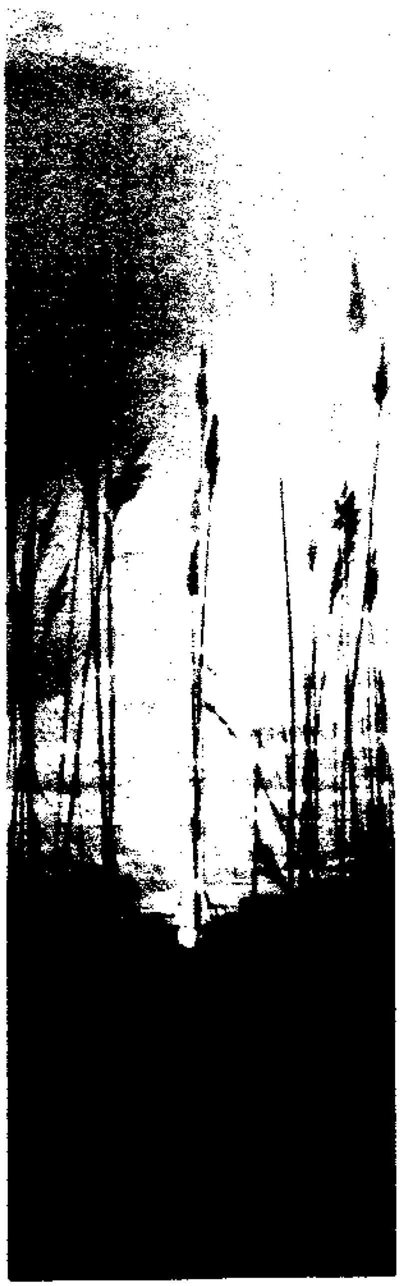 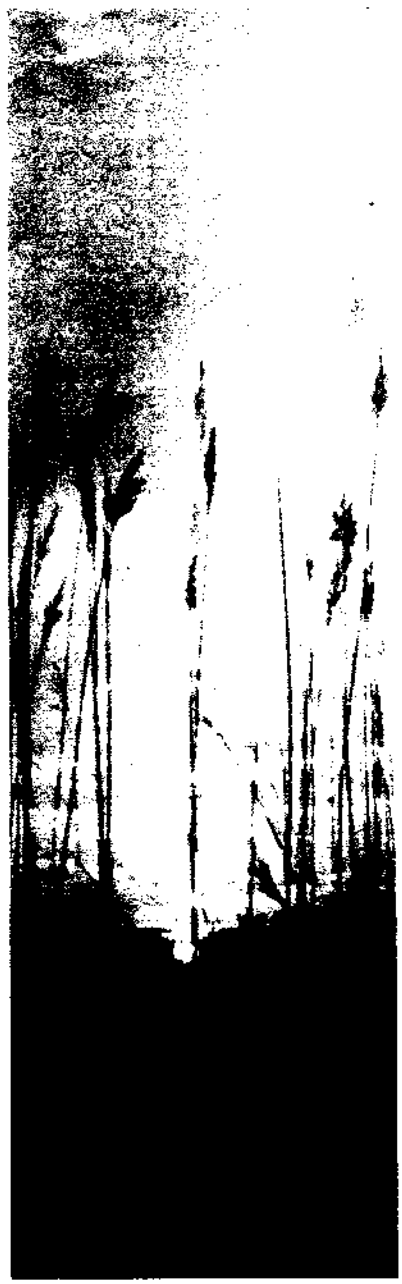 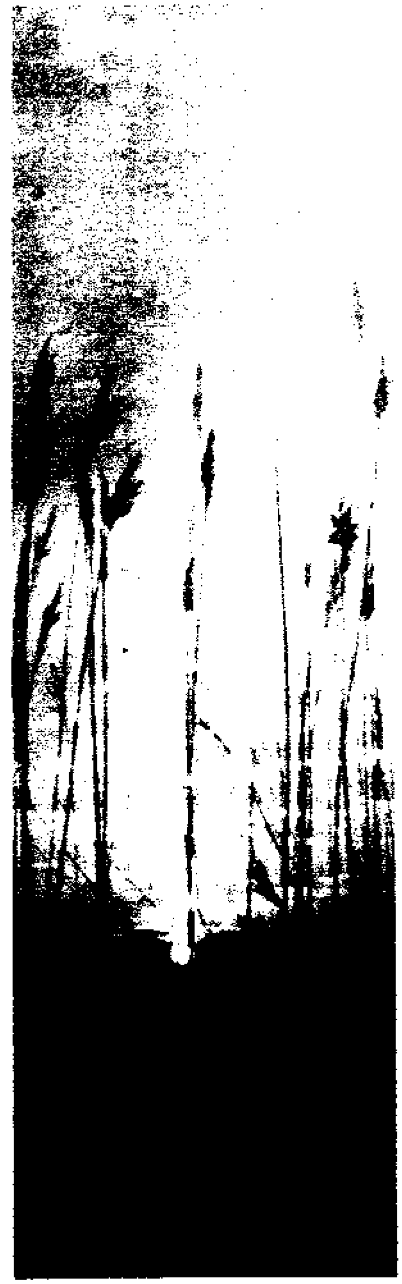

TRACE METALS IN CORES FROM THE GREAT MARSH

Lewes, Delaware

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DEL-SG-12-72
This work is a result of research sponsored by NOAA Office of Sea Grant, Dept. of Commerce, under Grant no. 2-35223

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ABSTRACT

Four twelve-foot cores and one eighteen-foot core were taken near Lewes, Delaware. Samples were taken at two-foot intervals down the core beginning at two feet below land surface. The samples were analyzed for zinc, copper, chromium, iron lead and cadmium. The levels of lead and cadmium were below the level of detectability by the methods used (i.e. less than 1 ppm in the sediment sample). Zinc showed a slight increase in average concentration with increasing depth. Copper and cadmium showed no significant changes with depth. There appears to be no significant difference in the metal concentrations between the $<63\mu$ and $>63\mu$ fractions.

ACKNOWLEDGMENTS

The work is the result of research sponsored by Sea Grant No. 2-35223. Mr. William Treasure assisted the authors in obtaining the cores from the Great Marsh.

INTRODUCTION

Four 12-foot cores and one 18-foot core were taken in the Great Marsh (Broadkill Marsh) near Lewes, Delaware, for the purpose of analyzing the areal and vertical changes in trace metal concentration in sediments deposited prior to the industrialization of the Delaware Bay watershed. Figure 1 shows the location of each of the five cores and the principal geographic features of the marsh.

Previous work has been done in the Great Marsh by Swain (1971) on the biogeochemistry of core samples; Elliott (1972), on the physiography, classification and geologic history of the Great Marsh, and Daiber and Beattie (1969, 1970), on the hydrographic parameters and flushing pattern of the tidal portion of the Broadkill River. Biggs, Miller, and Otley (1972) have reported on trace metals in a branch of the Broadkill River (Beaverdam Creek).

The sediments sampled for this study are all of marginal marine origin of brackish or salt-water conditions. The sediments of the Great Marsh were deposited during the Holocene marine transgression and deposition is apparently continuing unabated today. Lagoonal muds underlie the more recently formed salt-marsh materials. According to Kraft (1971), the coastal lagoon silted in during the late Holocene Epoch, possibly just prior to settlement of the area by Europeans, and salt-marsh conditions developed. Cores BB-2, BB-3

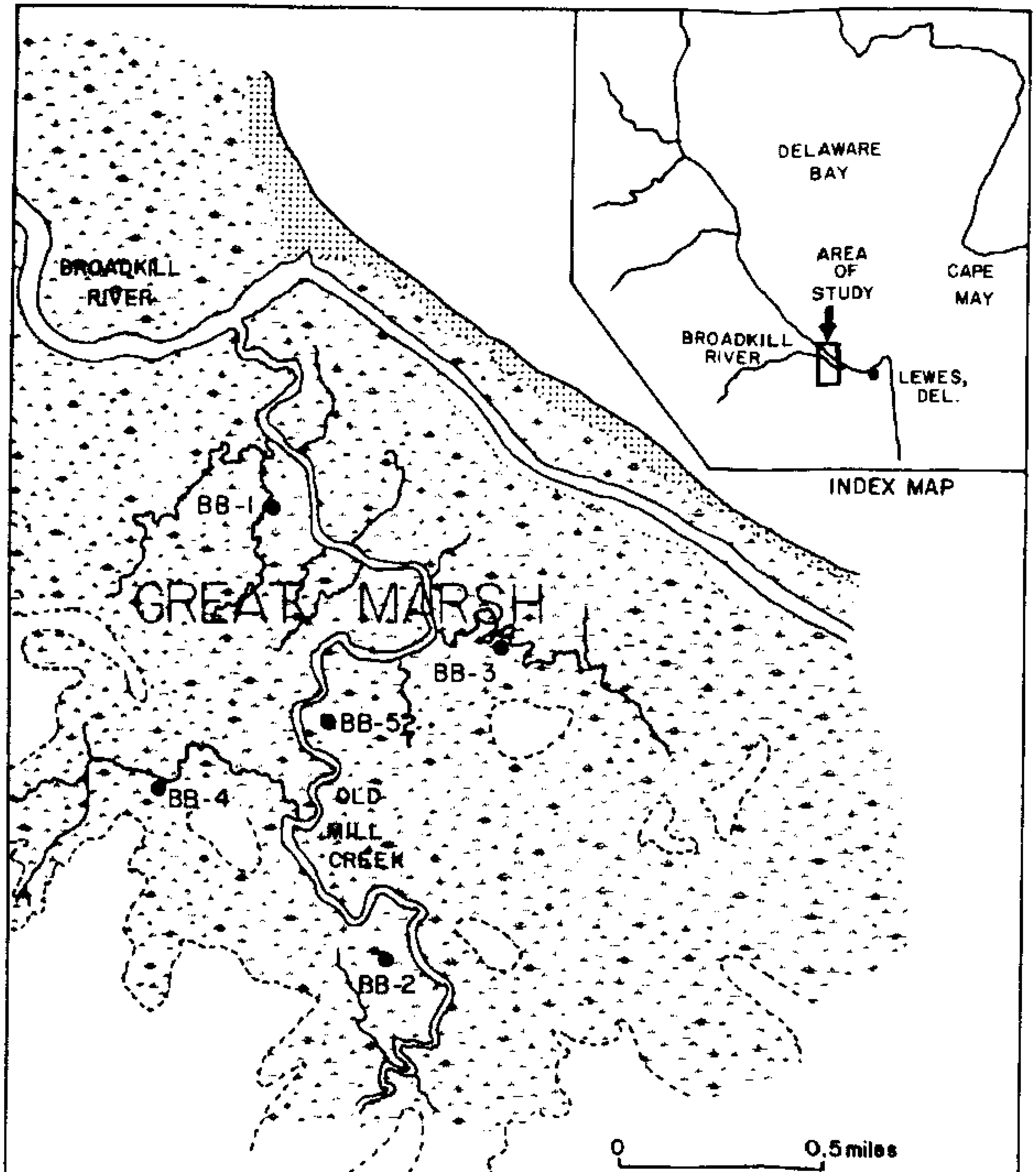

Figure 1 - Sample location map showing the area presently occupied by marsh.

and BB-5 have material in the lower halves of the cores which were deposited under open water (lagoonal ?) conditions whereas cores BB-1 and BB-4 contain materials in their lower sections which more closely resemble present day salt-marsh deposits.

METHODS

Coring operations: The cores were taken by hand driving lengths of 2 1/2" cellulose-acetate-butyrate plastic pipe into the sediment. After the pipe was extracted, it was cut into two-foot sections and a 6" sample was extruded from the lower end of each section. The Eh of the extruded sample was measured immediately using an Orion model 404 pH meter. The extruded samples were stored in plastic sample bags and returned to the laboratory for further study. The 2-foot sections of plastic pipe containing the remaining core material were also returned to the laboratory and described by visual examination. Color descriptions are based on comparison to the Rock Color Chart (Goddard, 1963). The log of each core is presented in Appendix I.

Sample numbering system: The following system was used for the identification of samples:

1. The first two letters of the sample identification "BB" refer to samples taken for this study.
2. The numeral following the letters and preceded by a dash refers to the core number from which the sample was taken.
3. The second numeral, preceded by a "#" refers to the sample number from that core, numbered from the top of the core downward.

Thus, sample BB-4#2 refers to the second sample from the top of the core (approximately four feet below land surface) from the fourth core taken for this project and BB-4#3 would refer to the third sample from the top (approximately six feet below land surface) of the same core.

Laboratory procedures: A fifty to one-hundred gram portion of the extruded sample was weighed and then separated by wet sieving on a 63μ sieve into two portions: a <63μ fraction and a >63μ fraction. Each portion was collected and the supernate water was removed by decanting and drying in a 70°C oven. The weight of each dry fraction was recorded and the difference between weight of the original sample and the combined dry weights of the <63μ and >63μ fractions was calculated. The weight loss thus calculated was assumed to be the loss of the water content of the original samples. The Eh, percent weight loss (H_2O), percent <63μ, and percent >63μ of each sample are recorded in Appendix II and are shown graphically in Figures 2 to 7. The large majority of the >63μ fraction in most samples was composed of organic fragments (peat) primarily (Swain, 1971) *Spartina* and *Disticlis*, with lesser quantities of *Phragmites* and pondweeds. The <63μ fraction was composed primarily of inorganic particles. It was hoped that it would be possible to determine whether the trace metals in the marsh were primarily bound in the organic or the inorganic fraction of the sediment by separating the samples into the "greater than" and "less than" 63μ fractions.

Three grams of each of the dry sample fractions were powdered in

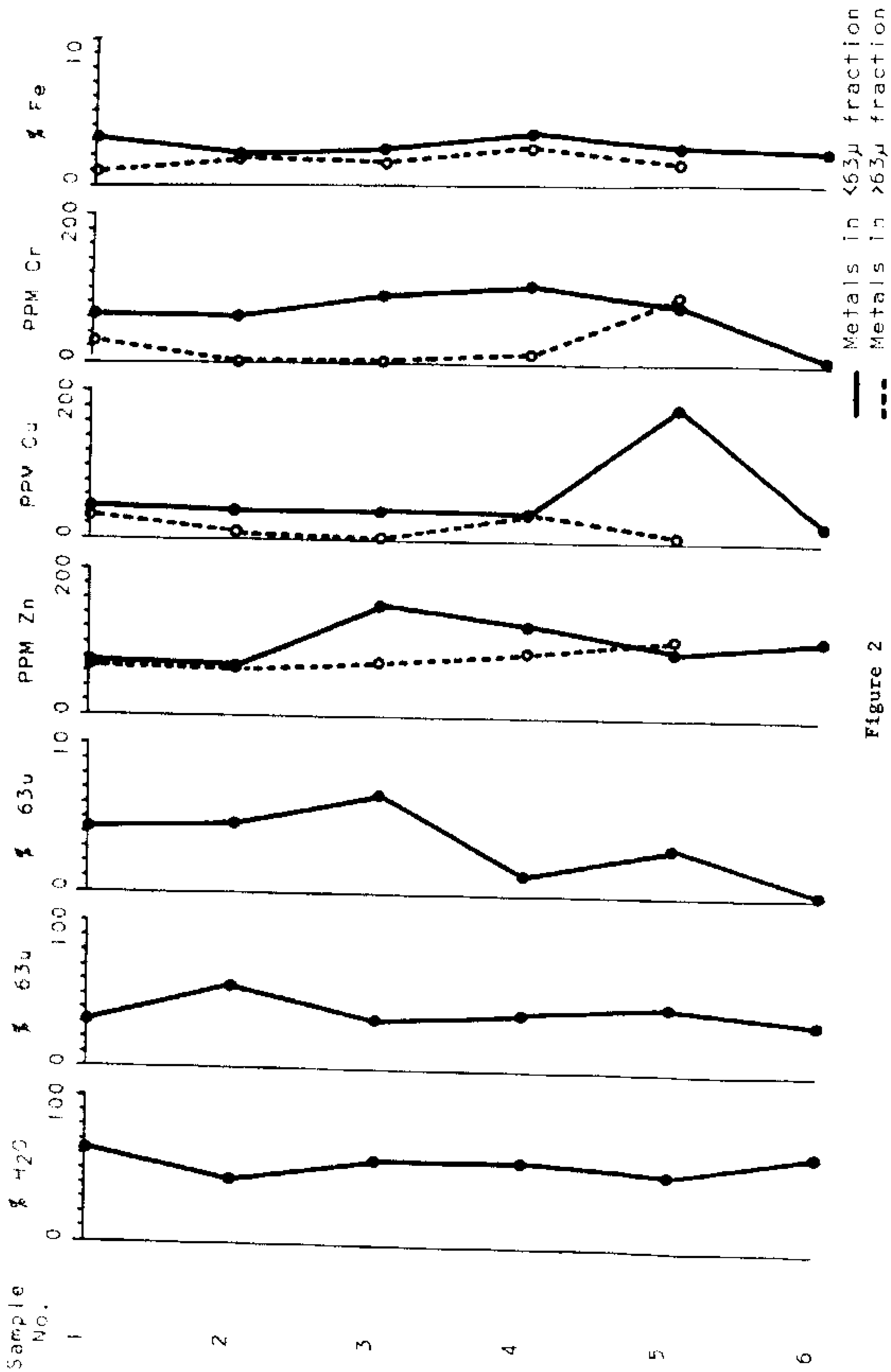
CORE BB-1
% Fe
PPM Cr
PPM Cu
PPM Zn
% 63u
% 63u
% H2O
Sample No.
1
2
3
4
5
6
0
10
0
200
0
200
0
200
0
10
0
100
0
100
Metals in <63μ fraction
Metals in >63μ fraction

Figure 2

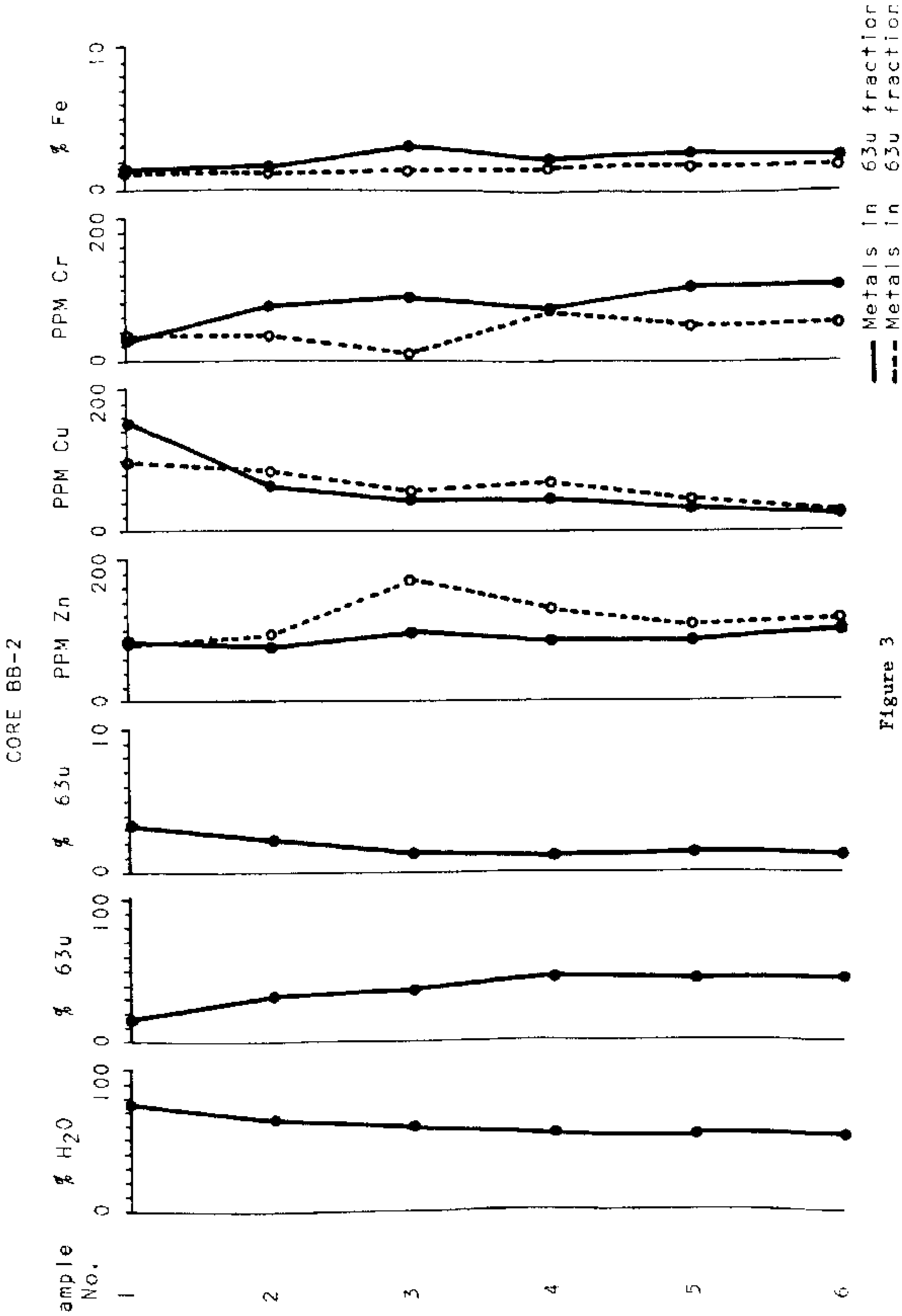
CORE BB-2
% Fe
PPM Cr
PPM Cu
PPM Zn
% 63u
% 63u
% H_2O
Sample No.
1
2
3
4
5
6
0
10
0
200
0
200
0
200
0
10
0
100
0
100
Metals in 63u fraction
Metals in 63u fraction

Figure 3

CORE BB-3

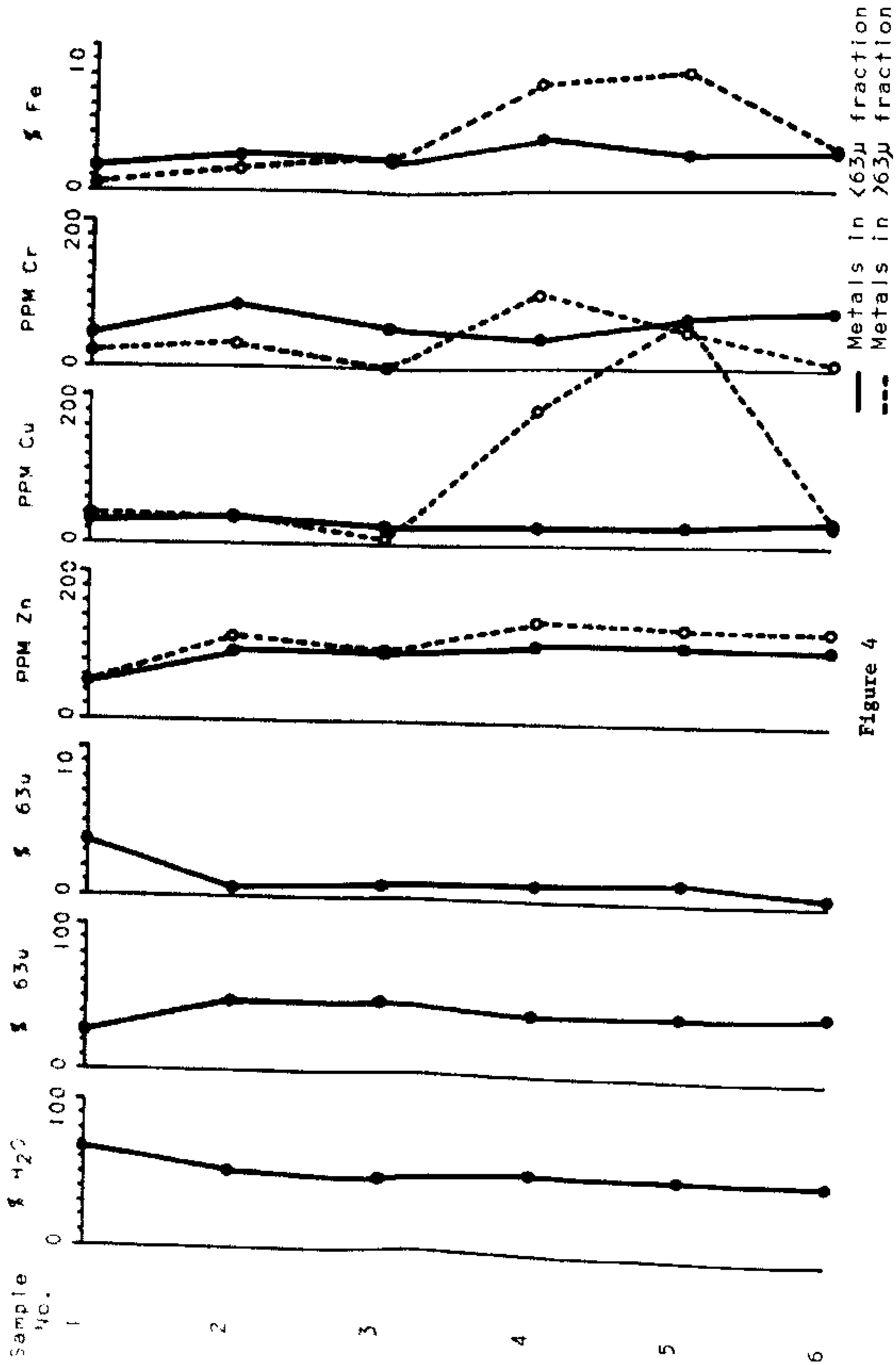

Figure 4

CORE BB-4

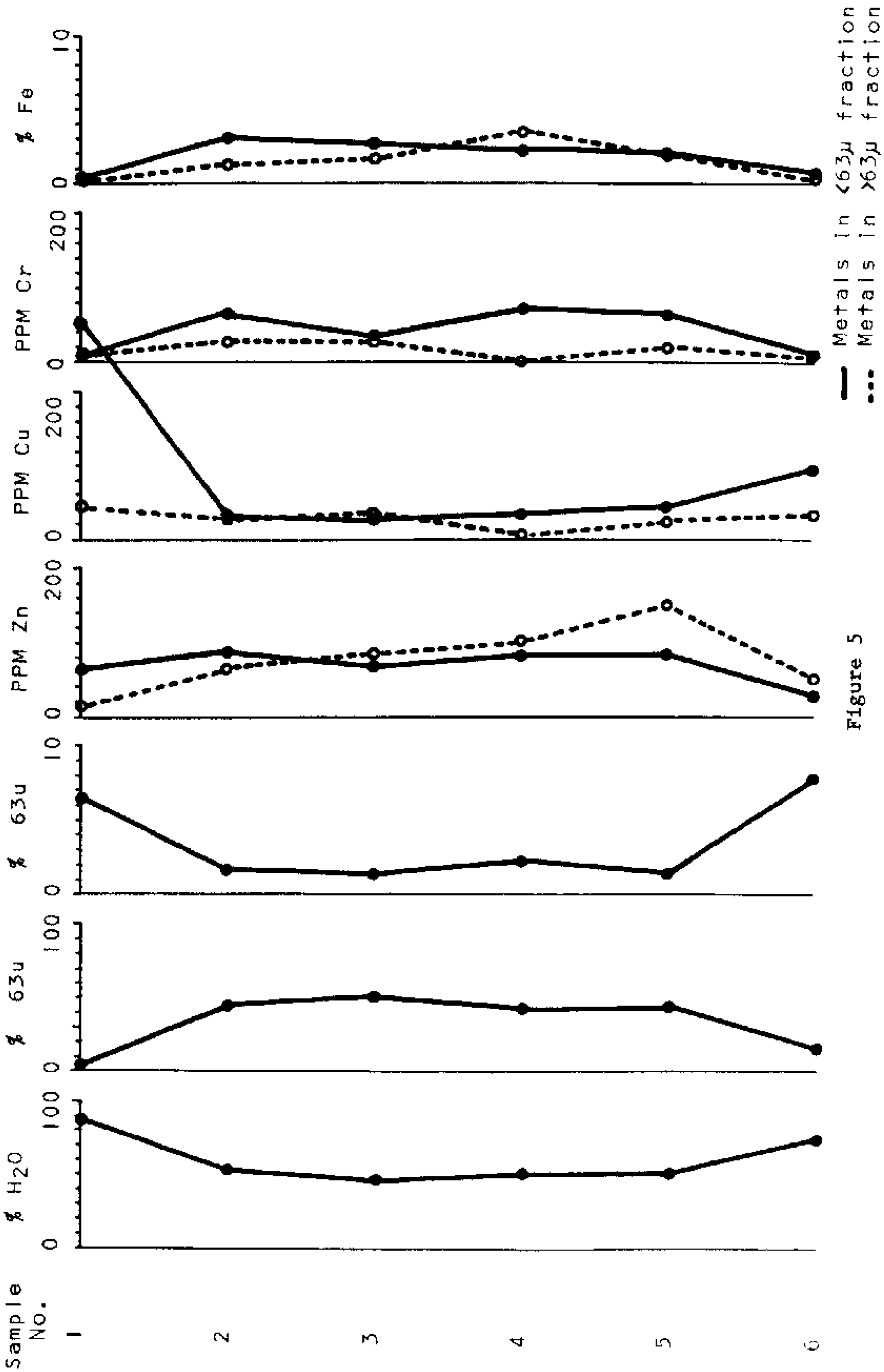

Figure 5

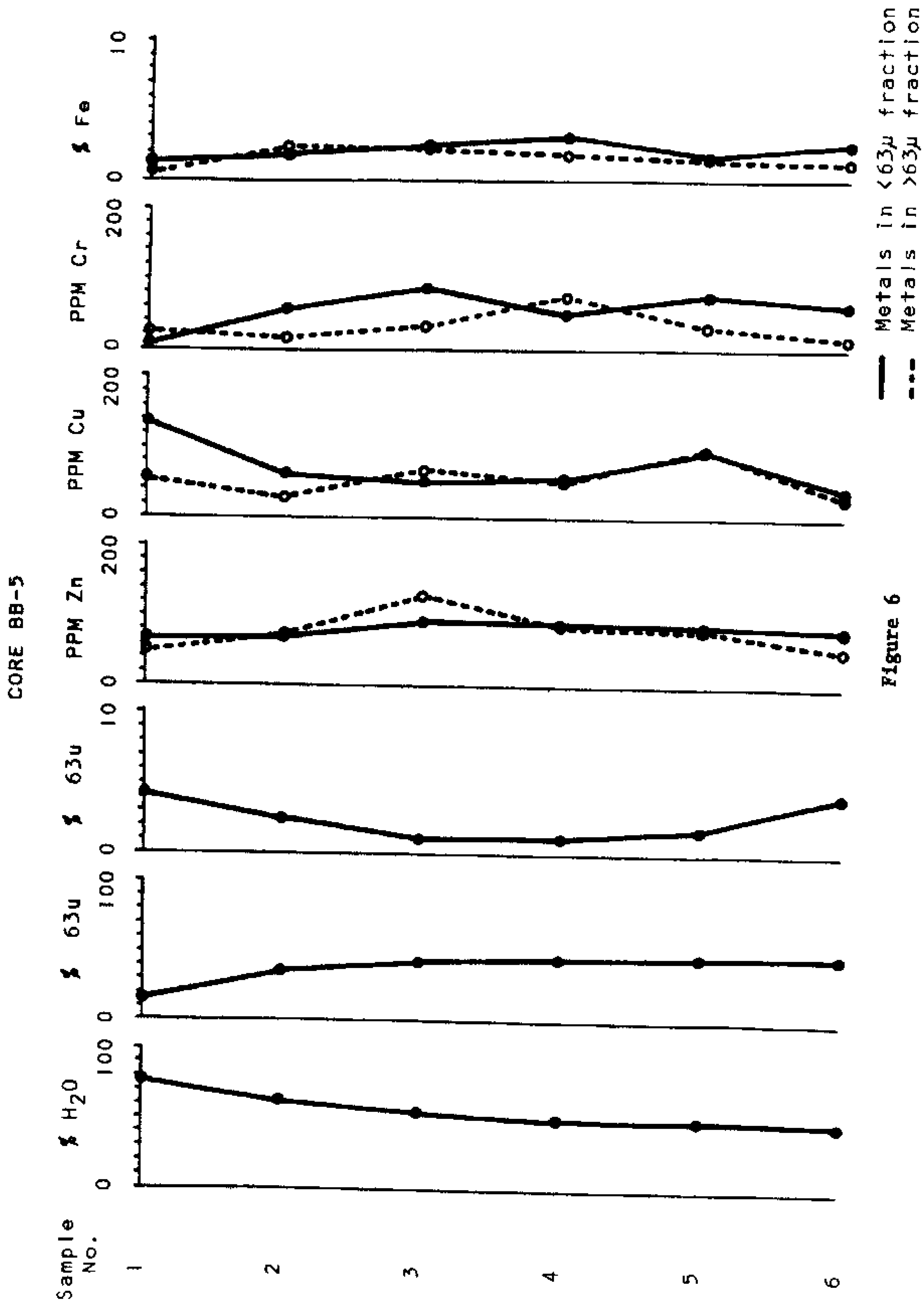
CORE BB-5
% Fe
PPM Cr
PPM Cu
PPM Zn
% 63u
% 63u
% H_2O
Sample No.
1
2
3
4
5
6
0
10
0
200
0
200
0
200
0
10
0
100
0
100
Metals in <63μ fraction
Metals in >63μ fraction

Figure 6

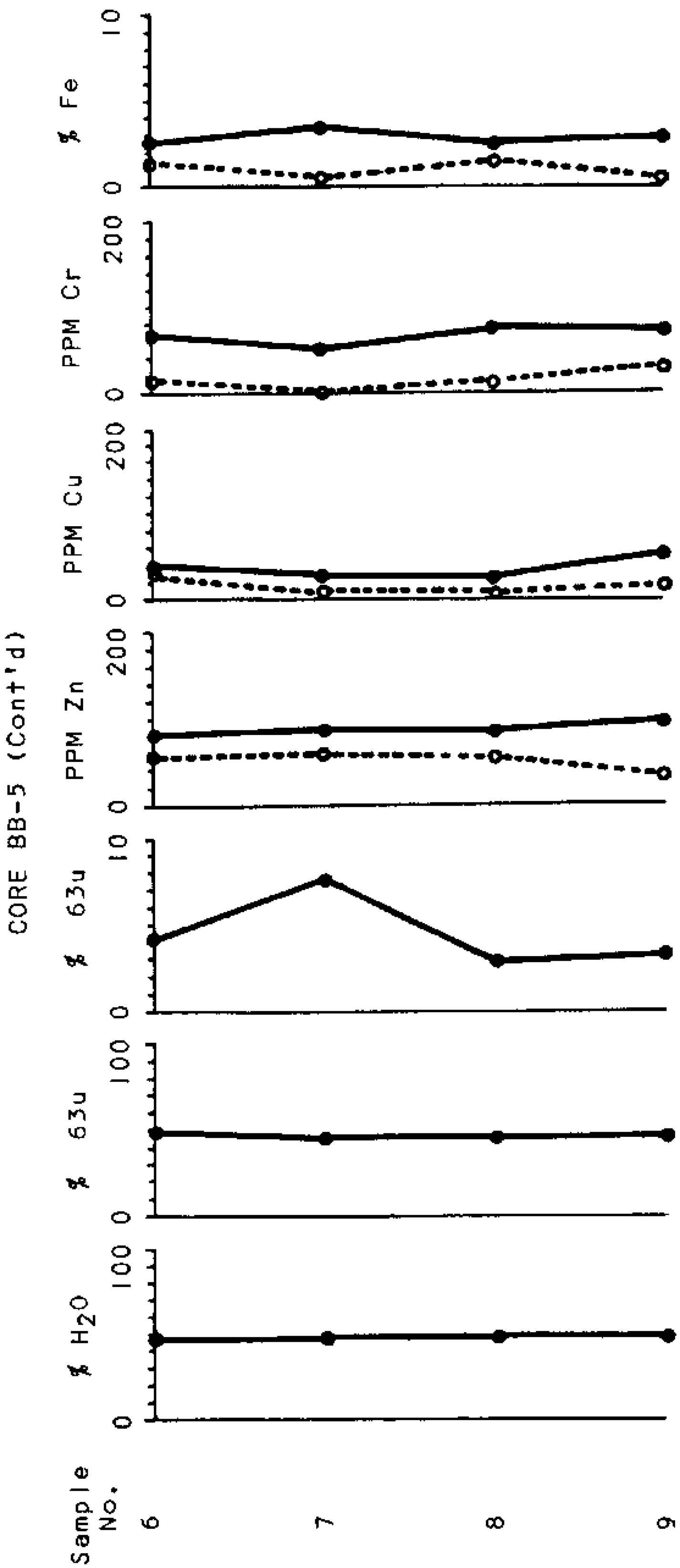
CORE BB-5 (Cont'd)
% Fe
PPM Cr
PPM Cu
PPM Zn
% 63u
% 63u
% H_2O
Sample No.
6
7
8
9
0
10
0
200
0
200
0
200
0
10
0
100
0
100

Figure 7

a ball mill and placed in 500 cc's of 10% HCl in a plastic bottle and heated for 96 hours in a 70°C oven to extract the metals. The material was filtered through a 0.47μ Millipore filter and the solution analyzed by atomic absorption techniques on a Jarrell-Ash model 800 Atomic Absorption Spectrophotometer for zinc, copper, chromium, iron, lead, and cadmium.

RESULTS

The water content of the cores decreases with depth in the cores. Typical values for water content range from 80% at -2' to 50% at -12'. Swain (1971, p. 550) feels that "...primary sorting by wave action rather than post-depositional compaction has been responsible for the low moisture values..." in the lower portions of the cores.

The procedures used for this study were too insensitive to determine the concentrations of lead and cadmium in the samples. Under the operating conditions used on the atomic absorption unit, 10 ppb (parts per billion) of these two elements were easily detectable in prepared standard solutions. In the solutions containing the metals from the sediment samples, lead and cadmium were not detectable. It was concluded therefore, that extractable lead and cadmium were below the levels in the standard solutions and therefore less than 1 ppm in the samples.

The results of the analyses for zinc, chromium, copper and iron are tabulated in Appendix II and are shown graphically in Figures 2 to 7.

The zinc, copper, and chromium content generally ranged from 10-200 ppm. No generalization can be made at this time concerning fractionation of the trace metals between the <63μ and the >63μ fractions: furthermore, there appear to be no major changes in concentration of these trace metals with depth in the core. Zinc does show a slight increase with depth from approximately 70 ppm at -2' to approximately 95 ppm at -12' in the core.

Iron was extracted from the materials studied in concentrations of 1-3% of the dry sample weight. In general, significantly more iron was extracted from the finer sample fraction than from the coarser fraction. It is believed that this is probably due to the solution of chlorite clay minerals by the warm HCl in the $<63\mu$ fraction. In samples BB-3#4 and BB-3#5 high iron concentrations in the $>63\mu$ fraction are also accompanied by anomalously high concentrations of copper (see Figure 4).

SUMMARY

The sediments analyzed for study show very little variation in the metals studied either areally or vertically. Contrary to expectation, there was little difference in the concentration of trace metals between the $<63\mu$ fraction, which was composed primarily of inorganic particles, and the $>63\mu$ fraction, which was composed primarily of organic (peat) fragments. Zinc did show a slight increase with depth and iron appeared to be more abundant in the $<63\mu$ fraction.

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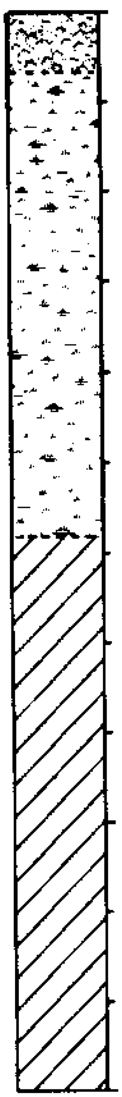
APPENDIX I

CORE DESCRIPTIONS

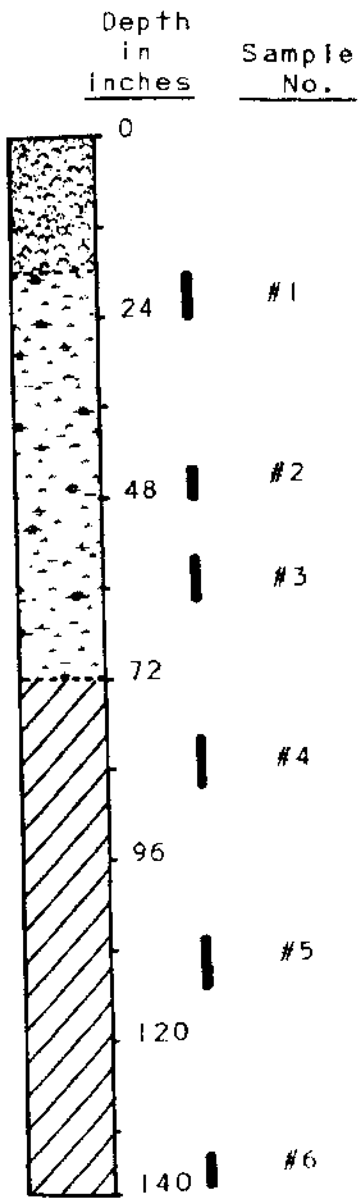
CORE BB-1



Depth in inches	Sample No.	Description
0		
	#1	0-8" *Peat*, muddy, dark grey (N-3).
		8-70" *Mud*, peaty to slightly peaty, soft, medium grey.
24		
	#2	
48		
	#3	70-144" *Mud*, slightly stiff to medium soft, mottled medium dark grey (N-4) to olive grey (5Y 4/1), occasional plant fragments and shells of *Nassarius obseletus Say* and *Mytilus edulis Linné*.
72		
	#4	
96		
	#5	
120		
144	#6	End of core.

Figure 8

CORE BB-2



Description

0-8" Peat, with very little mud grading downward into

8-18" Peat, muddy, greyish brown (5YR 2/2).

18-72" Mud, peaty, soft, mottled dark brown (5YR 3/2) and dark grey (N-3) grading into

72-86" Mud, soft with plant fragments mottled greyish brown (5YR 3/2) and olive grey (5Y 4/1).

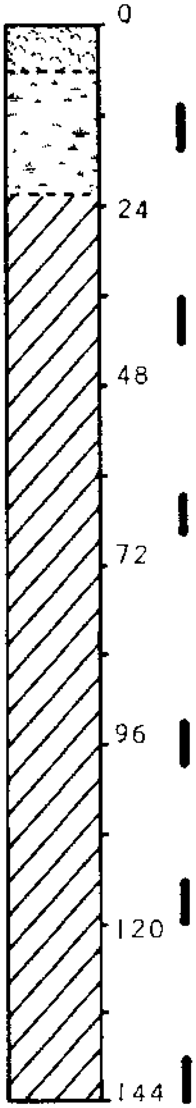
86-140" Mud, soft, with few plant fragments, olive grey (app. 5Y 3/1), shell fragments of *Nassarius obseletus Say* and *Periploma*? sp.

Mud becoming medium soft with increasing depth.

End of core.

Figure 9

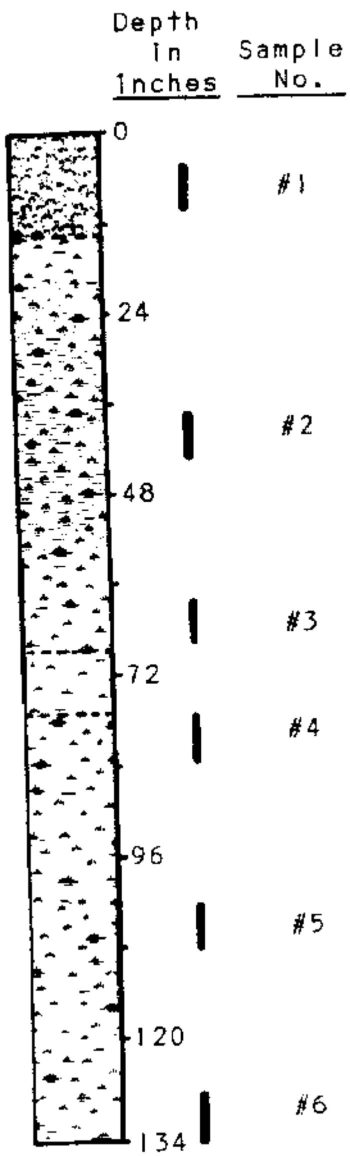
CORE BB-3



Depth in inches	Sample No.	Description
0		
	#1	0-6" Peat, muddy, grading into
		6-22" <u>Mud</u>, peaty, medium soft, olive grey (5Y 4/1) and brownish grey (5YR 4/1) grading into
24		
	#2	22-144" <u>Mud</u>, medium soft, olive grey (5Y 4/1) with occasional plant fragment (1mm). Uniform texture becoming slightly stiffer and slightly mottled olive grey (5Y 4/1) to dark grey (N-3).
48		
	#3	
72		
96	#4	Mud becoming stiff and dark olive grey (5Y 3/1) slightly mottled to dark grey (N-3).
	#5	
120		
144	#6	End of core.

Figure 10

CORE BB-4



Description

0-13" Peat, moderate brown (5YR 4/4) grading into

13-68" Mud, peaty, moderate soft to slightly stiff, mottled dark olive grey (5Y 3/1) and moderate brown (5YR 4/4).

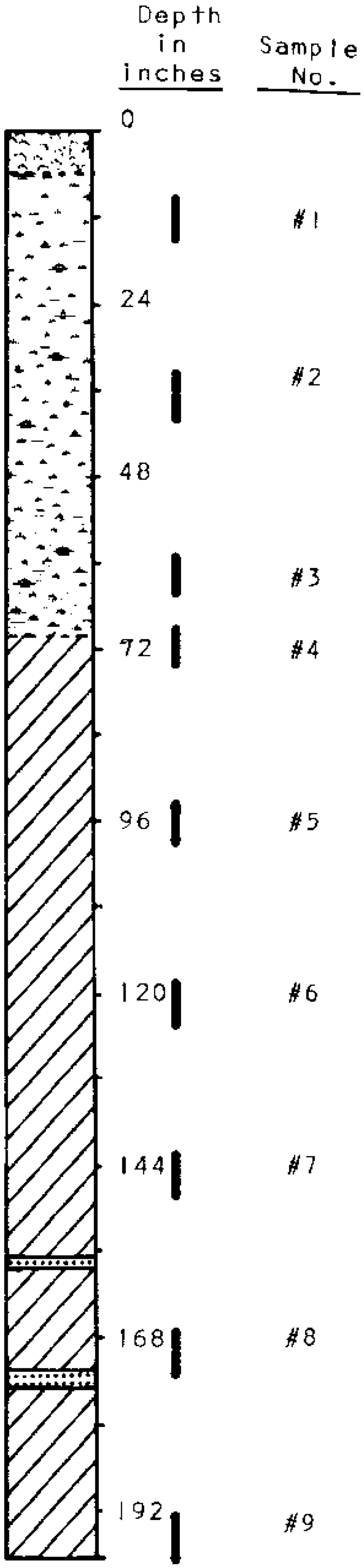
68-79" Mud, peaty, slightly stiff, olive black (5Y 2/1) grading into

79-134" Mud, peaty, slightly stiff, olive grey (5Y 3/1) and moderate yellowish brown (10YR 5/4).

Note: there was a loss of one foot of core, presumably due to compaction.

Figure 11

CORE BB-5



Description

0-6" Peat, brown to dark grey grading sharply into

6"-70" Mud, peaty, moderately soft, dark yellowish brown (10YR 4/2). Becoming mottled with dark grey (N-3) and moderate brown (5YR 3/4) to moderate yellowish brown (10YR 5/4), grading into

70-197" Mud, moderately soft to very slightly stiff, olive grey (5Y 4/1) with occasional allocthanous (?) plant fragment and clam shells (*Periploma?* sp.). Very even texture. Becoming sandier with depth.

Sand lenses at 157" and 172-173".

End of core (16'7").

Figure 12

APPENDIX II

RAW DATA

Sample No.	Eh mV	% H_2O	% <63μ	% >63μ	Zn (PPM) <63μ	Zn (PPM) >63μ	Cu (PPM) <63μ	Cu (PPM) >63μ	Cr (PPM) <63μ	Cr (PPM) >63μ	Fe (%) <63μ	Fe (%) >63μ
BB-1#1	-410	64.7	30.9	4.4	76	73	45	32	65	27	3.3	1.1
BB-1#2	-395	46.9	48.3	4.8	66	65	40	12	61	0.2	2.1	1.9
" #3	-395	59.3	33.8	6.9	150	79	40	5	90	3.3	2.6	1.7
" #4	-445	59.2	39.4	1.4	132	89	35	37	102	18	3.8	2.4
" #5	-440	51.4	45.4	3.3	88	108	180	7	78	87	2.7	1.7
" #6	-450	64.4	35.2	0.4	104	-	22	-	6.6	-	2.3	-
BB-2#1	-420	79.9	17.0	3.1	81	79	152	96	29	37	1.4	1.0
BB-2#2	-430	65.3	32.7	2.0	78	97	61	83	76	36	1.7	1.1
" #3	-450	61.0	37.8	1.3	97	173	41	54	91	10	3.1	1.4
" #4	-445	53.2	45.7	1.2	85	132	43	67	75	7	2.2	1.7
" #5	-450	54.5	44.3	1.2	83	110	33	43	106	54	2.9	1.8
" #6	-440	53.5	45.3	1.2	106	120	25	24	105	56	2.3	1.9
BB-3#1	-500	67.3	29.0	3.8	56	56	36	40	45	20	1.7	0.8
BB-3#2	-435	50.8	48.4	0.8	93	119	37	39	86	34	2.5	1.6
" #3	-435	49.9	49.1	1.0	89	93	22	8	56	0	2.3	2.3
" #4	-455	55.6	43.4	1.0	106	138	22	184	40	100	3.4	7.2
" #5	-465	54.9	43.8	1.3	105	133	25	265	63	50	2.3	7.8
" #6	-475	52.1	47.4	0.5	100	133	33	31	76	5	2.5	2.6
BB-4#1	-445	89.7	3.8	6.5	63	19	294	42	7	1	0.5	0.0
BB-4#2	-460	53.3	44.8	1.9	83	61	35	23	66	26	3.1	1.2
" #3	-440	48.1	50.6	1.3	70	85	27	39	38	25	2.8	1.8
" #4	-460	53.3	44.4	2.3	81	103	35	10	73	0	2.2	3.6
" #5	-445	52.7	45.6	1.6	84	153	45	21	64	20	2.1	2.1
" #6	-450	75.9	16.3	7.8	34	48	96	38	10	10	0.8	0.6
BB-5#1	-465	79.3	16.5	4.2	71	51	136	54	7	21	1.3	0.6
BB-5#2	-445	62.0	35.4	2.6	71	76	60	29	58	17	2.0	2.5
" #3	-430	55.7	43.3	1.1	93	130	48	65	84	32	2.5	2.4
" #4	-450	51.9	46.9	1.1	94	89	58	53	50	76	3.0	1.8
" #5	-460	50.1	48.0	2.0	86	80	92	97	77	31	1.9	1.5
" #6	-465	47.3	48.7	4.0	80	56	40	30	63	17	2.7	1.2
" #7	-475	46.8	45.6	7.6	83	60	27	10	53	0	3.3	0.7
" #8	-460	49.4	47.7	2.9	88	59	22	10	75	12	2.5	1.4
" #9	-445	49.1	47.8	3.0	98	33	50	17	75	29	3.0	0.7

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