

## Report on the Analyses of Five (5) Biscayne Bay Sediments

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### Introduction

Five sediment samples collected from Biscayne Bay were selected for an analysis of certain contaminants. In selecting these samples consideration was given to their hydrocarbon content (Corcoran, 1982) and their location within the Bay. The contaminants concentration chosen for examination were certain pesticides (aldrin, heptachlor epoxide, chlordane, dieldrin, DDE, DDD, DDT, endrin, toxaphene, methoxychlor, mirex), the herbicides (dowpon, dicamba, 2,4-D, silvex), the polychlorinated biphenyls, phthalates and trace metals cadmium, copper, mercury, lead, zinc, arsenic.

### Methods

The five selected cores (Stations 62, 101, 105, 137 and 147)\* were removed from the cold storage archive, unsealed and the top five centimeters was removed. All the sides were scraped free of possible contamination by the core liner, the sediment was placed in wide mouth jar, covered with aluminum foil and a screw top cap, and taken to the laboratory for analyses.

In the laboratory approximately 50 grams of wet sediment was weighed into a preextracted Soxhlet thimble. The thimble was placed in a Soxhlet apparatus and the sediment was extracted for 24 hours with a 1:1 mixture of hexane and acetone. The remainder of the sediment was placed in the freezer to be used later for dry weight determinations and trace metal analyses.

### Pesticide Analysis

The analyses for the organochlorine hydrocarbon pesticides were conducted according to the procedure described in the U.S. EPA manual, "Analysis of Pesticide Residues in Human and Environmental Samples" as revised by Joseph Sherma and Morton Beroza except the alumina clean-up was omitted.

The extract of acetone-hexane was carefully removed from the Soxhlet apparatus by washing with several rinses of hexane. The resultant extract was divided into two equal portions. One half was placed in a separatory funnel and the other half was acidified and set aside for the herbicide analyses. Organic free, distilled deionized water was added to the separatory funnel and the lipid soluble material was forced into the hexane layer. After washing the hexane layer several times with water the acetone-water extracts were discarded and the hexane extract was dried over anhydrous sodium sulfate, concentrated in a Kuderna-Danish apparatus and the chromatographed on a Florisil column. Six percent ether-hexane was used to collect the first fraction (this fraction contained most of the organochlorine pesticides and the polychlorinated

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biphenyls). Fraction two was obtained by using 15% ether-hexane (this fraction contained oxygenated organochlorine pesticides, e.g. heptachlor epoxide, dieldrin and some plasticizers), and to obtain fraction 3, 50% ether-hexane was used as an elutant. (Fraction 3 contained mainly the remainder of the plasticizers, e.g. phthalic acid esters.) Each fraction was concentrated to less than 5 mL and 5 µl portions were injected into a gas chromatograph equipped with Ni-63 electron capture detectors. Two 6-foot packed glass columns were used (1.5% OV17/1.95% OV210 and 4% SE-30/6% OV210). Identification and concentrations calculations were made from the use of standard curves prepared from pure compounds obtained from the EPA repository located in Research Triangle Park, North Carolina. Recovery of these compounds was from 85 to 94% as shown by recovery extractions run at the same time. The concentration of pesticide and phthalic acid ester concentrations are listed in Table 1.

#### Herbicide Analysis

The acidified portion of extract was washed into a separatory funnel using diethylether and was freed of acetone by using acidified organic-free, distilled, deionized water. The combined hexane-ether extract was dried over anhydrous sodium sulfate and was analyzed according to the procedure published in the Federal Register, 38, No. 75, part 2. In this procedure the chlorinated phenoxy acids and their esters are isolated and converted to the acid form. These isolated compounds were then changed to the potassium form by refluxing with potassium hydroxide. (In the potassium form these compounds are not soluble in ether and so can be washed free of interfering substances with ether.)

After these compounds were freed of interfering substances, the aqueous solution was acidified and the chlorinated phenoxy acids were extracted three times with ether. After drying a small amount of benzene was added to the ether extract and it was concentrated to approximately 0.5 mL. The concentrate was then esterified with boron trifluoride in methanol by holding it at 50 °C for 30 minutes. The esterified compounds in benzene were separated from the methanol by adding 5% sodium sulfate solution. The benzene solution was chromatographed on a micro Florisil column and the eluate was analyzed by gas chromatography at 180 °C. The methyl ester concentrations were calculated from standards made from pure compounds and are reported in Table 1.

#### Polychlorinated Biphenyl Analyses

Fraction 1 from the pesticide analysis was concentrated to less than one milliliter using a Kuderna-Danish concentrator in a steam bath. The remaining solvent was then removed under a stream of nitrogen at room temperature. Two milliliters of alcoholic potassium hydroxide was added, the condenser was re-attached and the mixture was saponified at 100 °C for thirty minutes. After cooling to room temperature, the condenser was removed, two (2) mL of water and five (5) mL of hexane were added and the mixture was mixed vigorously for 30 seconds on a vortex mixer. After the layers separated, two epiphan (hexane) was pipetted into a concentrator tube. This process was repeated twice more using additional 5 mL portions of hexane. The hexane extracts were combined and concentrated. Analysis was made with gas chromatography using Aroclors 1222 through 1268 including 1016 as standards for identification. Aroclor 1254 was used to evaluate the PCB.

## Trace Metal

The sediments were weighed out into silica dishes and placed in a drying oven at 60 °C. (Sixty degrees was used to prevent loss of mercury.) The sediments were removed from the oven and cooled in a desiccator. After reaching room temperature the sediments were homogenized and replicate samples were weighed into tared silica flasks. Half the samples were covered with concentrated nitric acid and the other half were covered with nitric acid-sulfuric mixture. Cold fingers were inserted in the mouths of each flask and they were placed under a bank of infra-red lamps to digest. After digestion the residues were dissolved in dilute nitric acid. The analyses were done by atomic absorption spectrophotometer using standards prepared from pure metals for evaluation. Cold vapor atomic absorption spectrophotometry was used for the mercury samples. Table 2 shows the results obtained.

## Results and Conclusion

While all the five sediments were contaminated with pesticides, PCBs, PAEs, and heavy metals, the sediment from station 137 (located near the mouth of Little River) contained the greatest concentration. This sample also contained the highest concentration of organic matter and the greatest percentage of silt-day fraction. So it might be expected to be the most contaminated. However, the sediments from the Miami River area (station 62) contained higher concentrations of petroleum hydrocarbons, and since most of the contaminants measured are lipid-soluble, it is a little unusual to find the higher concentrations in the sediment from station #137.

The findings from the pesticide analysis were also a little unusual in that DDT residues along with DDD [WERE FOUND], but no DDE. Usually when DDT degrades in the environment, the first product formed is DDE. Also unusual was the finding of endosulfan I. This compound is probably relatively a newcomer to the sediment while the DDT residues have probably been there for some time. Because of the large amount of termite control in this area, it was expected that chlordane residues and heptachlor epoxide would be found. No heptachlor epoxide and only a trace of chlordane were found.

Although dowpon, dicamba, 2,4-D, and silvex were looked for in all the sediments only one contained 2,4-D. All the chromatograms were checked very carefully for silvex. No silvex was found, but 2,4,5-T was found in three of the sediments. Since silvex is the propionic ester of 2,4,5-T there is the possibility that silvex was hydrolyzed to the acid and then the methyl ester was measured. Because dowpon is used so extensively as a grass killer along fences and driveways, it would be expected some of this compound would show. However, all of these samples were from industrial areas so possibly dowpon would be more prevalent in the residential areas.

The Aroclors in sediments from stations #62 (Miami River Month) and #137 (Little River Month) and possibly #147 were definitely Aroclor 1254. Since Aroclor 1254 has been a definite constituent of industrial oils such as insulating transformer oils, brake fluids, etc., it was no surprise to find this compound in the sediments of these areas.

At the present time, phthalic acid esters seem to be ubiquitous, even samples from pristine areas contain some plasticizers. However, the unusual find was that only butyl benzyl phthalate [BBP] and diethylhexyl phthalate [DEHP] were found in these sediments. Usually, there are concentrations of diisobutyl phthalate and dibutyl phthalate present, however, these compounds hydrolyze rather readily and are also attacked by bacteria. The hydrolysis products are alcohols which are toxic. The BBP and DEHP are much more refractory, thus they remain as sedimentary constituents.

While the concentrations of the heavy metals are not extremely high, they are high enough to be of some concern. For example, the mercury content in sediments from stations #137 and #147 are values that resemble those of heavily polluted areas around a boat yard. The copper and lead concentrations of station #137 are also indicative of a polluted area.

Although these measurements are of a preliminary nature, the findings are such that a more extensive monitoring program is indicated.

Table 1. Pesticides, PCBs, PAEs [TABLE CAPTION INCOMPLETE IN DOCUMENT STORED AT THE UNIVERSITY OF MIAMI.]

	Sample #62	Sample #101	Sample #105	Sample #137	Sample #147
Organic matter (%)	7.5	15.8	7.6	12.5	6.7
Silt/clay (%)	52.5	81.0	34.0	37.0	64.0
Aldrin	ND	ND	ND	ND	ND
Heptachlor epoxide	ND	ND	ND	ND	ND
Chlordane	ND	ND	ND	TR	ND
Endosulfan (ng/g)	124.2	71.5	14.5	1014.3	30.5
DDE (ng/g)	ND	ND	2.3	ND	ND
DDD (ng/g)	2.3	ND	0.1	ND	ND
DDT (ng/g)	2.2	5.8	ND	52.7	ND
Toxaphene	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	ND
Dowpon	ND	ND	ND	ND	ND
Dicamba	ND	ND	ND	ND	ND
2,4-D (ng/g)	ND	33.8	ND	ND	ND
2,4,5-T (ng/g)	ND	11.4	ND	44.6	35.0
Silvex	ND	ND	ND	ND	ND
Aroclor 1254 (ng/g)	58.6	15.0	17.4	21.4	3.6
Butyl benzyl phthalate	156.0	308.8	156.0	450.4	75.2
Diethyl hexyl phthalate	113.0	521.8	1175.0	12,390.0	2037.4

Table 2. Trace metals (ppm dry weight)

Sample	Moisture (%)	Mercury	Iron	Copper	Cadmium	Lead	Zinc
62	33	0.07	547	3.1	0.1	2.2	4.3
101	68	0.05	1130	5.1	0.1	2.9	10.5
105	51	0.03	628	2.0	0.1	1.0	4.4
137	64.7	0.16	2580	7.7	0.1	32.0	34.0
147	48.6	0.10	1720	2.2	0.1	2.2	72.0

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