x
72	04/23/82	25	37	29.4	80	17	59.9		x	
73	04/23/82	25	40	32.5	80	15	25.7		x	
74	04/28/82	25	46	14.0	80	10	50.4		x	
75	04/28/82	25	45	46.8	80	8	23.0	x		
78	04/30/82	25	52	26.2	80	9	23.4		x	
92	05/11/82	25	28	17.4	80	11	29.9		x	
96	05/11/82	25	23	40.3	80	13	57.1	x		
101	05/13/82	25	32	3.4	80	19	31.4			x
102	05/13/82	25	31	7.5	80	19	55.7			x
103	05/13/82	25	29	21.0	80	20	21.4			x
105	05/13/82	25	26	10.0	80	20	10.0			x
106	05/13/82	25	26	51.7	80	20	0.0	x		
113	05/16/82	25	22	12.5	80	16	51.4	x		
119	05/16/82	25	20	32.5	80	18	24.3		x	
124	05/16/82	25	20	42.9	80	20	0.0			x
130	05/18/82	25	28	21.3	80	15	18.6		x	
132	05/18/82	25	36	10.1	80	13	1.4	x		
137	05/27/82	25	50	46.8	80	10	34.3			x
140	05/27/82	25	49	33.5	80	7	25.7			x
143	05/27/82	25	48	32.5	80	8	2.9			x
145	05/29/82	25	58	31.2	80	7	27.1			x
147	05/29/82	25	56	39.0	80	7	41.4	x		
149	05/29/82	25	56	0.0	80	8	40.0			x
152	05/29/82	25	54	2.6	80	8	2.9		x	
155	05/29/82	25	51	48.3	80	8	37.1	x		
218	07/18/83	25	46	45.0	80	12	27.0			x
232	08/02/83	25	32	13.0	80	20	9.0			x

TABLE 3. Collection site description and corresponding DERM water quality stations.

Station Number	Site Description	Water Quality Station
NORTH BAY		
32	Between San Marino and Hibiscus Islands	18
35	North of Di Lido Island	
36	West end of Venetian Causeway	
38	ICW, north of Julia Tuttle Causeway	15
43	South of North Bay Island	14
44	Bird Key	
47	ICW, opposite Haulover Park	4
74	East of Miami River mouth	
75	Government Cut, Belcher oil slip	24
78	Spoil island east of Biscayne Canal	9
145	Dade/Broward county line	1
147	Dumfoundling Bay	
149	Center of Maule Lake	
152	Haulover Inlet, north of spoil island	6
155	Biscayne Point	
CENTRAL BAY		
4	Entrance to Crandon Marina	
8	ICW, south of Key Biscayne	31
17	ICW, Featherbed channel	38
23	Northeast of Dinner Key	
27	ICW, south of Rickenbacker Causeway draw bridge	
72	Dredge spoil north of Chicken Key	
73	Matheson Hammock Marina, southern entrance	
132	Northwest of Soldier Key	
SOUTH BAY		
92	Elliott Key, Coon Point	
96	Caesars Creek, western mouth of channel	43
113	ICW, Card Sound	
119	Middle of Card Sound	47
130	ICW, south of Featherbed Bank	

TABLE 3. Collection site description and corresponding DERM water quality stations (cont.).

CANALS AND RIVERS

North Bay

46	Mouth of Oleta River	3
51	North mouth of Arch Creek	5
54	South mouth of Arch Creek	
61	Miami River, south of interstate 95	
62	Mouth of Miami River	20
137	Little River	12
140	Indian Creek	
143	Indian Creek, south	
218	Seybold Canal, Miami River	

Central Bay

66	Mouth of Coral Gables Waterway	
101	Intersection of Goulds Canal and Black Creek	30
102	Mouth of C-102 canal	39
232	Goulds Canal	

South Bay

103	Mouth of Military Canal	
105	Mouth of Mowry Canal	40
106	Mouth of Florida City Canal	
124	Mouth of Turkey Point cooling canal	

foil over both ends of the core tube. The circular liner plates were fitted into the caps and then secured to the ends of the core tube.

The core tubes and liner plates were washed, rinsed in tap water and burned at 500° C in a kiln to remove any sources of organic contamination. Immediately after being removed from the kiln the core tubes were sealed with clean aluminum foil. The foil was secured in place with plastic core caps lined with aluminum discs. This insured a contaminant free container for sample collection.

During collection of the sediment samples the core tubes were kept sealed until they were fully submerged, this eliminated possible contamination by the water column and/or surface micro layer. Immediately after collection the cores were resealed with the foil and aluminum disc lined plastic core caps. Care was taken to keep the collected samples in a vertical position at all times to maintain its internal integrity. Immediately after being brought on board the support vessel the plastic caps were secured with tape to prevent the sample from falling out of the collection tube and to prevent tampering. The core was labeled as to station number and vertical orientation. The collected cores were under the direct responsibility and supervision of the field supervisor during collection and storage.

Three types of coring procedures were used for the collection of the sediment samples. These were short, long and remote coring. Short and long cores were collected by divers equipped with SCUBA and remote coring was done from onboard the collection vessel.

Short cores were obtained when sediment thickness was less 20 cm. The tube was submerged and the core caps removed. The short tubes were inserted by hand to bedrock, capped, withdrawn from the sediment and transported to the support vessel in an upright position.

Long push cores (1.3 m in length) were collected by securing an adjustable "T" handle near the top of the capped core tubes. The core caps were removed only when the assembled coring apparatus was submerged below the water surface. The tube was pushed into the sediment, the aluminum lined caps were placed over the top of the core tube prior to, and under the core tube bottom after removal from the sediment. The core was then transported to the support vessel in an upright position.

Areas that represented possible health hazards to divers were sampled by remote coring. This process involved the use of a 1.3 m length of aluminum core tubing connected to a reusable extender equipped with a one-way valve. The sampling device was pushed into the sediment and the valve was closed by inserting a solvent rinsed stainless steel sphere (7 cm diameter) into the extension tube. During the extraction of the core tube from the sediment the sphere created a vacuum which retained the sediment in the tube until capped at the surface. The remote coring method was preferred to box coring and grab sampling because: 1) possible sample exposure to contaminants emanating from the sampling vessel, surface films and water-borne pollutants were eliminated; 2) the sample does not contact any lubricated moving parts; 3) undisturbed samples are easily and quantitatively obtained.

After collection all core tubes and caps were coded, sealed with tape, signed and dated. Any undue disturbance during this process necessitated repeating the procedure until intact samples were obtained.

At each station the latitude and longitude in degrees, minutes and seconds as well as proximity of navigational and prominent landmarks, station number, sample number, type of collection methodology used, date and time were recorded in permanently bound waterproof field notebooks.

Great care was taken during the sampling and subsampling process to insure that contamination was kept to a minimum and chain of custody was maintained. This was accomplished by adhering to strict clean procedures, keeping all samples under lock and key and maintaining detailed field and lab records.

The samples were returned to the laboratory and transferred immediately to a locked, refrigerated core locker. The samples were stored in an upright position until they could be subsampled.

SUBSAMPLING

The cores, after being cooled and dewatered were opened and subsampled. All materials coming into contact with the samples during subsampling were cleaned to remove organic contaminants by being hexane rinsed or burned at 500° C. Within 48 hours of collection the water above the sediment in the core tubes was removed with a large pipette. Once the water had been removed, the core tubes were split by making two shallow longitudinal cuts with an electric circular saw. Samples for synthetic organic and metal analyses were collected by subsampling from only the center of the core. This was done by removing a 5-cm long cylinder shaped subsample, with hexane rinsed stainless steel spatulas, and placing it on clean aluminum foil.

An inner 2-cm diameter plug was removed by inserting a cleaned, organic-free 50-mL glass beaker through the center of the subsample. These samples were placed in burned, glass screw top jars with aluminum foil liners. The jars were stored in a locked freezer at -20° C until analyses could be performed.

CHEMICAL ANALYSES

The clean procedures and quality assurance guidelines discussed in Thompson (1977), EPA (1979) and Plumb (1981) were followed for both metals and synthetic organics. Materials used in the analytical determinations for metals were made of glass or teflon and were acid washed to insure that they were contaminant free. Materials used for synthetic organic compounds were always glass, teflon or metal. These apparatus were either solvent rinsed or burned at 500° C to remove all organic contaminants.

Synthetic organics and metals were determined using modifications of methods developed by the US. Environmental Protection Agency. Pesticides and polychlorinated biphenyls (PCB) were determined following the method of Thompson (1977). Herbicides and phthalate acid esters (PAE) followed those discussed by Plumb (1981) and metals were determined using those outlined in EPA (1979).

Synthetic Organics

A weighed sample of approximately 70 - 75 g of wet sediment was transferred to a pre-extracted cellulose thimble. The thimble was placed in a Soxhlet extraction apparatus and allowed to reflux with a 1:1 (v/v) mixture of acetone and hexane for 8 hrs. The acetone:hexane mixture was placed in a large separatory funnel with acidified organic-free H₂O for the purpose of removing the acetone. The water/acetone fraction was discarded and the hexane fraction was split into two equal subsamples. One to be used for the determination of pesticides, polychlorinated biphenyls and phthalic acid esters and the other for herbicides.

Insecticides and polychlorinated biphenyls

The fraction for insecticide and PCB determination was cleaned and fractionated by use of a Florisil column. Activated Florisil was added to a depth of 80 mm in the chromatographic column (25 mm OD, 22 mm ID, and 400 mm in length) equipped with a teflon stopcock. Ten mm of anhydrous sodium sulfate (previously burned at 500° C to remove any organic contaminants) was added on top of the Florisil. The concentrated sample was added to the Florisil column and separated into three fractions. The column was first eluted with 200 mL of 6 percent diethyl ether in hexane (fraction 1), then with 200 mL of 15 percent diethyl ether (fraction 2) and finally with 100 mL of 50 percent diethyl ether in hexane (fraction 3). Fraction 1 contained heptachlor epoxide, toxaphene, methoxychlor, aldrin, endosulfan, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT and the PCBs. Fraction 2 and 3 contained the PAEs.

Fraction 1 was further subdivided into a fraction containing primarily the PCBs by saponification (dehydrohalogenation). About 20 mL of fraction 1 was placed into a boiling flask fitted with a standard taper ground glass joint. A mixture of 5 g of KOH dissolved in 50 mL of ethanol was added and the flask was fitted with a Snyder condenser. The mixture was placed on a water bath and allowed to reflux for 30 minutes. The contents of the flask were placed in a separatory funnel along with 100 mL of organic free water (prepared by passing distilled water through an XAD-2 resin column), 50 mL of hexane was added and the sample was shaken for 5 minutes. The aqueous layer was discarded and the organic layer washed with two 100-mL

portions of water. The saponified fraction was then concentrated using a Snyder condenser and water bath and analyzed by gas chromatography (GC).

The other portion of the hexane subsample, to be used for herbicide analysis, was poured into a 300-mL round-bottom flask with diethyl ether, 15 mL H₂O, 2 mL of 37% KOH solution and two to three teflon boiling chips. A three-ball Snyder column was fitted. The ether was evaporated in a water bath for 30 minutes. The basic aqueous solution was transferred to a 125-mL separatory funnel, washed twice with 20-mL portions of diethyl ether and the ether discarded. The aqueous layer was acidified with 2 mL of 25% H₂SO₄, extracted with 20 mL, and extracted twice with 10 mL of diethyl ether. The ether extracts were combined and dried over 1 g of acidified anhydrous sodium sulfate. Then the extracts were transferred to a 25-mL evaporator tube and 0.5 mL of benzene was added. A Snyder column was fitted and the contents were concentrated in a water bath. The concentrated extracts were removed from the water bath and allowed to cool before adding 0.5 mL of 14% boron trifluoride-methanol esterification reagent. They were again placed in the water bath for 30 minutes at 50° C. After removal 4.5 mL of 5% sodium sulfate solution was added and they were mixed on a vortex mixer.

A glass Pasteur disposable pipette was packed with a small wad of pre-extracted glass wool, 2.5 cm of Florisil, 1 cm of anhydrous sodium sulfate and a thin layer of Nuchar-Attaclay. The contents in the evaporator tube were added to a 5 mL volumetric flask and the benzene layer was pipetted from the flask and placed on the Florisil column. More benzene was added to the volumetric flask and the operation was repeated until 5 mL of sample was collected in an 8-mL vial. The samples were then analyzed by GC.

Gas Chromatography Analysis

The samples were analyzed with a Tracor Model 222 Gas Chromatograph. The unit was equipped with two electron capture ⁶³Ni detectors. Packed columns, 2.0 m long, 6 mm OD, and 2 mm ID were used. Column 1 was packed with 1.5 percent SP2250, 1.95 percent SP2401 on 100/120 mesh Supelcoport and column 2 with 4 percent SE-30, 6 percent SP2401 on 100/120 mesh Supelcoport (both were prepared by Supelco, Bellefonte, Pennsylvania 16823). Column 1 was used for quantification of the compounds, while column 2 was used for verification. The carrier gas was purified nitrogen with a flow rate of 80 mL/min. The temperatures for the injectors, column and detectors were 225, 205 and 285° C, respectively. Column temperature was lowered to 180° C for herbicide determination.

Hard copy printout of the GC results were obtained with two Hewlett-Packard integrators, Model 3390A. The integrators were programmed to record the retention time, areas under the peaks and to calculate the quantity of compound present. Calibration standards were run daily and the integrators adjusted as needed.

The insecticides, PCBs, herbicides and PAEs were identified and quantified by comparison of retention times and peak heights of the samples with those of standards received from the US. Environmental Protection Agency repository located at Research Triangle Park, North Carolina. Standards were analyzed with each day's sample run. The detection limits were determined by the measurement of the smallest peak that could be quantifiable under the operating conditions used during the project. Table 4 lists the detection limits for the compounds quantified.

The o,p' and p,p'-DDT, DDE and DDD compounds were determined separately. For reporting purposes these compounds were combined and are presented as total DDT, total DDE and total DDD.

Table 4. Detection limits for synthetic organic compounds.

Compounds	Detection limits (pg)	Compounds	Detection limits (pg)
<u>Pesticides</u>		<u>Phthalic acid esters</u>	
Aldrin	10	Butylbenzyl	3000
o,p'-DDE	10	Butylglycol	3000
p,p'-DDE	10	Di-butyl	3000
o,p'-DDD	15	Di-ethylhexyl	3000
p,p'-DDD	15	Di-ethyl	3000
o,p'-DDT	20	Di-isobutyl	3000
p,p'-DDT	20	Di-methyl	3000
Dieldrin	10		
Endosulfan	10	<u>Herbicides</u>	
Heptachlor epoxide	10	2,4-D	20
Toxaphene	40	Silvex	20
Methoxychlor	40	2,4,5-T	20
<u>Polychlorinated biphenyls</u>			
Aroclor 1016	200		
Aroclor 1254	200		
Aroclor 1260	200		

The PCB's presented a somewhat more difficult quantification problem in that these compounds were characterized by multiple peaks and in many cases there was more than one PCB present. The identification of these compounds was done by comparison with known standards and quantified by the summation of the dominant peaks.

Metal Analyses

A 25-g sample of sediment was dried at 60° C for 48 hrs. This sample was used to determine moisture content for dry weight conversions (synthetic organics) and metal analyses. The low temperature (60° C) was used to ensure that Hg was not vaporized and thus lost.

The determination of metals involved their dissolution with acids and quantification by atomic absorption spectroscopy. The metals were digested using nitric acid and hydrogen peroxide. This procedure was followed for all metals except As and Hg. Arsenic was determined by the arsine generation technique and Hg by the cold vapor procedure.

The 25 g dried sample was pulverized, homogenized and split into three samples for Hg, As and the remaining metal analyses. The procedure followed for the nitric acid and hydrogen peroxide digestion and subsequent analysis by flame atomic absorption spectroscopy for Cd, Cr, Cu, Pb, and Zn is explained in detail by EPA (1979). Mercury and As were determined using the methods described by Plumb (1981).

Table 5. Detection limits for metals ($\mu\text{g/g}$).

Metals	Detection limits
Arsenic	1
Cadmium	5
Chromium	5
Copper	5
Mercury	0.1
Lead	10
Zinc	5

The instrumentation used for the determination of the metals was a Varian Model 475 atomic absorption spectrometer. Hard copy print out was obtained from a strip chart recorder. Peak heights were quantified against a standard curve which was verified daily. Table 5 presents the detection limits for the metals analyzed.

RESULTS AND DISCUSSION

PHTHALIC ACID ESTERS

Phthalic acid esters are a group of plasticizers used in the production of polyvinyl chloride and copolymers. These compounds are added to synthetic plastics to impart flexibility and improve the natural properties of these materials. In 1971 3.44 billion pounds of polyvinyl chloride products were produced (Zitko, 1977) and as much as 40% of these products are PAEs. PAEs have become ubiquitous in the environment because of their general usage and have been found in ground water, river water, drinking water, open ocean water, air, fish, crustaceans, seals, birds, soil, and sediments (both lake and marine). Experimental data have shown toxic effects due to large doses of phthalates, although low doses have not demonstrated any acute toxicity (Lawrence and Tuell, 1979). It was originally believed that exposure to doses high enough to cause toxicity were very unlikely, although Hanson (1983) reported that recent research has indicated that DEHP may be a carcinogen and exposure to extremely high levels of this compound are possible, particularly in small children. It is estimated that in 1980 5.3 to 12.9 million lbs of DEHP was used in items such as pacifiers, crib bumper pads, baby mattresses and DEHP concentrations in these products can be as high as 40%. PAEs were detected in 43 of the 45 samples collected from Biscayne Bay (see Table 6). The compounds identified were butylbenzyl, di-butyl, di-ethylhexyl, and di-ethyl. There were no butylglycolbutyl, di-isobutyl or di-methyl detected. The two samples which indicated no detectable levels of PAEs were located in north bay between San Marino and Hibiscus Islands (32) and in the ICW north of Julia Tuttle Causeway (38). Di-ethylhexyl showed the highest concentrations, maximum value 55.21 $\mu\text{g/g}$ (Card Sound, 119), which would be expected since this is the most common plasticizer in use and is not easily degraded by bacteria. Butylbenzyl occurred in all the samples except three.

Table 7 shows the distribution of PAEs in Biscayne Bay. The maximum values detected for butylbenzyl were recorded in the canals and rivers, di-butyl in north bay, for di-ethylhexyl and di-ethyl south bay. The distribution of these compounds does not seem to be correlated with

Table 6. Concentration of phthalic acid esters in Biscayne Bay surface sediments.

Station number	Phthalic acid esters ($\mu\text{g/g}$)*						
	BBP	BGBP	DBP	DEHP	DEP	DIBP	DMP
NORTH BAY							
32	ND	ND	ND	ND	ND	ND	ND
35	0.10	ND	ND	ND	ND	ND	ND
36	0.46	ND	ND	1.69	ND	ND	ND
38	ND	ND	ND	ND	ND	ND	ND
43	0.12	ND	ND	ND	ND	ND	ND
44	0.56	ND	ND	4.99	ND	ND	ND
47	0.11	ND	ND	0.65	ND	ND	ND
74	0.95	ND	ND	0.77	ND	ND	ND
75	1.20	ND	6.36	3.35	ND	ND	ND
78	0.55	ND	ND	4.22	ND	ND	ND
145	1.79	ND	48.35	11.25	ND	ND	ND
147	0.08	ND	ND	2.04	ND	ND	ND
149	0.07	ND	ND	5.81	ND	ND	ND
152	0.29	ND	ND	0.62	2.04	ND	ND
155	0.08	ND	3.18	15.53	ND	ND	ND
CENTRAL BAY							
4	0.12	ND	ND	6.48	ND	ND	ND
8	0.27	ND	ND	ND	ND	ND	ND
17	1.06	ND	ND	3.40	ND	ND	ND
23	0.41	ND	0.81	1.48	ND	ND	ND
27	0.68	ND	5.86	3.08	ND	ND	ND
72	1.19	ND	3.83	4.60	ND	ND	ND
73	0.86	ND	ND	4.97	ND	ND	ND
132	1.49	ND	12.62	4.77	ND	ND	ND
SOUTH BAY							
92	1.35	ND	5.35	1.57	ND	ND	ND
96	ND	ND	ND	1.11	2.74	ND	ND
113	0.73	ND	3.20	0.90	ND	ND	ND
119	1.29	ND	3.97	55.21	ND	ND	ND
130	0.20	ND	0.44	7.17	ND	ND	ND

Table 6. Concentration of phthalic acid esters in Biscayne Bay surface sediments (cont.).

Station number	Phthalic acid esters ($\mu\text{g/g}$)*						
	BBP	BGBP	DBP	DEHP	DEP	DIBP	DMP
CANALS AND RIVERS							
NORTH BAY							
46	2.05	ND	ND	13.28	ND	ND	ND
51	1.94	ND	ND	18.40	ND	ND	ND
54	1.16	ND	ND	7.74	ND	ND	ND
61	0.77	ND	ND	1.70	ND	ND	ND
62	0.16	ND	ND	0.11	ND	ND	ND
137	0.45	ND	ND	12.39	ND	ND	ND
140	0.29	ND	ND	1.38	ND	ND	ND
143	0.19	ND	ND	2.05	ND	ND	ND
218	2.59	ND	ND	4.44	ND	ND	ND
CENTRAL BAY							
66	0.08	ND	2.04	0.75	ND	ND	ND
101	0.31	ND	ND	0.52	ND	ND	ND
102	0.09	ND	ND	ND	ND	ND	ND
232	2.39	ND	ND	3.95	ND	ND	ND
SOUTH BAY							
103	5.98	ND	ND	44.55	ND	ND	ND
105	0.16	ND	ND	1.18	ND	ND	ND
106	0.90	ND	2.79	ND	ND	ND	ND
124	4.82	ND	8.40	5.18	ND	ND	ND

* BBP = Butylbenzyl phthalate
 BGBP = Butylglycolbutyl phthalate
 DBP = Di-butyl phthalate
 DEHP = Di-ethylhexyl phthalate
 ND = None detected.

DEP = Di-ethyl phthalate
 DIBP = Di-isobutyl phthalate
 DMP = Di-methyl phthalate

Table 7. Distribution of phthalic acid esters concentrations in Biscayne Bay surface sediments ($\mu\text{g/g}$).

Compounds	North Bay (14)*	Central Bay (8)	South Bay (5)	Canals and Rivers (17)
BBP	<0.5 - 1.8 (13)	<0.5 - 1.5 (8)	<0.5 - 1.4 (4)	<0.5 - 6.0 (15)
DBP	<0.5 - 48.4 (3)	<0.5 - 12.6 (4)	<0.5 - 5.3 (4)	<0.5 - 8.4 (3)
DEHP	<0.5 - 15.5 (11)	<0.5 - 6.5 (7)	<0.5 - 55.2 (5)	<0.5 - 44.5 (15)
DEP	<0.5 - 2.0 (1)	<0.5 (0)	<0.5 - 2.7 (1)	<0.5 (0)

* Number of samples analyzed from designated area.

Number of samples analyzed which contained detectable amounts.

BBP = Butylbenzyl phthalate

DBP = Di-butyl phthalate

DEHP = Di-ethylhexyl phthalate

DEP = Di-ethyl phthalate

any one locality or source. Since these compounds are so prevalent in the environment this type of distribution would be expected.

Table 8 shows PAE concentrations from other localities for comparison purposes. The concentrations of PAEs in Biscayne Bay sediments are much higher than those from Texas, the Mississippi delta and the Gulf coast. Although they are comparable to values found in several rivers in the Netherlands.

INSECTICIDES

The insecticides (see Table 9) were not as widely distributed as the PAEs. Aldrin, toxaphene and methoxychlor were below detection limits in all the sediment samples. Heptachlor epoxide and dieldrin were only detected in two and one samples respectively.

The most widely distributed compound was DDE (maximum concentration 52.7 ng/g) which was detected in 10 (22%) of the samples. The highest insecticide concentration was 1014.3 ng/g for endosulfan. Detectable levels of insecticide residues were determined in 17 of the 45 sediment samples (38%).

The insecticides determined were all organochlorine compounds which can be further divided into three subgroups, DDT and related compounds; cyclodiene compounds; and chlorinated terpenes. The first group includes DDT, DDE, DDD and methoxychlor. The cyclodienes include heptachlor (epoxide), aldrin, dieldrin and endosulfan. The chlorinated terpenes include toxaphene.

Table 8. Phthalic acid esters in surface sediments for selected locations ($\mu\text{g/g}$).

Location	Phthalic acid esters ($\mu\text{g/g}$)			
	DBP	DEHP	DEP	DIBP
<u>USA</u>				
Chesapeake Bay*	0.027 - 0.89	0.012 - 0.180	0.022 - 0.042	0.006
Galveston Bay		<0.001 - 0.110		
Mississippi Delta ⁺	<0.0001 - 0.052	<0.0001 - 0.248		
Gulf Coast ⁺	<0.0001 - 0.015	<0.003 - 0.014		
<u>NETHERLANDS</u> [▼]				
Meuse River	0 - 2	1 - 17		
IJssel River	0 - 7	2 - 50		
Rhine River	0 - 7	2 - 50		

DBP = Di-butyl phthalate; DEHP = Di-ethylhexyl phthalate; DEP = Di-ethyl phthalate; DIBP = Di-isobutyl phthalate.

* Peterson and Freeman, 1982.

Murray *et al.*, 1981.

⁺Giam *et al.*, 1978.

[▼]Schwartz *et al.*, 1979.

DDT was praised by Sir Winston Churchill as the "miraculous DDT powder" for its unprecedented effectiveness in halting a louseborne typhus outbreak in 1943 and reviled as the "elixir of death" by Rachel Carson. DDT has received extensive use worldwide as an agricultural insecticide and to eliminate disease carrying insects, although its persistence, bioaccumulation and the development of insect resistance has resulted in its restriction and banning in North America. It is still used, although to a much lesser degree than previously, for vector control in developing countries. DDT has been shown to be extremely toxic to insects and fish, and moderately toxic to mammals and birds.

Total DDT (the sum of o,p'-DDT and p,p'-DDT) was detected in five samples all of which were located in canals and rivers entering Biscayne Bay. The highest concentration 52.7 ng/g was from the Little River (137). Other detectable values ranged from 2 to 6 ng/g and were located in the Oleta River, Miami River, Goulds Canal/Black Creek and at Turkey Point.

Total DDE and DDD are both breakdown (dehydrochlorination) products of DDT. DDE has only slight insecticidal properties but is highly persistent in the environment. DDD has been synthesized and marketed as an insecticide. It is less toxic than DDT to mammals but is more toxic to some insects. It is persistent in the environment and does bioaccumulate. Its use in North America has been discontinued.

Table 9. Concentrations of insecticides in Biscayne Bay surface sediment (ng/g).

Station number	Aldrin	Heptachlor epoxide	Dieldrin	Endo-sulfan	Toxaphene	Methoxy-chlor	DDT	DDE	DDD
NORTH BAY									
32	ND	ND	ND	ND	ND	ND	ND	ND	ND
35	ND	ND	ND	ND	ND	ND	ND	ND	ND
36	ND	ND	ND	ND	ND	ND	ND	ND	ND
38	ND	ND	ND	ND	ND	ND	ND	10.0	ND
43	ND	ND	ND	ND	ND	ND	ND	15.0	ND
44	ND	31.8	ND	ND	ND	ND	ND	ND	ND
47	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	ND	ND	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND	ND
78	ND	ND	ND	ND	ND	ND	ND	ND	ND
145	ND	ND	ND	ND	ND	ND	ND	ND	ND
147	ND	ND	ND	30.5	ND	ND	ND	ND	ND
149	ND	ND	ND	ND	ND	ND	ND	ND	ND
152	ND	ND	ND	ND	ND	ND	ND	ND	ND
155	ND	ND	ND	ND	ND	ND	ND	ND	ND
CENTRAL BAY									
4	ND	ND	ND	ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND	ND	ND	ND	ND
17	ND	ND	7.2	ND	ND	ND	ND	ND	ND
23	ND	ND	ND	ND	ND	ND	ND	ND	ND
27	ND	ND	ND	ND	ND	ND	ND	ND	ND
72	ND	ND	ND	ND	ND	ND	ND	13.9	ND
73	ND	ND	ND	ND	ND	ND	ND	6.3	ND
132	ND	ND	ND	ND	ND	ND	ND	10.0	ND
SOUTH BAY									
92	ND	ND	ND	ND	ND	ND	ND	ND	ND
96	ND	18.8	ND	ND	ND	ND	ND	17.3	ND
113	ND	ND	ND	ND	ND	ND	ND	ND	ND
119	ND	ND	ND	ND	ND	ND	ND	6.4	ND
130	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 9. Concentrations of insecticides in Biscayne Bay surface sediment (ng/g) (cont.).

Station number	Aldrin	Heptachlor epoxide	Dieldrin	Endo-sulfan	Toxaphene	Methoxy-chlor	DDT	DDE	DDD
CANALS AND RIVERS									
NORTH BAY									
46	ND	ND	ND	ND	ND	ND	4.5	9.8	3.8
51	ND	ND	ND	ND	ND	ND	ND	ND	ND
54	ND	ND	ND	ND	ND	ND	ND	ND	ND
61	ND	ND	ND	ND	ND	ND	ND	ND	ND
62	ND	ND	ND	124.2	ND	ND	2.2	ND	2.3
137	ND	ND	ND	1014.3	ND	ND	52.7	ND	ND
140	ND	ND	ND	ND	ND	ND	ND	ND	ND
143	ND	ND	ND	ND	ND	ND	ND	ND	ND
218	ND	ND	ND	ND	ND	ND	ND	ND	ND
CENTRAL BAY									
66	ND	ND	ND	ND	ND	ND	ND	3.0	ND
101	ND	ND	ND	71.5	ND	ND	5.8	ND	ND
102	ND	ND	ND	ND	ND	ND	ND	ND	ND
232	ND	ND	ND	ND	ND	ND	ND	ND	ND
SOUTH BAY									
103	ND	ND	ND	ND	ND	ND	ND	ND	ND
105	ND	ND	ND	14.5	ND	ND	ND	2.3	0.1
106	ND	ND	ND	ND	ND	ND	6.2	12.3	ND
124	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = None detected.

DDE occurred more frequently than any of the other insecticides and was distributed in all four of the geographical regions of the bay. It was detected in 11 samples and detectable values ranged from 2.3 to 17.3 ng/g. The most probable explanation for this broad occurrence is that the DDE is the remnant of its parent compound (DDT) which was widely used in Dade county. DDD was detected in three samples, all of which were located in canals and rivers. The Oleta River (46) sample contained 3.8 ng/g, the sample from the mouth of the Miami River (62) contained 2.3 ng/g and the Mowry Canal (105) sample contained 0.1 ng/g.

Methoxychlor is a widely used but non persistent insecticide. It accumulates in most animals, although molluscs, crustaceans and fish do not metabolize it as rapidly as higher animals, therefore, some accumulation may occur. Methoxychlor has a low toxicity to mammals and birds, but is highly toxic to fish.

As stated earlier methoxychlor was not detected in any of the samples. This would be expected since it is rapidly degraded.

Heptachlor is one of the several compounds which comprise technical grade chlordane. Its major use is as an insecticide against soil living insects and is more toxic than its parent compound (chlordane). Heptachlor degrades rapidly and is metabolized by birds, insects, microorganisms, mammals and plants to form an epoxide. This product (heptachlor epoxide) is as toxic as heptachlor and can bioaccumulate in animal tissue. The use of this compound is restricted in the US.

Heptachlor epoxide was detected in only two samples, near Bird Key and Caesars Creek. Detected concentrations ranged from 18.8 to 31.8 ng/g.

Aldrin and its epoxide dieldrin have extensive use as soil insecticides. They are more toxic to insects and mammals than chlordane. In the environment aldrin is short lived but dieldrin persists and can accumulate in animal tissue. Dieldrin has been found in tissues of many birds and humans, and mothers' milk. Dieldrin has been used extensively to eradicate the fire ant in the southeast United States. The use of aldrin and dieldrin are restricted in the US.

Aldrin was below detection limits for all the samples. Dieldrin was detected only at the Featherbed channel (17).

Endosulfan is used mostly as a foliar insecticide and is only moderately persistent in the environment. It is of moderate toxicity to mammals and birds, but fish are highly susceptible and contamination of lakes and streams has resulted in fish kills. Endosulfan has been used as an effective chemical for removal of fish in small lakes. Unlike dieldrin and heptachlor (epoxide) endosulfan does not bioaccumulate.

Endosulfan was detected in five samples, four of these were located in canals and rivers. The Miami River (62), C-102 Canal (102), Mowry Canal (105) and Little River (137) all had detectable levels of Endosulfan. The other area where this compound occurred was Dumfoundling Bay (147).

Toxaphene is used mainly as a foliar insecticide and is considered to be persistent in the environment. It is moderately toxic to mammals and birds and is extremely toxic to fish. Toxaphene was not detected in any of the samples.

Table 10 presents a summation of the insecticide values by location and the results of a previous study conducted in canals located in the Florida Keys. The Keys are industrially and agriculturally undeveloped and the major source for these compounds would be small scale homeowner usage and mosquito control. Thus these values were used for comparison purposes. In comparison all of the compounds (endosulfan, toxaphene and methoxychlor values are not available) except DDT were below the range of values reported by Chesher (1974). The lower values in Biscayne Bay may be the result of the restricted use of many of these compounds for the past several years and their gradual degradation.

Concentration of total DDTs (summation of DDT and DDE isomers) for Galveston Bay ranged from 0.01 to 1.4 ng/g (Murray *et al.*, 1981). Concentrations from the Mississippi delta and the Gulf coast ranged from 0.2 to 9.3 and 0.2 and 4.0 ng/g, respectively (Giam *et al.*, 1978). The detectable values found in Biscayne Bay sediment (total DDT) ranged from <2 to 17.3 ng/g (excludes canal and river data). Again the values for DDT are slightly higher than values detected in similar environments

Table 10. Distribution of insecticide concentrations in Biscayne Bay surface sediments and surrounding areas (ng/g).

Compounds	Present study				Previous study
	North Bay (15)*	Central Bay (8)	South Bay (5)	Canals and Rivers (17)	Florida Keys canals♦ (12)
Aldrin	<5 (0)	<5 (0)	<5 (0)	<5 (0)	7 - 44 (12)
Heptachlor epoxide	<5 - 32 (1)	<5 (0)	<5 - 19 (1)	<5 (0)	8 - 29 (12)
Dieldrin	<5 (0)	<5 - 7 (1)	<5 (0)	<5 (0)	4 - 40 (12)
Endosulfan	<0.5 - 30 (1)	<5 (0)	<5 (0)	<5 - 1014 (4)	-
Toxaphene	<5 (0)	<5 (0)	<5 (0)	<5 (0)	-
Methoxychlor	<5 (0)	<5 (0)	<5 (0)	<5 (0)	-
DDT	<2 (0)	<2 (0)	<2 (0)	<2 - 53 (5)	ND - 30 (12)
DDE	<2 - 15 (2)	<2 - 14 (3)	<2 - 17 (2)	<5 - 13 (4)	15 - 90 (12)
DDD	<0.1 (0)	<0.1 (0)	<0.1 (0)	<0.1 - 4 (3)	10 - 349 (11)

* Number of samples analyzed from designated area.

♦ Chesher (1974).

Number of samples analyzed which contained detectable amounts.

These higher values for DDT may be the result of its more extensive usage in the agricultural regions of Dade county, its persistence in the environment or its continued usage. This last statement is supported by the recent toxic cleanup program sponsored by the State of Florida Department of Environmental Regulation in which over 1400 lbs of DDT were recovered in Dade county.

Endosulfan occurred in higher concentrations than any of the other compounds (Little River 1014.3 ng/g and Miami River 124.2 ng/g). These elevated values are in the same order of magnitude as the maximum values found in agricultural soil in the US. Stevens *et al.* (1970) reported a maximum value from orchard soils of 4600 ng/g and Wiersma *et al.* (1972)

reported 400 ng/g from soil used for growing vegetables. The high concentrations detected in these two areas may its continued use since it is only moderately persistent in the environment. The occurrence of high concentrations of endosulfan in nonagricultural regions is not unexpected since approximately 50% of its production is used by farmers (McEwen and Stephenson, 1979), leaving the remainder to be distributed by the homeowner.

HERBICIDES

The chlorine-substituted phenoxy herbicides, 2,4-D, 2,4,5-T and silvex were found in 78% of the Biscayne Bay sediments sampled (see Table 11). These three herbicides as a result of their selectivity for certain plants combined with their non persistence in the environment has resulted in extensive use. They are rapidly degraded by bacteria in the environment. Their persistence in soil is 4 weeks to a year. During the last several years their use has become regulated due to birth defects observed in mice injected with 2,4,5-T and the presence of dioxins.

The highest concentrations found for 2,4-D, Silvex and 2,4,5-T were 33.00, 15.81 and 44.60 ng/g, all were collected in canals and rivers. The highest concentrations in the bay proper for 2,4-D were detected at Bird Key (44), Silvex in Card Sound (113) and for 2,4,5-T Dumfoundling Bay (147). Table 12 summarizes the distribution of the herbicide results.

POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls, prior to 1970, were used as plasticizers, hydraulic fluids and dielectric for transformers and large capacitors. Due to their wide usage, persistence and toxicity, use has been restricted in the US. Table 13 presents the PCB results for the Biscayne Bay sediments. Table 14 summarizes these results by location. The PCBs were widely distributed throughout the bay, they were detected in 69% of the collected samples. The most widely distributed PCB was Aroclor 1254 which was detected in 16 of the samples. Aroclor 1016 was found in only 4 samples and Aroclor 1260 was detected in 7 samples. The highest concentrations for 1254 and 1260 were detected in the canals and rivers, the highest detected value for 1016 was found in north bay.

Concentrations for total PCBs in sediment for Galveston Bay (Murray *et al.*, 1981), the Mississippi delta and the Gulf coast (Giam *et al.*, 1978) are <0.14 - 7.1, 0.2 - 35, and 0.2 - 6 ng/g. These much lower than those detected in Biscayne Bay (excludes canals and rivers) which ranged from <2 to 307.49 ng/g. The lowest detectable value was 3.6 ng/g.

METALS

Table 15 presents the results of the metal analyses. Nine (20% of the samples collected) contained no detectable concentrations of the target metals, although two of these samples were not analyzed for arsenic and chromium. Two of the sites were marinas (73, Matheson Hammock and 4, Crandon), three were in the mouths of canals entering the bay (62, Miami River, 66, Coral Gables Waterway and 105, Mowry Canal), two in the Intracoastal Waterway (8 and 130), one north of Chicken Key (72) and one in Card Sound (119). Arsenic and cadmium were below detection limits (<1 and <5 µg/g) in all samples. Mercury values above detection limits (<0.1 µg/g) ranged from 0.1 to 0.9 µg/g and were found in five samples collected from the Oleta River (46), Arch Creek (51), Military Canal (103), Little River (137) and Dumfoundling Bay (47). Chromium, copper and zinc were the most widely distributed elements occurring in 19 (48%), 27 (60%), and 29 (64%) of the samples, respectively. The detectable concentrations for chromium, copper and zinc ranged from 7 to 22, 5 to 117, 6 to 252 µg/g. Lead was detected in 11 (24%) of the samples. Detectable values ranged from 12 to 520 µg/g. The highest concentrations of lead, zinc and copper occurred in two samples, 218 and 232.

Table 11. Herbicide concentrations in Biscayne Bay surface sediment (ng/g).

Station number	2,4-D	Silvex	2,4,5-T
NORTH BAY			
32	ND	0.46	ND
35	ND	0.44	ND
36	ND	ND	3.42
38	1.28	0.53	ND
43	ND	0.28	ND
44	8.04	1.54	ND
47	0.11	0.22	0.11
74	ND	ND	ND
75	6.86	3.68	ND
78	6.06	ND	1.92
145	ND	ND	ND
147	ND	ND	35.00
149	ND	1.29	1.14
152	MD *	ND	ND
155	ND	ND	2.58
CENTRAL BAY			
4	ND	0.51	ND
8	0.61	0.51	ND
17	ND	1.34	3.48
23	1.67	0.37	0.60
27	4.42	ND	1.34
72	ND	ND	2.42
73	ND	ND	ND
132	ND	ND	1.99
SOUTH BAY			
92	5.04	2.29	ND
96	4.55	4.26	1.70
113	ND	9.24	4.09
119	ND	ND	ND
130	0.30	1.30	ND

Table 11. Herbicide concentrations in Biscayne Bay surface sediment (ng/g) (cont.).

Station number	2,4-D	Silvex	2,4,5-T
CANALS AND RIVERS			
NORTH BAY			
46	0.50	ND	0.26
51	ND	ND	ND
54	ND	ND	ND
61	ND	4.07	ND
62	ND	ND	ND
137	ND	ND	44.60
140	ND	ND	ND
143	ND	ND	ND
218	3.09	3.97	ND
CENTRAL BAY			
66	ND	0.60	3.79
101	33.80	ND	11.40
102	32.68	ND	1.24
232	3.51	15.81	ND
SOUTH BAY			
103	15.19	8.36	30.60
105	ND	ND	ND
106	3.58	4.66	11.64
124	ND	13.84	10.57

ND = None detected.
 * MD = Missing data.

Table 12. Distribution of insecticide concentrations in Biscayne Bay surface sediments and surrounding areas (ng/g).

Compounds	Present study			
	North Bay (14)*	Central Bay (8)	South Bay (5)	Canals and Rivers (17)
2,4-D	<0.1 - 8 (5)	<0.1 - 4 (3)	<0.1 - 5 (3)	<0.1 - 34 (7)
Silvex	<0.1 - 4 (8)	<0.1 - 1 (4)	<0.1 - 9 (4)	<0.1 - 16 (7)
2,4,5-T	<0.1 - 35 (6)	<0.1 - 3 (5)	<0.1 - 4 (2)	<0.1 - 45 (8)

* Number of samples analyzed from designated area.
 Number of samples analyzed which contained detectable amounts.

Sample 218 was collected from Seybold Canal which drains into the Miami River and sample 232 was collected from Goulds Canal. The highest concentrations of chromium (22 µg/g) were detected in the Miami River (61) and Maule Lake (149).

Manker (1975) conducted a survey of the distribution and concentration and established background concentrations for selected metals in the upper Keys, Florida Bay, and Biscayne Bay. Segar and Pellenbarg (1973) conducting work to evaluate the possible elevation of metals due to the construction and operation of the Turkey Point power generating plant established background stations in Card Sound for comparison purposes. In addition, Chesher (1974), during his evaluation of the impact of canal systems in the Florida Keys, collected metal data from these environments. This earlier information will be used to compare and contrast the data collected during this study since they offer background values collected approximately ten years ago.

Arsenic compounds, which are highly poisonous to mammals, do not occur naturally at high concentrations in the marine environment. The main sources of arsenic arise from its use in herbicides and insecticides and also in certain mining and manufacturing waste products. In particular, it is used in the production of glass, paints and alloys and is a by-product in several smelting products. Its use in insecticides and wood preservatives pose a possible local source.

Cadmium is of great concern primarily because of its cumulative toxic effects in mammals. It can become concentrated in selected organs to a level which can cause detrimental effects or death. It enters the environment as an industrial waste product, especially from industries involved in pigment, electroplating, galvanizing, battery and alloy manufacturing.

Arsenic and cadmium were not detected in any of the sediments analyzed in this study. Segar and Pellenbarg (1973) reported values of 0.07 and 0.2 for Card Sound and Turkey Point. These values were lower than those reported by Riley and Chesher (1971) for deep sea clays (0.42

Table 13. Concentrations of polychlorinated biphenyls (PCBs) found in Biscayne Bay surface sediment (ng/g).

Station number	Aroclor 1016	Aroclor 1254	Aroclor 1260
NORTH BAY			
32	ND	ND	64.00
35	ND	ND	49.15
36	124.78	ND	ND
38	ND	ND	ND
43	ND	ND	ND
44	ND	ND	ND
47	ND	37.22	ND
74	ND	54.61	ND
75	ND	ND	ND
78	ND	170.96	ND
145	ND	122.82	ND
147	ND	3.6	ND
149	ND	ND	86.98
152	ND	218.55	ND
155	ND	26.10	ND
CENTRAL BAY			
4	ND	81.40	ND
8	ND	33.79	ND
17	ND	ND	ND
23	ND	307.49	ND
27	33.86	ND	ND
72	ND	ND	ND
73	ND	ND	ND
132	ND	ND	ND
SOUTH BAY			
92	ND	277.18	ND
96	ND	ND	ND
113	ND	ND	ND
119	ND	ND	ND
130	48.22	ND	ND

Table 13. Concentrations of polychlorinated biphenyls (PCBs) found in Biscayne Bay surface sediment (ng/g) (cont.).

Station number	Aroclor 1016	Aroclor 1254	Aroclor 1260
CANALS AND RIVERS			
NORTH BAY			
46	ND	ND	ND
51	ND	234.82	ND
54	ND	31.06	ND
61	ND	464.12	ND
62	ND	58.60	ND
137	ND	21.40	ND
140	ND	204.93	ND
143	ND	ND	51.28
218	ND	ND	5961.60
CENTRAL BAY			
66ND	ND	ND	
101	ND	15.00	ND
102	2.02	ND	ND
232	ND	1549.80	ND
SOUTH BAY			
103	ND	ND	2044.30
105	ND	17.40	ND
106	ND	ND	ND
124	ND	ND	10.26

ND = None detected.

Table 12. Distribution of polychlorinated biphenyls in Biscayne Bay surface sediment (ng/g).

Compounds	Present study			
	North Bay	Central Bay	South Bay	Canals and Rivers
	(15)*	(8)	(5)	(17)
Aroclor 1016	<2 - 125 (1)	<2 - 34 (1)	<2 - 48 (1)	<2 - 2 (1)
Aroclor 1254	<2 - 218 (6)	<2 - 307 (3)	<2 - 277 (1)	<2 - 1550 (9)
Aroclor 1260	<2 - 87 (3)	<2 (0)	<2 (0)	<2 - 5962 (4)

* Number of samples analyzed from designated area.
 Number of samples analyzed which contained detectable amounts.

µg/g). The higher values near Turkey Point are believed to be from the construction and operation of the nuclear power plants (Segar and Pellenbarg, 1973). The values reported in this study for this area of Biscayne Bay area are all below the detection limits.

Chromium is essential to many biochemical activities and widely distributed in soils and vegetation, although the concentrations are generally very low. It is toxic to animals, particularly in the hexavalent state, and, also plants, but to a lesser degree. It is used in industrial processes such as electroplating, corrosion inhibition (chromate paints and primers), printing, aluminum-anodizing, fungicides, wood preservatives and the manufacture of alloys. Another major source is the particle emission from coal, wood and rubbish burning. Cuffe and Gerstle (1967) have shown that particle emission from coal burning plants can contain 2.3 to 31.0 ppm chromium. Maximum values detected during this study were 23 to 28 µg/g. Chesher (1974) working in canals in the Florida Keys detected maximum values of 10 to 15 µg/g. The background established by Manker (1975) for chromium is 7 to 8 µg/g.

Copper is an important element in many biological processes. It is essential to animals including the settling of barnacles, spinning of bissus threads in mussels, biosynthesis of hemoglobin, respiratory pigments in invertebrates and also in the activation of certain enzymes in plants, although it can become harmful in excessive amounts particularly in the aquatic environment. Copper is used as a fungicide and insecticide and also in metallurgical and ceramic industries and anti fouling paints for boats. Copper ranged from <5 to 117 µg/g in the sediments collected. Segar and Pellenbarg (1973) reported average values in Card Sound of 2 and near Turkey Point of 11 µg/g. Values for selected canals in the Keys ranged from 1 to 3 µg/g.

Mercury is used in a number of industrial processes which include chlor-alkali plants, pulp mills, plastic and drug manufacturing and wood preservation. Industries such as these, however, are largely absent in the vicinity of the study area. The second major source of

Table 15. Metal concentrations in Biscayne Bay surface sediment ($\mu\text{g/g}$).

Station number	As	Cd	Cr	Cu	Hg	Pb	Zn
NORTH BAY							
32	ND	ND	8	14	ND	60	18
35	ND	ND	11	14	ND	30	20
36	ND	ND	ND	ND	ND	ND	8
38	ND	ND	ND	16	ND	ND	ND
43	ND	ND	9	ND	ND	ND	ND
44	ND	ND	ND	5	ND	ND	6
47	ND	ND	ND	25	ND	25	ND
74	ND	ND	ND	8	ND	ND	ND
75	ND	ND	ND	19	ND	12	16
78	ND	ND	ND	6	ND	ND	9
145	ND	ND	18	18	ND	ND	44
147	NA	ND	NA	ND	0.1	ND	72
149	ND	ND	22	16	ND	10	67
152	ND	ND	ND	ND	ND	ND	11
155	ND	ND	ND	24	ND	ND	25
CENTRAL BAY							
4	ND	ND	ND	ND	ND	ND	ND
8	ND	ND	ND	ND	ND	ND	ND
17	ND	ND	7	ND	ND	ND	ND
23	ND	ND	9	ND	ND	ND	8
27	ND	ND	ND	6	ND	ND	6
72	ND	ND	ND	ND	ND	ND	ND
73	ND	ND	ND	ND	ND	ND	ND
132	ND	ND	8	ND	ND	ND	ND
SOUTH BAY							
92	ND	ND	16	7	ND	ND	10
96	ND	ND	ND	5	ND	ND	9
113	ND	ND	12	5	ND	ND	12
119	ND	ND	ND	ND	ND	ND	ND
130	ND	ND	ND	ND	ND	ND	ND

Table 15. Metal concentrations in Biscayne Bay surface sediment ($\mu\text{g/g}$) (cont.).

Station number	As	Cd	Cr	Cu	Hg	Pb	Zn
CANALS AND RIVERS							
NORTH BAY							
46	ND	ND	9	12	0.1	60	15
51	ND	ND	19	45	0.9	ND	36
54	ND	ND	10	ND	ND	ND	ND
61	ND	ND	22	55	ND	50	25
62	NA*	ND	NA	ND	ND	ND	ND
137	NA	ND	NA	8	0.2	32	34
140	ND	ND	10	12	ND	ND	20
143	ND	ND	10	ND	ND	80	10
218	ND	ND	9	52	ND	520	252
CENTRAL BAY							
66	ND	ND	ND	ND	ND	ND	ND
101	NA	ND	NA	5	ND	ND	10
102	ND	ND	ND	12	ND	ND	78
232	ND	ND	20	117	ND	88	98
SOUTH BAY							
103	ND	ND	ND	65	0.3	ND	158
105	NA	ND	NA	ND	ND	ND	ND
106	ND	ND	ND	6	ND	ND	21
124	ND	ND	10	6	ND	ND	10

ND = None detected.

* NA = Not analyzed.

Table 16. Distribution of metal concentrations in Biscayne Bay surface sediments and surrounding areas ($\mu\text{g/g}$).

Metals	Present study				Previous study			
	North Bay (15)*	Central Bay (8)	South Bay (5)	Canals and Rivers (17)	Central Bay [❖]	South Bay [❖]	Upper Keys etc. [❖]	Florida Keys Canals [◆]
As	<1 (0)	<1 (0)	<1 (0)	<1 (0)	-	-	-	-
Cd	<5 (0)	<5 (0)	<5 (0)	<5 (0)	-	0.07 [▲] , 0.2 [◆]	-	-
Cr	<5 - 22 (5)	<5 - 9 (3)	<5 - 12 (2)	<5 - 22 (10)	6 - 7	5 - 8	3 - 30 (7 - 8) [✱]	10 - 18
Cu	<5 - 25 (11)	<5 - 6 (1)	<5 - 7 (3)	<5 - 117 (12)	-	<2 [▲] , 25 [◆]	-	1 - 30
Hg	<0.1 - 0.1 (1)	<0.1 (0)	<0.1 (0)	<0.1 - 0.9 (4)	0.2 - 0.3	0.1 - 0.2	0.1 - 5.8 (0.2)	0.1 - 0.3
Pb	<10 - 60 (5)	<10 (0)	<10 (0)	<10 - 250 (6)	12 - 30	14 - 25	12 - 361 (16)	0.1 - 1.5
Zn	<5 - 72 (11)	<5 - 8 (2)	<5 - 12 (3)	<5 - 252 (13)	1 - 6	1 - 22	1 - 100 (2)	10 - 54

* Number of samples analyzed from designated area.

❖ Manker (1975)

◆ Chesher (1974)

▲ Segar and Pellenbarg (1973) Card Sound

◆ Segar and Pellenbarg (1973) Turkey Point

✱ Manker (1975) Background values in parenthesis

Number of samples analyzed which contained detectable amounts.

mercury contamination is sewage. The mercury content of sewage is the result of incidental disposal by individuals and businesses. The sources include: water based paints, paper products, cosmetics, broken thermometers, discarded pharmaceuticals and runoff containing agriculture and lawn insecticides. Five samples contained detectable mercury concentrations. Manker established the background for this to be 0.2 $\mu\text{g/g}$ and detected values which ranged from 0.1 to 5.8 $\mu\text{g/g}$. Chesher reported values from 0.1 to 0.3 $\mu\text{g/g}$. A comparison of Manker's corresponding samples in south Biscayne Day shows a range of 0.1 to 0.3 $\mu\text{g/g}$. Values determined for this project ranged from 0.1 to 0.9 $\mu\text{g/g}$.

Lead is toxic to many plant species and is a cumulative poison in mammals. The two most widespread inputs of lead into the environment are the discharge of exhaust fumes from

internal combustion engines and its use in many paints. Lead is also widely distributed through its use in batteries, pigments, dyeing, glass and pesticides (lead arsenate). Values for this study ranged from <10 to 520 µg/g. Manker and Chesher reported values from 12 to 391 and 0.1 to 1.5, respectively. Manker established background lead values for this area at 16 µg/g. Segar and Pellenburg reported average values of 1 µg/g in Card Sound sediments and 3 µg/g in sediment near Turkey Point.

Zinc is essential for many organisms as it activates certain enzyme systems, but can be a serious pollutant in elevated quantities. The major input of zinc into the environment is through sewage systems. Zinc and its compounds have numerous commercial and domestic applications (e.g., soaps, paints, paper products, dyes, corrosive inhibitors for pipe lines and a combustion product of fossil fuels). The values for this study ranged from <5 to 252 µg/g. Manker and Chesher reported values from 1 to 100 and 10 to 54, respectively. Manker established background for this area at 2 µg/g. Segar and Pellenburg showed average values of 4 µg/g for Card Sound and 12 µg/g for Turkey Point.

Table 16 characterizes the distribution, concentration and compares the results of this study with the three previous studies conducted in Biscayne Bay and surrounding localities.

Comparing the range of values (Manker, 1975; and Segar and Pellenburg, 1973) detected in central and south bay and the background levels established for the upper Keys, Florida Bay and Biscayne Bay (Manker 1975) it is evident that central and south bays are within the limits and that north bay and the canals and rivers are, in some cases, in excess. Chromium, copper and zinc values in south and central bays are comparable in both ranges and background values, while lead and mercury are less than previously established values. In north bay two of the values for chromium, five for lead and seven for zinc were elevated above the maximum values detected in south and central bays, although they did not exceed the maximum values reported by Manker (1975) for the upper Keys, Florida Bay and Biscayne Bay area. Nine of the 14 sediment copper values were in excess of the maximum values detected in this study for south and central bays, although none exceeded the average value reported by Segar and Pellenburg (1973) for Turkey Point.

The canals and rivers which empty into Biscayne Bay showed the highest concentration of metals. The high values exceeded those reported by Manker (1975) and Chesher (1974) except for mercury and chromium. The maximum values for chromium, mercury, lead and zinc were detected in canals in north bay. The maximum value for copper was found in Goulds Canal. The values for chromium, copper, mercury and lead exceeded those reported by Chesher (1974) for a sanitary landfill in Key West.

SUMMARY AND CONCLUSIONS

The contaminants analyzed in this study can be grouped into two categories, 1) those compounds which do not occur naturally in the environment, the synthetic organic compounds and 2) those which do occur naturally but can be elevated to a level of toxicity, the metals.

In Biscayne Bay the order of occurrence (i.e., the number of samples in which the compound occurred) for the synthetic organics is:

PAE (96%) > herbicides (78%) > PCB (69%) > insecticides (38%)

The distribution of the PAEs is not surprising since these compounds are used extensively. Their concentration though is much higher than similar environments in the US. Their toxicity

and effect on the environment is still an area of scientific debate. The control of their usage and eventual input to the environment would take governmental regulations.

The herbicides were the second most frequently occurring compound. This would be expected since they are used extensively by both agricultural interests and the homeowner. Due to their rapid degradation it is unlikely that the parent compounds will pose a serious hazard, although their usage has been restricted to some degree.

The distribution of PCBs was predominantly concentrated in north bay and the canals and rivers. The concentrations of these compounds in Biscayne Bay were much higher than similar areas in the US.

This group of compounds has received much scientific attention which has resulted in the restriction of their usage. Large quantities of these compounds are used and their input to the environment will continue, although, hopefully, it will be on the decrease.

Most of the organochlorine insecticides found are no longer used or are restricted in use. Their occurrence should be on the decline however, this will take time because of their limited biodegradability. The high concentrations of endosulfan though may cause a problem because of its high toxicity to fish. The concentrations of DDT also would appear to be elevated in comparison to the values reported for the Florida Keys and other estuarine areas.

The evaluation of metal contamination is difficult since these elements occur naturally in the environment. The use of the results from previous studies in the Florida Keys and Card Sound to establish estimated natural background levels was presented to help interpret these data. The metals which exceeded these background values were chromium, copper, mercury, lead and zinc.

All of these above background values were detected in the canals and rivers entering Biscayne Bay.

In general, the high concentrations for both groups (synthetic organic compounds and metal) occurred in north bay (north of Rickenbacker Causeway) and in the canals and rivers entering the bay. The only exception to this was the PAEs which were ubiquitous. The elevated concentrations in north bay would be expected since this is the area of greatest urbanization and industrialization. The high concentrations in the canals entering central and south bay represent a source of pollutants into what is considered a relatively pristine portion of Biscayne Bay.

This study has documented the occurrence, distribution of metals and synthetic organic compounds in Biscayne Bay sediment and possible major sources. Since sediments yield an integrated long term record, the present status of these inputs is still not answered (i.e., are these contaminants still entering the bay?).

LITERATURE CITED

- Biscayne Bay Management Plan. 1981. Biscayne Bay Management Plan. Metropolitan Dade County Department of Environmental Resources Management and Department of Planning, 909 SE. First Avenue, Miami, Florida. p. 114
- Chesher, R. H. 1974. Canal Survey Florida Keys. Society for Correlation of Progress and Environment. Big Pine Key, Florida. p. 173.

- Corcoran, E. F., M. S. Brown, F. R. Baddour, S. A. Chasens and A. D. Freay. 1983. Biscayne Bay Hydrocarbon Study. State of Florida Dept. of Natural Resources, 100 Eight Avenue, SE., St. Petersburg, Florida 33701. Final Report. 327 p.
- Cuffe, S. T., and R. W. Gerstle. 1967. Emission from coal-fired plants. Public Health Service Pub. 999-AP-35. P. 26.
- Duke, T. W., J. N. Willis and T. J. Price. 1966. Cycling of trace elements in the estuarine environment. I. Movement and distribution of zinc 65 and stable zinc in experimental ponds. Chesapeake Science. 7(1):1-10.
- Edwards, C. A. 1966. Insecticide residues in sails. Residue Rev. 13:83-132.
- Environmental Protection Agency. 1979. Methods for Chemical Analysis of Water and Wastes. US. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268. EPA-60074-79-020.
- Giam, C. S., H. S. Chan, G. S. Neff and E. L. Atlas. 1978. Phthalate ester plasticizers: a new class of marine pollutant. Science. 199:419-421.
- Hanson, D. 1983. Plasticizer scrutinized for possible health risks. C & E News. Feb. 28. pp. 36-37.
- Lawrence, W. H. and S. F. Tuell. 1979. Phthalate esters: the question of safety- an update. Clinical Toxicology. 15(4):447-466.
- McEwen, F. L. and G. R. Stephenson. 1979. The Use and Significance of Pesticides in the Environment. John Wiley & Sons, New York. p. 538.
- Manker, J. P. 1975. Distribution and Concentration of Mercury, Lead, Cobalt, Zinc and Chromium in Suspended Particulates and Bottom Sediments - Upper Florida Keys, Florida Bay and Biscayne Bay. Ph.D. Thesis. Rice University, Houston, Texas. p. 114.
- Murray, H. E., L. R. Ray and C. S. Giam. 1981. Phthalic acid esters, total DDTs, and polychlorinated biphenyls in marine samples from Galveston Bay, Texas. Bull. Environ. Contam. Toxicol. 26:769-774.
- Peterson, J. C., and D. H. Freeman. 1982. Phthalate ester concentration variations in dated sediment cores from the Chesapeake Bay. Environ. Sci. Technol. 16(8):464-469.
- Plumb, Jr., R. H. 1981. Procedures for Handling and Chemical Analysis of Sediment and Water Samples. Environmental Laboratory, US. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, Mississippi 39108. Contract No. EPA-4805572010.
- Riley, J. P. and R. Chesher. 1971. Introduction to Marine Chemistry. Academic Press, London.
- Roessler, M. A., and G. L. Beardsley. 1975. Biscayne Bay: its environment and problems. Fla. Sci. 37(4):186-203.
- Schwartz, H. E., C. J. M. Anzion, H. P. M. Van Vliet, J. W. Copius Peeredooms and U. A. Th. Brinkman. 1979. Analysis of phthalate esters in sediments from Dutch rivers by means of high performance liquid chromatography. Intern. J. Environ. Anal. Chem. 6:133-144.

- Segar, D. A., and R. E. Pellenbarg. 1973. Trace metals in carbonate and organic-rich sediments. *Mar. Poll. Bull.* 4(9):138-142.
- Stevens, L. J., C. W. Collier and D. M. Woodham. 1970. Monitoring pesticides in soils from areas of regular, limited and no pesticide use. *Pestic. Monit. J.* 4:145-166.
- Thompson, J. F. 1977. *Manual of Analytical Methods for the Analysis of Pesticides Residues in Human and Environmental Samples.* U.S. Environmental Protection Agency, Toxicology Division, Research Triangle Park, N.C. 27711.
- Wiersma, G. B., W. B. Mitchell and C. L. Stanford. 1972. Pesticide residue in onions and soil. *Pesti. Monit. J.* 5:345-347.
- Wurster, C. F. 1969. Chlorinated hydrocarbon insecticides and the world ecosystem. *Biol. Conser.* 1:123-129.
- Zitko, V. 1972. Determination, toxicity, and environmental levels of phthalate plasticizers. Fisheries Research Board of Canada, Technical Report No. 344. p. 37.