

1962

Chemistry of Chesapeake Bay Sediments

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<https://dx.doi.org/doi:10.25773/v5-tjbc-1c97>

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CHEMISTRY OF CHESAPEAKE BAY SEDIMENTS

by

DAVID KENNETH YOUNG

A THESIS

Submitted to the School of Marine Science
of the College of William and Mary
in partial fulfillment of the requirements
for the degree of
MASTER OF ARTS

1962

APPROVED

Thomas L. Brecken

ABSTRACT

Areal differences and vertical variations in Chesapeake Bay sediments of organic carbon, inorganic carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium were observed in fourteen cores from sand to silty clay sediment types in five to thirty-four meters of water. Eh and pH measurements indicate that the muds are predominantly reducing and alkaline. No laminations or texture changes were observed with depth of sediment.

Organic carbon contents below the surface sediments suggested incomplete carbon decomposition and oxidation. Amounts of organic carbon from 0.15% to 2.01% in the surface sediments implied lower organic matter contents of Chesapeake Bay sediments than previously assumed. Inorganic carbon contents reflected variations in shell accumulations. Direct relationships were indicated between organic carbon and total iron. Highest quantities of total iron and organic carbon were found in the deepest water sediments.

Phosphorus concentrations in the surface sediments indicated aerobic hydrosol conditions. Lesser sorptive capacities of all cations were suggested in the large-size sediments fractions. An inverse relationship between calcium

and magnesium content from deep to shoal sediments implies that these cations in the sediments were determined by the salinity of overlying waters. Sodium and potassium in the sediments showed little variation.

ACKNOWLEDGMENTS

The writer wishes to express his sincere thanks to Dr. Morris L. Brehmer for his personal guidance and assistance throughout the entire course of this investigation. Grateful acknowledgment is also due to Dr. Maynard M. Nichols and Dr. Wyman Harrison for their interest and help in the geological aspects of the study, to Dr. Edwin B. Joseph and Miss Evelyn Wells for their aid in editing the manuscript, to Mr. Robert S. Bailey and Mr. Frank Pine for the photographic work, to Mrs. Audrey Jordan for typing the manuscript, and to the students and staff of the Virginia Institute of Marine Science for their assistance and encouragement. The writer appreciates the financial support from a U. S. Army Corps of Engineers grant, contract no. DA-44-CIVENG-61-181.

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INTRODUCTION

Chesapeake Bay lies within the Atlantic Coastal Plain. Freshwater streams tributary to the bay drain an area of almost 74,000 square miles and extend their headwaters into the Piedmont physiographic province. The character of the recent bottom sediments of Chesapeake Bay has been determined largely by the material carried to the bay by these streams (Stephenson et al., 1932).

Sediments of Chesapeake Bay grade progressively from a near-shore sandy facies along the margins into a clayey-silt facies in the central areas (Ryan, 1953). Fine-fraction analyses of Chesapeake Bay sediments made by Carritt and Goodgal (1954, p. 235) exhibited the following range of composition: "kaolinite less than 5% to 15%; illite less than 10% to 40%; chlorite-like montmorillinite 20% to 90%; amorphous silica less than 5% to 35%; quartz less than 5% to 20%."

Since Pliocene time the Chesapeake Bay region has undergone crustal warping and has been subjected to transgressions and regressions of the sea with attendant erosion and deposition. The present form of the Chesapeake Bay estuarine system can be closely related to ancient drainage pattern formed during the Pleistocene epoch (Hack, 1957). During glacially lowered sea levels, the Susquehanna River

cut a valley in the bottom of Chesapeake Bay and flowed over the exposed continental shelf to the sea. The valley of the Pleistocene Susquehanna coursed through the present bay entrance in the vicinity of Fisherman's Island (Harrison, 1962). A worldwide rise in sea level since the last glacial maximum of the Wisconsin Stage, about 18,000 years ago, resulted in the drowning of the Susquehanna River and its tributaries.

Ryan estimates that the average rate of sedimentation in Chesapeake Bay during the last 10,000 years is over six million cubic yards per year. One quarter of this amount probably represents erosion of the ancient shore line (Carpenter, 1957). By measuring present amounts of suspended solids, Carpenter has estimated a sedimentation rate of 0.1 cm per year for the bay. Powers (1954) estimated the average sedimentation rate for the bay to be 0.25 cm per year. Average sedimentation estimates for the bay are of limited value, however, as the rate of sedimentation has not been uniform throughout time and space.

Ryan found the highest sedimentation rates in the lower part of the bay where about 90% of the Pleistocene valley has been filled. This rapid rate of sedimentation can be readily understood because the principal rivers

contribute most of the sedimentary material that enters Chesapeake Bay (Burt, 1955), and all of the major tributaries with the exception of the Susquehanna River drain into this part of the bay.

Shoal areas in the lower bay have been recently subjected to dredging in order to allow for the passage of deeper draft vessels. This investigation will review an area of sediment accumulation, the Rappahannock Shoal, which was dredged by the U. S. Army Corps of Engineers during 1961 for the deepening of the Baltimore Ship Channel. An associated area, the spoil disposal site of the dredged material, will also be considered.

Although the variability in the estuarine environment has been well documented, little work has been done on the chemistry of estuarine sediments. Even in such an important waterway and seafood source as the Chesapeake Bay, chemical analyses of the sediments are rare. The purpose of this study is to contribute to the general knowledge of the chemistry of estuarine sediments in Chesapeake Bay and to relate these chemical findings to associated physical, chemical, and biological conditions in the bay.

THE DIAGENETIC ENVIRONMENT

At the instant of deposition an estuarine sediment may consist of loose mineral particles, colloidal mud, and organic debris. In shallow areas windwave-mixing and tidal-scouring may bring this material back into suspension. Modifications of particles occur as the sediment is buried by subsequent depositions. The postdepositional change of the sediment is termed diagenesis.

The nature of the diagenetic environment and the rapidity of postdepositional change depends upon the medium of deposition and the kind of sediment being deposited. Estuarine sediment dispersal and deposition has been shown to depend predominantly on physical characteristics of the current systems that operate in the estuary (Nelson, 1960). The medium of deposition in estuaries is influenced by the effects of changing salt concentration in the overlying water and the action of tides.

The diagenetic environment usually shows the most pronounced changes within several centimeters below the sediment-water interface (Krumbein and Sloss, 1953). The top two or three centimeters of marine and estuarine sediments contain the highest numbers of bacteria (Zobell, 1942) and benthic invertebrates (Sanders, 1960). Shepard and

Moore (1955) have stated that organisms in the sediments are the greatest single factor in changing the physical character of newly deposited material.

Decreasing water content and increasing salt content has been shown with increasing depth in estuarine sediments (Nelson, 1960). Ion exchanges take place between the sediments, the interstitial water, and the overlying water. The composition of the exchangeable ion content is primarily determined by the amount of fresh or salt water present. Adsorption of the cations onto clay particles in sea water has been explained (Carroll and Starkey, 1959) by the Law of Mass Action. It has been theorized (Jarusov, 1937) that the cations with the higher free-bonding energy occupy the exchange sites on the clay lattices with the highest bonding energy. In general, the bonding energies of the cations are in the order: $\text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+ > \text{Na}^+$ (Carroll and Starkey, 1959; Kelley, 1939). However, this order may vary with the nature and concentration of the clay mineral as well as the nature and concentration of the ions involved (Grim, 1953).

Changes progress downward from the sediment-water interface in the oxidizing or reducing nature, acid or alkaline character, and dissolved gas content of estuarine sediments. This dynamic nature of the diagenetic environment is

due to complex interactions of organic activity, ion exchange, and many other associated variables operating within a sediment. The diagenetic environment may be effectively interpreted in terms of vertical variations in the physical and chemical properties of the sediments.

METHODS AND MATERIALS

Sampling Program

A series of core samples were taken on transects covering the Rappahannock Shoal area and spoil disposal site (Fig. 1) during the period from July 1961 through June 1962. A number of these cores were examined in the field for color and structure changes with depth of sediment.

Nineteen cores taken during the January-February 1962 cruise of the R/V Pathfinder were selected for organic and inorganic carbon analyses. Fourteen of these cores were analyzed for sodium, potassium, calcium, magnesium, total iron, and total phosphorus. These selected cores were representative of the varying depths and sediment types (Table 1) that were encountered in the survey (VIMS, 1962).

The bottom cores were taken with two modified gravity-type corers having diameters of 1.5 and 2 inches. Cores of sediments were obtained up to 90 cm in length. The coring tubes would generally not retain sediments of high sand content.

Bottom samples collected in such coring tubes are probably slightly compacted, the amount varying between 25 and 50 % (Wrath, 1936). The compaction ratio varies with sediment type and the diameter of coring tube. Therefore,

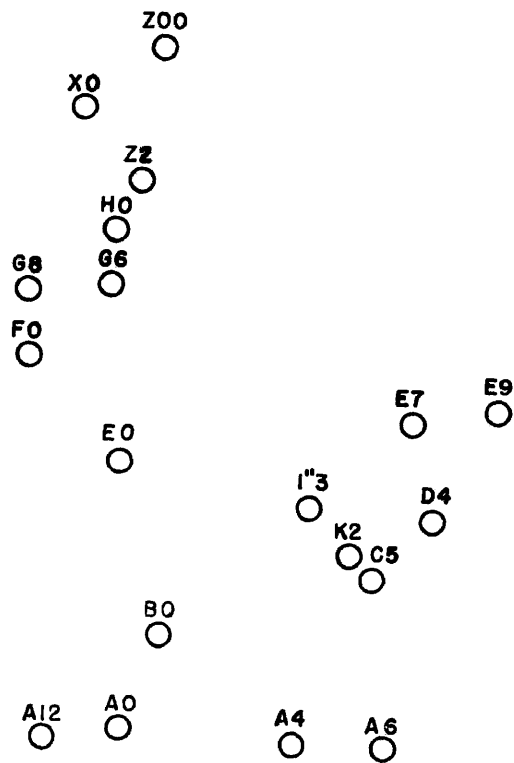


Figure 1. Map of study area and locations of cores analyzed.

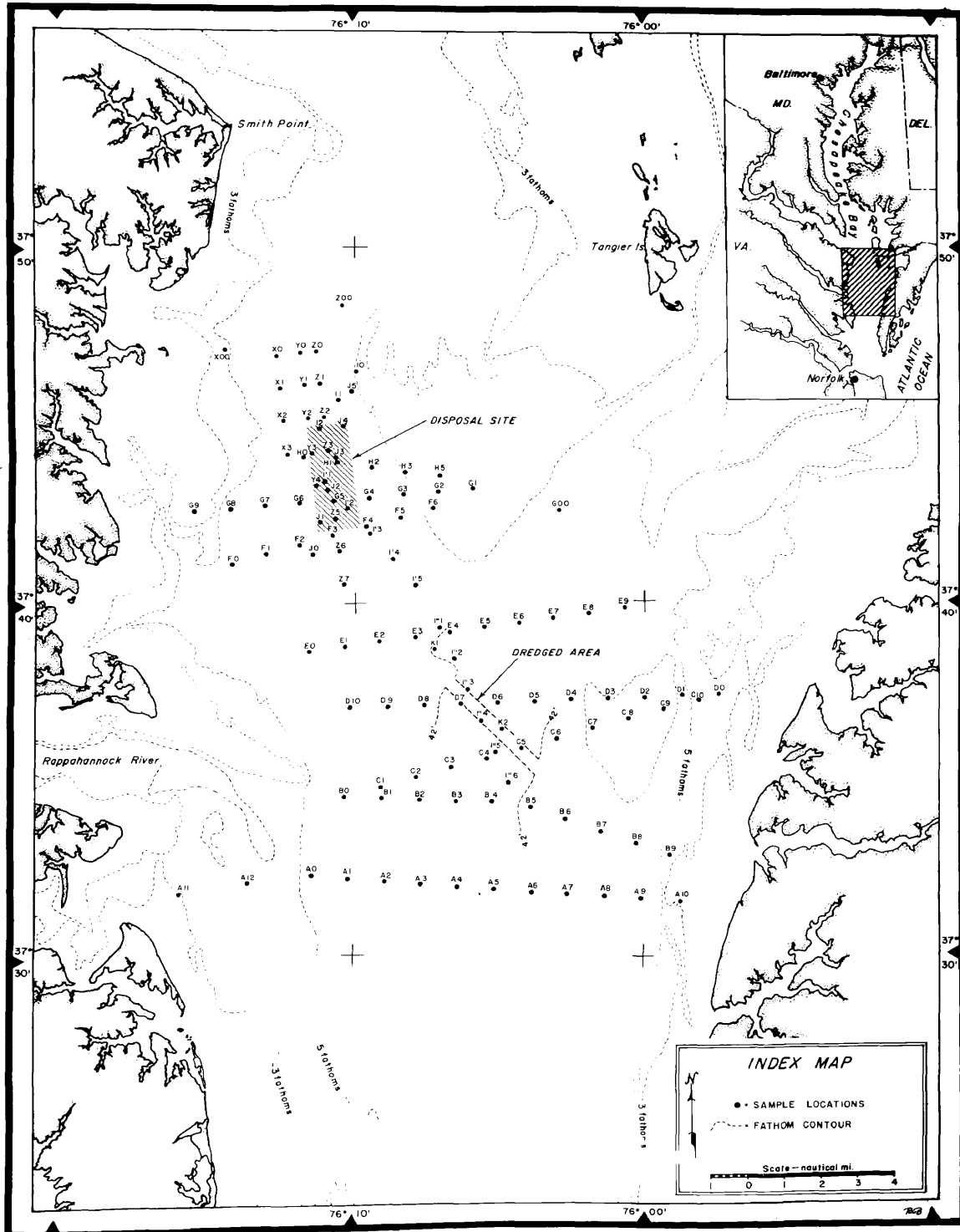


Table 1

Textural classes and size analyses of survey sediments taken during July 1961 (analyzed by R. W. Batten)

<u>Station no.</u>	<u>Station depth, meters</u>	<u>Textural class (Shepard, 1954)</u>	<u>Median diameter, mm.</u>
A0	11	Clayey silt	0.017
A4	12	Sand-silt-clay	0.0365
A6	14	Sand-silt-clay	0.0295
A12	10	Clayey silt	-
B0	13	Clayey silt	0.013
C5	13	Clayey silt	0.0195
D4	21	Silty sand	0.165
E0	13	Clayey silt	0.0096
E7	13	Sand	0.465
E9	13	Clayey silt	-
F0	12	Sandy silt	0.0225
G6	18	Clayey silt	0.0068
G8	5	Sand	0.31
H0	29	Silt	0.0096
I"3	16	Clayey silt	0.018
K2	16	Clayey silt	-
X0	20	Sand	0.178
Z00	34	Clayey silt	-
Z2	34	Clayey silt	0.0051

the listed sediment depth as stated in the analyses (Table 2, Column 1) is only a relative index of the depth in the natural sediment.

The 1.5 inch cores were used for the geochemical determinations. These cores, contained in their plastic core liners, were immediately frozen and subsequently stored in a freezer until analysis. Samples treated in such a manner have biochemical activity reduced to a very low level. Reliable results should be reached if the analyses are performed within a reasonable time after collection (Eggler et al., 1961).

Hydrogen ion concentration (pH) and the redox potential (Eh) of the sediments were measured in the field. These measurements were made immediately by direct probing in seven of the 2 inch cores by use of a Beckman pH meter and suitable electrode systems.

Sample Preparation

Each plastic core liner containing the sediment core was removed from the freezer and sectioned with a saw at 10- or 20-cm intervals. The sand sediments were sampled only at the surface and bottom of the cores. Approximately 10 g of sediment were removed at each core depth.

Table 2

Chemical data, percent by weight

Sample	Organic carbon	Inorganic carbon	Total P	Total Fe	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
A4 - surf.	0.66	0.07	0.0604	2.489	2.141	1.036	0.125	0.184
- 10 cm	0.54	0.32	0.0438	2.651	2.326	0.935	0.131	0.152
- 20 cm	0.35	0.21	0.0498	2.631	1.271	0.804	0.134	0.155
A0 - surf.	0.85	0.39	0.0563	3.065	2.745	1.063	0.105	0.177
- 10 cm	1.03	0.23	0.0544	3.195	0.924	1.063	0.137	0.168
- 20 cm	1.03	0.20	0.0542	3.497	1.424	1.284	0.141	0.173
- 30 cm	0.78	0.31						
K2 - surf.	0.60	0.20	0.0614	2.944	0.898	0.973	0.116	0.189
- 10 cm	0.64	0.22	0.0655	3.070	0.850	0.975	0.126	0.189
- 20 cm	0.75	0.16	0.0702	3.348	0.859	1.084	0.137	0.189
- 30 cm	0.70	0.11	0.0616					
- 40 cm	0.63	0.16						
X0 - surf.	0.32	0.02	0.0260	1.640	0.330	0.480	0.042	0.057
E7 - surf.	0.15	0.11	0.0124	1.118	0.220	0.384	0.021	0.046
- 7 cm	0.21	0.05						
G8 - surf.	0.16	0.03	0.0315	1.349	0.699	0.385	0.011	0.067
- 9 cm	0.26	0.04						
D4 - surf.	1.27	0.08	0.0622	3.494	1.249	1.148	0.095	0.147
- 10 cm	1.35	0.19	0.0623	3.418	0.809	1.124	0.095	0.156
- 20 cm	1.45	0.49	0.0602	3.672	2.051	1.251	0.109	0.154
- 37 cm	1.56	0.07						

Table 2 (continued)

Sample	Organic carbon	Inorganic carbon	Total P	Total Fe	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
I ³ - surf.	0.56	0.03	0.0615	2.980	2.325	1.150	0.093	0.192
- 10 cm	0.76	0.16	0.0615	3.268	0.809	1.024	0.097	0.194
- 20 cm	0.80	0.05	0.0591	3.447	0.809	1.024	0.126	0.168
- 36 cm	0.64	0.03						
A6 - surf.	0.89	0.16	0.0670	4.070	0.745	0.935	0.093	0.171
- 10 cm	1.01	0.03	0.0580	3.895	0.759	0.974	0.088	0.168
- 20 cm	0.87	0.01	0.0579	4.398	0.725	0.935	0.099	0.192
- 31 cm	0.78	0.08						
A12- surf.	1.14	0.13	0.0705	3.929	0.565	0.875	0.088	0.143
- 10 cm	1.52	0.10	0.0654	4.899	1.280	1.065	0.084	0.158
- 20 cm	1.10	0.10	0.0631	4.149	0.610	0.955	0.074	0.179
- 31 cm	0.86	0.02						
H0 - surf.	1.17	0.19	0.0746	4.500	0.610	1.125	0.105	0.200
- 10 cm	1.60	0.05	0.0687	4.046	0.594	1.024	0.076	0.198
- 20 cm	1.60	0.08	0.0663	4.380	1.460	1.105	0.080	0.204
- 40 cm	1.53	0.26						
Z00- surf.	1.76	0.11	0.0615	4.500	0.700	1.105	0.074	0.219
- 10 cm	2.12	0.01	0.0583	4.400	0.610	1.065	0.074	0.221
- 20 cm	2.17	0.03	0.0570	4.658	0.675	1.200	0.075	0.225
- 45 cm	1.57	0.06						
Z2 - surf.	1.83	0.09	0.0676	4.210	1.000	1.175	0.078	0.206
- 10 cm	1.99	0.11	0.0558	3.780	0.610	1.065	0.078	0.185
- 20 cm	1.88	0.03	0.0559	3.924	1.323	1.123	0.080	0.194
- 40 cm	1.87	0.08	0.0559	4.149	0.885	1.150	0.084	0.194
- 53 cm	1.46	0.11	0.0560	3.868	0.645	1.220	0.084	0.204

Table 2 (continued)

Sample	Organic carbon	Inorganic carbon	Total P	Total Fe	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
G6 - surf.	2.01	0.11	0.0672	4.450	0.610	1.150	0.084	0.212
- 10 cm	1.97	0.18	0.0600	4.480	0.625	1.200	0.084	0.202
- 20 cm	1.72	0.17	0.0587	4.479	0.710	1.330	0.084	0.192
- 40 cm	1.75	0.02	0.0547	4.445	0.700	1.425	0.080	0.215
- 60 cm	1.64	0.05	0.0590	4.470	0.610	1.220	0.074	0.232
- 90 cm	1.37	0.04	0.0607	4.496	0.609	1.249	0.074	0.223
F0 - surf.	1.82	0.07						
- 10 cm	1.85	0.12						
- 55 cm	1.49	0.12						
C5 - surf.	1.14	0.13						
- 10 cm	1.12	0.61						
- 30 cm	1.23	0.39						
- 52 cm	1.01	0.15						
E0 - surf.	0.85	0.19						
- 10 cm	0.96	0.07						
- 36 cm	0.69	0.10						
B0 - surf.	1.43	0.15						
- 10 cm	1.47	0.06						
- 32 cm	1.16	0.18						
E9 - surf.	1.37	0.21						
- 10 cm	1.28	0.31						
- 37 cm	1.01	0.02						

The sediment samples were divided into two portions. One was dried without treatment and the other was dried after being washed with distilled water. The two portions were ground in a mortar and pestle, redried, placed in vials, and stored in desiccators.

The splits were prepared for analyses by the procedure outlined in Fig. 2.

Split A

The procedure for the rapid analysis of silicate rocks developed at the U. S. Geological Survey by Shapiro and Brannock (1956) provided a basis for determination of sodium, potassium, iron, magnesium, and calcium more rapid, simple, and direct than the classical methods of quantitative separations.

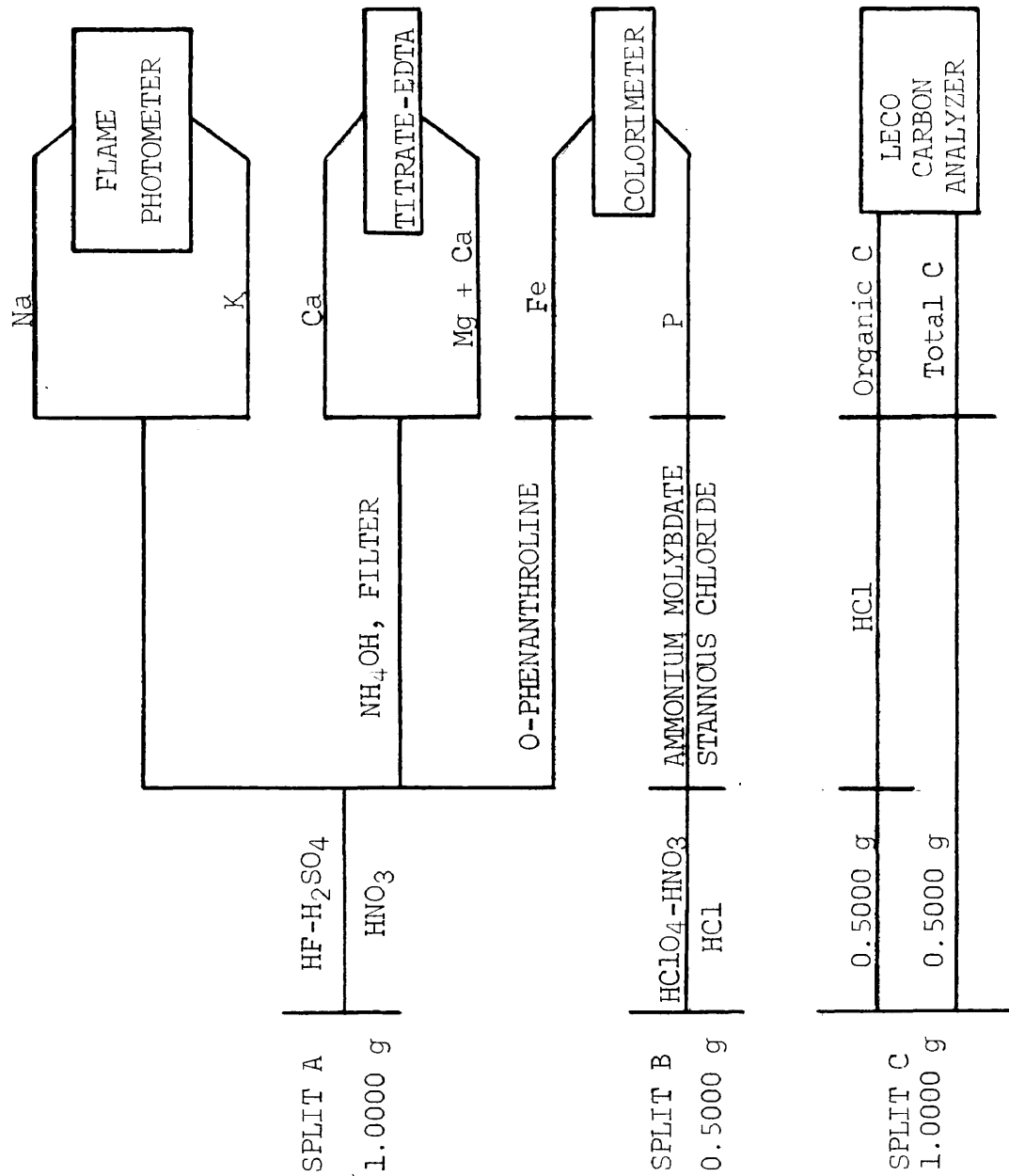
The complete digestion of the sediment samples was performed with modifications from a variety of basic methods (Shapiro and Brannock, 1956; Fitch and Rosenfeld, undated; Jackson, 1958; and Carey and Jackson, 1953).

It was desirable to minimize those variations due to differences in the amount of interstitial or pore water contained by each sediment type. Therefore, only washed samples were used.

Figure 2

Flow diagram of analytical procedures for the determinations of sodium, potassium, calcium, magnesium, iron, phosphorus, organic carbon, and total carbon

FLOW DIAGRAM OF ANALYTICAL PROCEDURES



Approximately 1 g of washed sediment was weighed in a 30 ml platinum crucible. Following a moistening of the sediment with distilled water, 15 ml conc. HF, 2 ml conc. HNO₃, and 10 ml conc. H₂SO₄ were added. The crucible was placed in a sand bath having a temperature of 200° to 225°C, and the contents were digested for 8 to 10 hours. The temperature was then raised to 325° to 350°C, and the solution was evaporated to a low volume.

The contents were transferred to a 250 ml vycor beaker containing 100 ml distilled water and 2 ml HCl. This solution was diluted to 250 ml after having been boiled for several minutes to digest the remaining solids. Aliquots from this final solution were taken for the determinations of sodium, potassium, calcium, magnesium, and iron.

Sodium and Potassium.--Sodium and potassium were determined by flame spectroscopy with a Beckman DU Spectrophotometer using an oxy-acetylene mixture as fuel. Spectral interference of common ions with sodium and potassium was largely eliminated by using a minimal slit width (Porter and Wyld, 1955). The addition of ammonium sulfate to both the standards and the samples served to minimize anion interference (Fitch and Rosenfeld, undated).

A 25 ml aliquot from the HF digestate was diluted to 50 ml after the addition of 5 ml 25% $(\text{NH}_4)_2\text{SO}_4$. Both Na and K were determined from this solution. Instrument settings used were:

	<u>Na</u>	<u>K</u>
Working range, ppm	0-100	0-100
Selector switch	0.1	0.1
Phototube	blue	red
Phototube load resistor	2	3
Photomultiplier sensitivity	full	0
Zero suppression	0	2
Wave length, μ	589	768
Slit width, mm	0.02	0.10
Oxygen pressure, psi	10	10
Acetylene pressure, psi	4	4

The concentrations of Na and K in mg l^{-1} were read from log-log calibration curves of Na and K standards.

Calcium and Magnesium.--Calcium and magnesium were determined by the versene or EDTA (disodium dihydrogen ethylenediamine tetra acetic acid) titration procedure of Schwarzenbach and Biedermann (1948). The reaction of Ca and Mg with EDTA has been shown to be stoichiometrical within a relative error of 0.1% (Bladel and Knight, 1954).

Since EDTA forms chelated complexes with many metal cations, any metal whose versene complex is less dissociated than of Ca or Mg would be preferentially complexed and included in the titration. Some of the interfering ions were removed by ammonium hydroxide separation and precipitation

in a buffered solution (Fitch and Rosenfeld, undated). The remaining ions were complexed and withdrawn from the reaction by the addition of cyanide (Jackson, 1958).

Calcium was determined at pH 11.5-12.0 using EDTA of known normality as the titrant and murexide (acid ammonium purpurate) as the indicator. Magnesium does not change the color of ammonium purpurate at this pH, thus permitting the titration of calcium in the presence of magnesium.

Magnesium and calcium were complexed with EDTA of known normality at pH 9.5-10.0 using eriochrome black T as the indicator. Magnesium was determined by the difference between the EDTA titration values with murexide and with eriochrome black T.

For separation, a 25 ml aliquot from the HF digestion was transferred to a 150 ml beaker. The pH was adjusted to 5.0 ± 0.2 by adding a gradation of NH_4OH dilutions. The solution was diluted to 50 ml, mixed, and allowed to stand for 30 minutes. The solution was filtered through a Whatman No. 40 filter paper. The filtrate was preserved for the Ca and Mg determinations.

In the titration for Ca, two 5 ml aliquots of the filtrate were transferred into 350 ml porcelain dishes and each was diluted to about 80 ml. The solutions were titrated

with EDTA to a color change from pink to purple after the addition of 25 ml of a murexide indicator-buffer. The color change is gradual which necessitated the second titration for comparison purposes.

In the titration for Ca plus Mg, two 5 ml aliquots of the filtrate were transferred into 400 ml beakers and each was diluted to about 150 ml. After 10 drops of eriochrome black T indicator and 10 ml of NH_4OH buffer solution were added, the solutions were titrated with EDTA to a color change from red to blue. The second titration was used for a color comparison of the endpoint.

Iron.--Total iron was determined colorimetrically after a reduction by hydroxylamine hydrochloride and the formation of a stable orange-red complex with 0-phenanthroline. A slightly acidic solution was used due to the interference of cations in the alkaline ranges by precipitation of their hydroxides (Fortune and Mellon, 1938).

A 5 ml aliquot from the HF digestion was diluted to 200 ml. A subsequent 5 ml of the dilutant was treated with the following reagents: 2 ml 10% hydroxylamine hydrochloride, 25 ml 2% 0-phenanthroline in ethanol, and 5 ml 10% ammonium chloride.

The pH of the solution was adjusted to 3.5 ± 0.5 with dilute HCl. The absorption of the resulting complex was measured in a Klett-Summerson colorimeter using a green filter with maximum transmittance at 515 m μ .

The concentration of iron in mg l⁻¹ was read directly from an iron standard calibration curve.

Split B

Phosphorus.---Total phosphorus was determined colorimetrically following complete oxidation with perchloric acid. Both washed and unwashed sediment samples were initially measured for phosphorus. The unwashed samples, as a general rule, gave slightly higher values of total phosphorus than washed samples. These inconsistencies were attributed either to a weight difference of residual salts, an actual phosphorus difference, or to a salt error affecting color development of the reduced phosphomolybdate complex (Hansen and Robinson, 1953). Thereafter, only washed samples were utilized in all phosphorus determinations in order to maintain consistency between subsample characteristics.

The perchloric acid digestion procedure was adapted mainly from Jackson (1958) with minor modifications from Hansen and Robinson (1953).

Under certain conditions perchloric acid can react violently with organic matter. The immediate danger of explosion was overcome by effecting preliminary oxidation of the organic matter in the samples with concentrated nitric acid. A Kjeldahl digestion flask fume collector coupled by glass and teflon joints through a sodium hydroxide trap to a glass water pump, effectively evacuated the fumes. All the perchloric acid digestions were heated on a sand bath and carried out in a fume hood.

A 0.5 g washed sediment sample from a selected depth was weighed and then transferred to a 30 ml micro-Kjeldahl flask. Initial oxidation was performed by adding 5 ml conc. HNO_3 and heating slowly until reddish nitric acid fumes were no longer evolved. Oxidation was completed by adding 5 ml 70% HClO_4 .

Arsenic interference in the phosphorus colorimetric determination, reported by Hansen and Robinson (1953), was eliminated by adding and rapidly fuming off 2 ml conc. HCl after five minutes of HClO_4 digestion.

Digestion was continued at 120° to 140°C until the solution became colorless and white dense fumes were evolved. The digestion supernatant was filtered through a No. 41 H Whatman paper into two 200 ml volumetric flasks. The white

silica residue was washed to bring the volume of the solution to 200 ml. Aliquots from this final solution were taken for analysis.

The ceruleomolybdic method of Deniges (1920) for orthophosphate was used for total phosphorus determinations. Reagent preparations were adapted from Ellis, Westfall, and Ellis (1948) and from Standard Methods for the Examination of Water and Wastewater (1960). All reagents were freshly prepared before each set of determinations.

A 10 ml aliquot from the HClO_4 digestion was diluted to 100 ml. One drop of phenolphthalein was added to a 50 ml aliquot of this dilutant. In order to remove residual oxidizing reagents and acidity, saturated NaOH was added dropwise until a faint pink color persisted.

Upon the addition of 2 ml acidified ammonium molybdate, a phospho-molybdate complex was formed which was reduced by 0.25 ml stannous chloride reagent to a blue colored solution. After color development was complete, the absorbancy of the resulting solution was measured with a Klett-Summerson Colorimeter using a red filter with maximum transmittance at 660 m μ . Concentrations of phosphorus were read directly in mg l^{-1} from a phosphorus standard calibration curve.

Split C

Carbon.--Total carbon was measured gasometrically with a Leco Carbon Analyzer. Organic carbon was also determined by this method after a preliminary removal of carbonates by a digestion with dilute hydrochloric acid. The difference between total carbon and organic carbon was taken as the measure of inorganic carbon.

Both washed and unwashed sediment samples were initially measured for the carbon fractions. Inconsistencies were found in the carbon measurements from unwashed samples; therefore, only washed samples were used in subsequent determinations. These inconsistencies could be attributed to considerable weight differences in residual salts and possible differences in carbon and carbonate contents of the retained interstitial water.

A 0.5 g washed sample was weighed in a Leco carbon-free crucible and measured for total carbon content in a Leco Carbon Analyzer after ignition to 3000°F in an induction furnace. A 0.5 g unwashed sample from the same depth and station was treated for 12 hours with 1:1 HCl. The sample was analyzed for organic carbon content after washing with distilled water, filtering, and drying at 60°C.

The readings obtained for each carbon determination, along with temperature-pressure correction factors, were used to calculate the percent of each carbon fraction in the sample.

RESULTS

The sediments were analyzed by observing the physical differences and measuring the chemical variations with increasing depth of burial.

Color and Texture

The most obvious physical change with depth in the sediments was the variation in firmness. In most of the finer sediment cores the upper one or two centimeters consisted of a brownish-colored fluid layer. Shepard and Moore (1956) refer to this layer as a "mobile" zone and question as to whether it is an integral part of the sediment column. Most of the sediments were loosely integrated in the surface layers, and the coherence increased noticeably with depth, particularly in the clayey cores.

A homogeneous, dark, greenish-gray and brownish-gray coloration was characteristic of nearly all the clayey cores. Homogeneity of sediment texture and similarity in size distribution was noted with depth in most cores. Laminations were absent in the sediments that were sampled. A lack of mineralogical changes with depth of sediment has been found to be characteristic of Chesapeake Bay sediments (Ryan, 1953) and Rappahannock River sediments (Nelson, 1959).

pH - Eh

Previous studies have cast some doubts as to the authenticity of pH and Eh measurements taken directly in sediments (Eggler et al., 1961). Only relative comparisons can be made between stations and absolute potentials cannot be assured within each core (Fig. 3).

Eh values from stations Z2 and Z00 indicated the presence of reducing conditions below the upper two or three centimeters of the sediment. The reducing potentials were shown to increase with depth in these cores. The pH readings indicated slightly alkaline conditions in all the cores that were examined.

Chemistry

All results from chemical analyses (Table 2) were expressed in percentage of the sediment sample weight. Post-depositional conditions in all constituents were investigated in eleven cores (Figs. 4-10).

Organic and Inorganic Carbon.---Eighteen cores were examined for changes in organic and inorganic carbon content with depth. All but three of these cores (A4, G6, and E9) had the highest organic carbon contents at 10 and 20 cm depths. In only one core (D4) was there an increase of

Figure 3

**Eh and pH values of sediments at stations Z00,
Z2, A0, A4, A6, I*3, and K2**

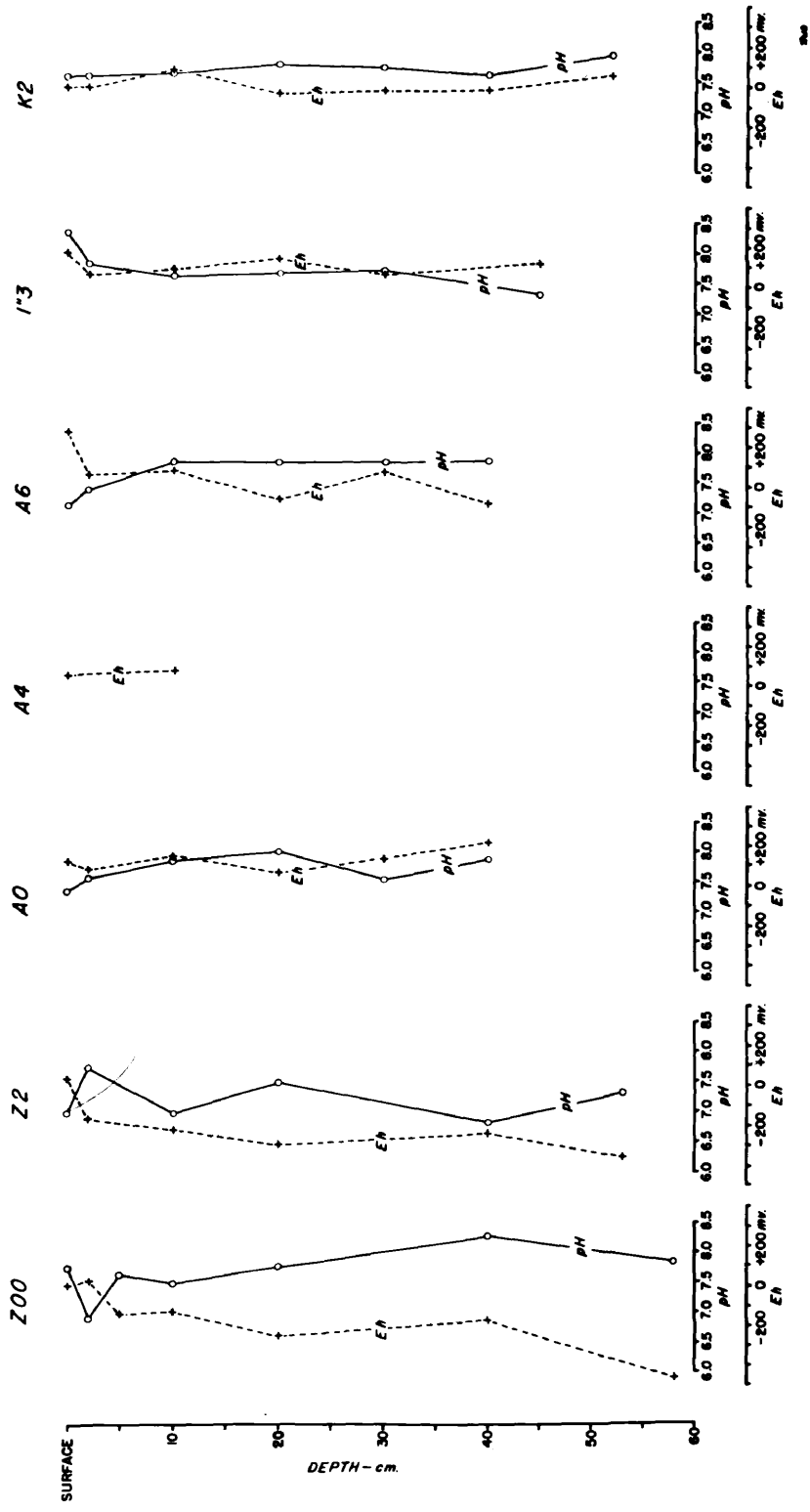
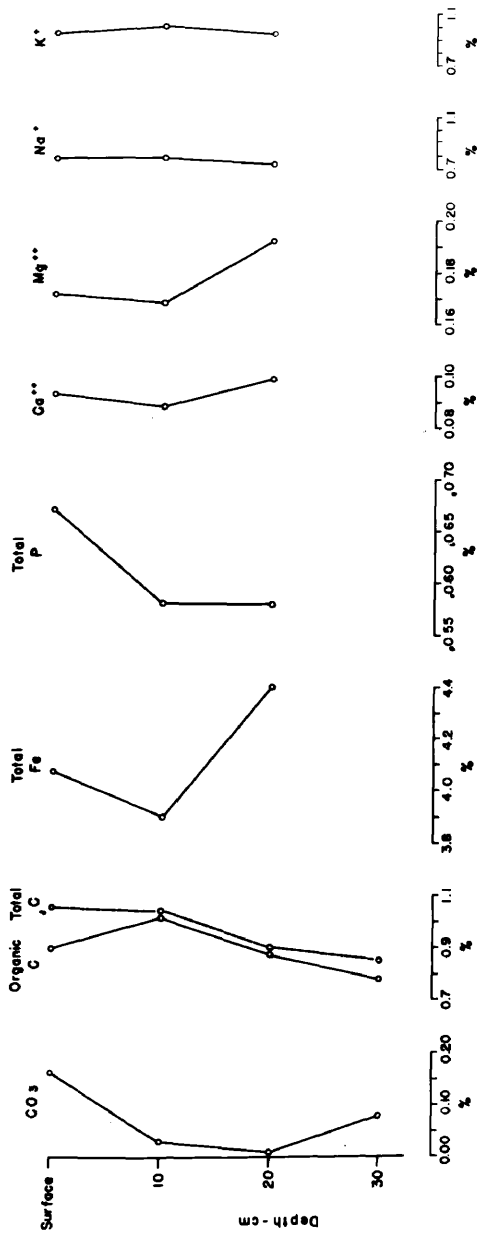


Figure 4

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at stations A4 and A6 of a sand-silt-clay sediment type

STATION A6



STATION A4

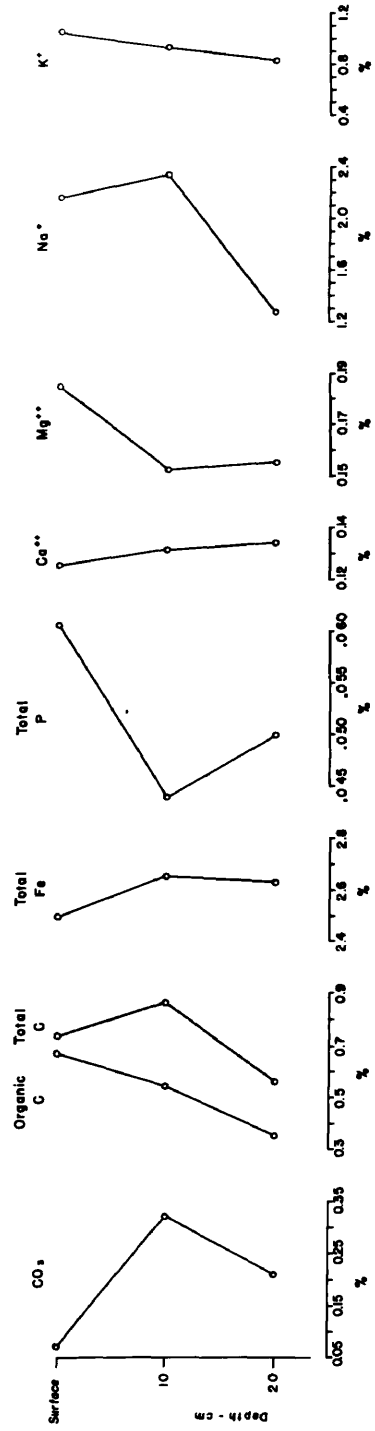
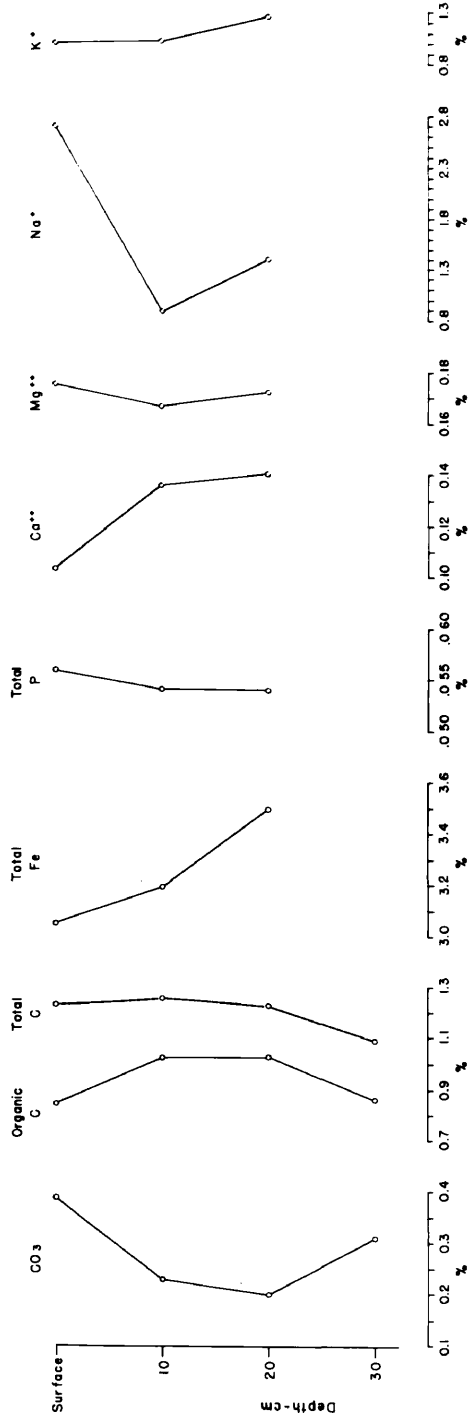


Figure 5

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at stations A0 and A12 of a clayey silt sediment type

STATION A0



STATION A12

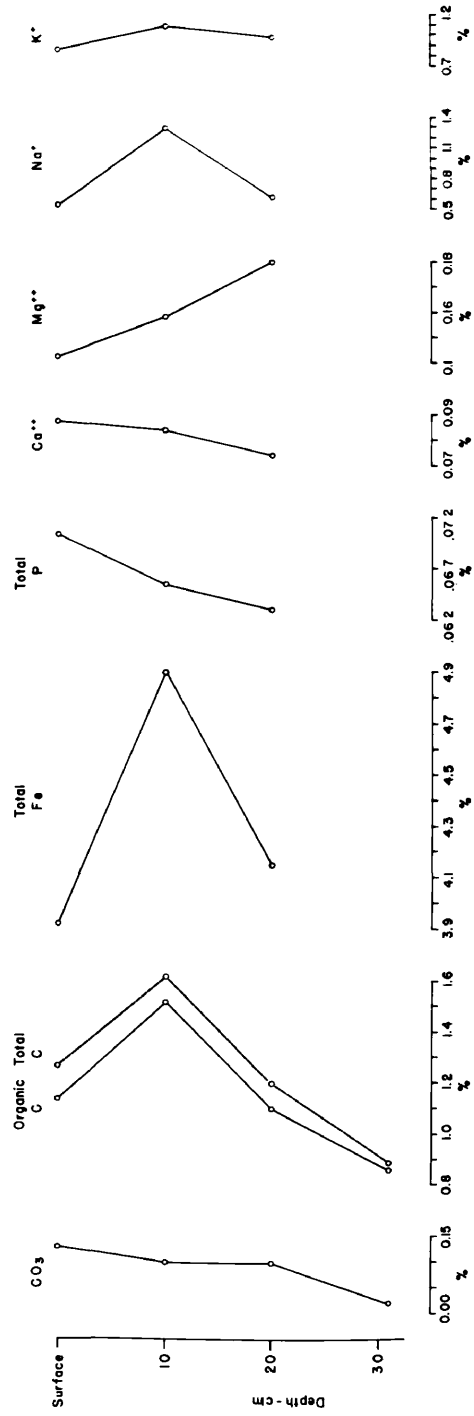
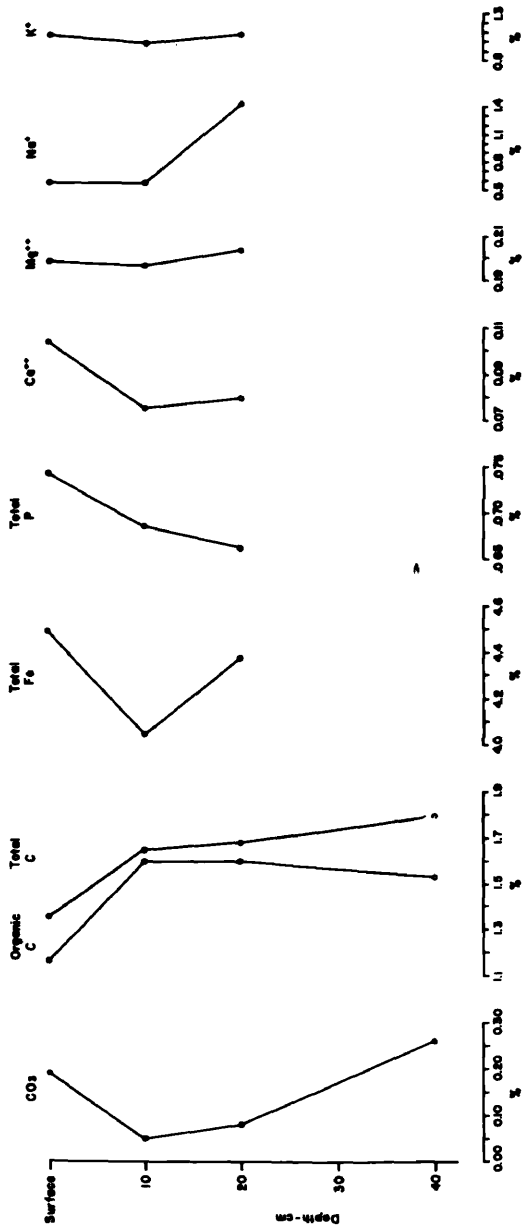


Figure 6

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at stations H0 and D4 of silt and silty sand sediment types

STATION HO



STATION D4

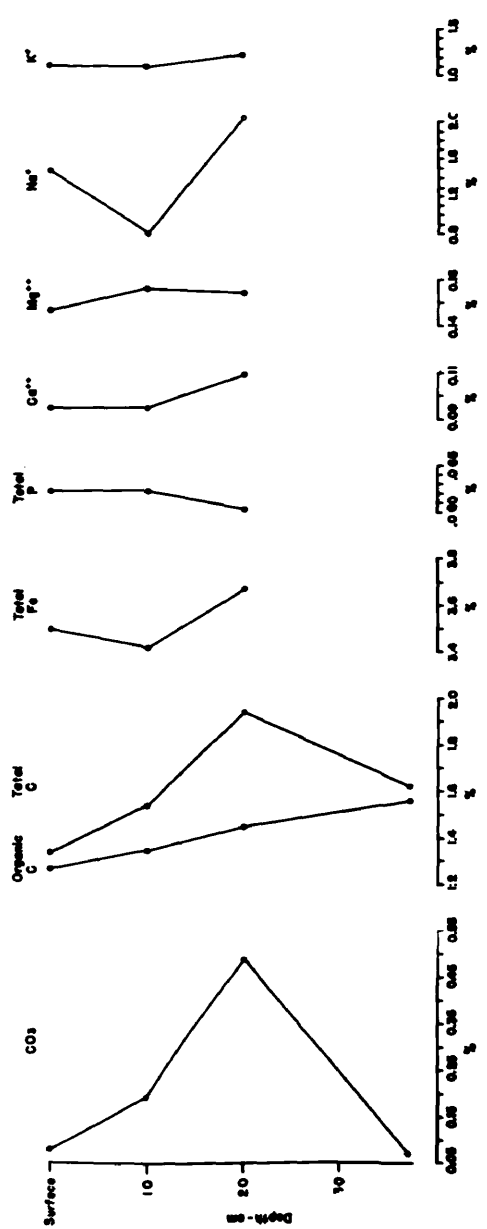
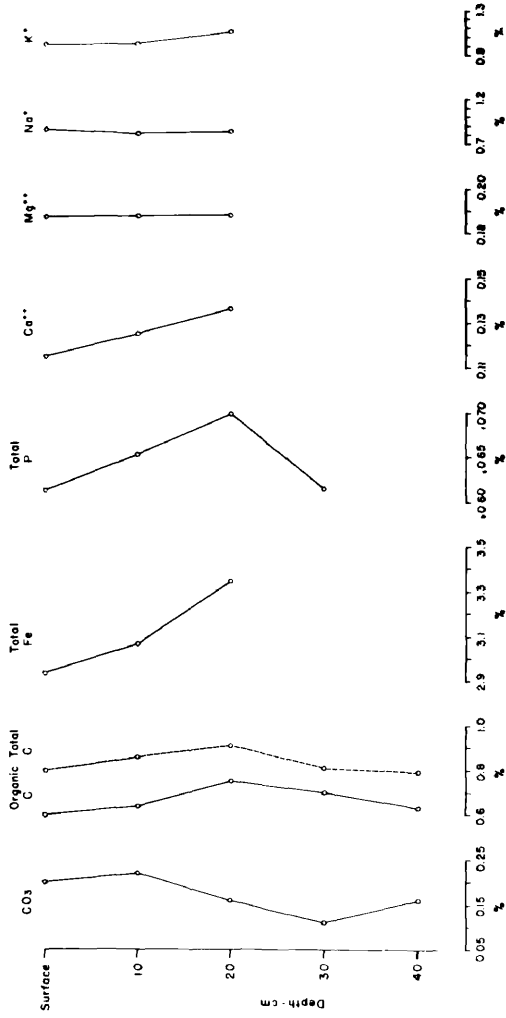


Figure 7

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at stations K2 and I³ of a clayey silt sediment type

STATION K2



STATION I#3

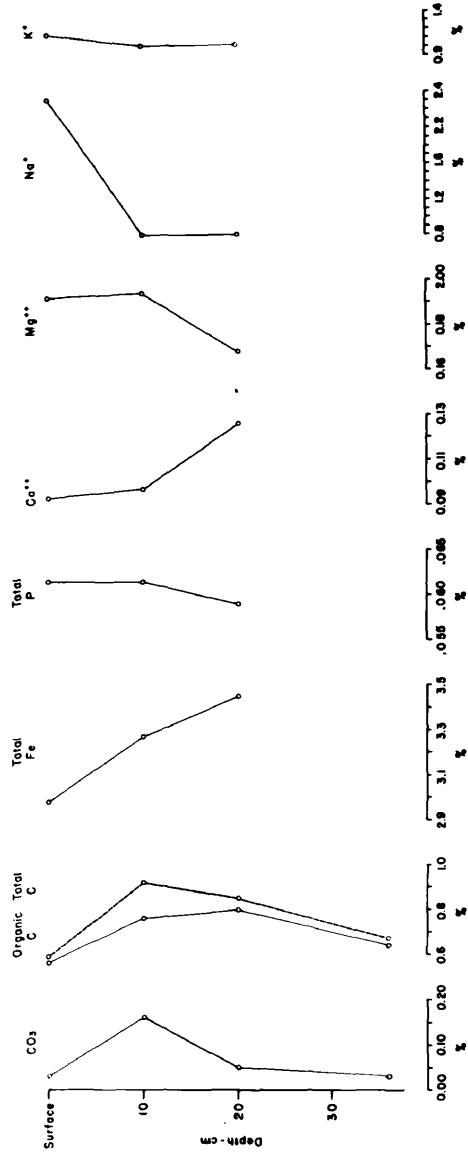


Figure 8

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at station G6 of a clayey silt sediment type

STATION 66

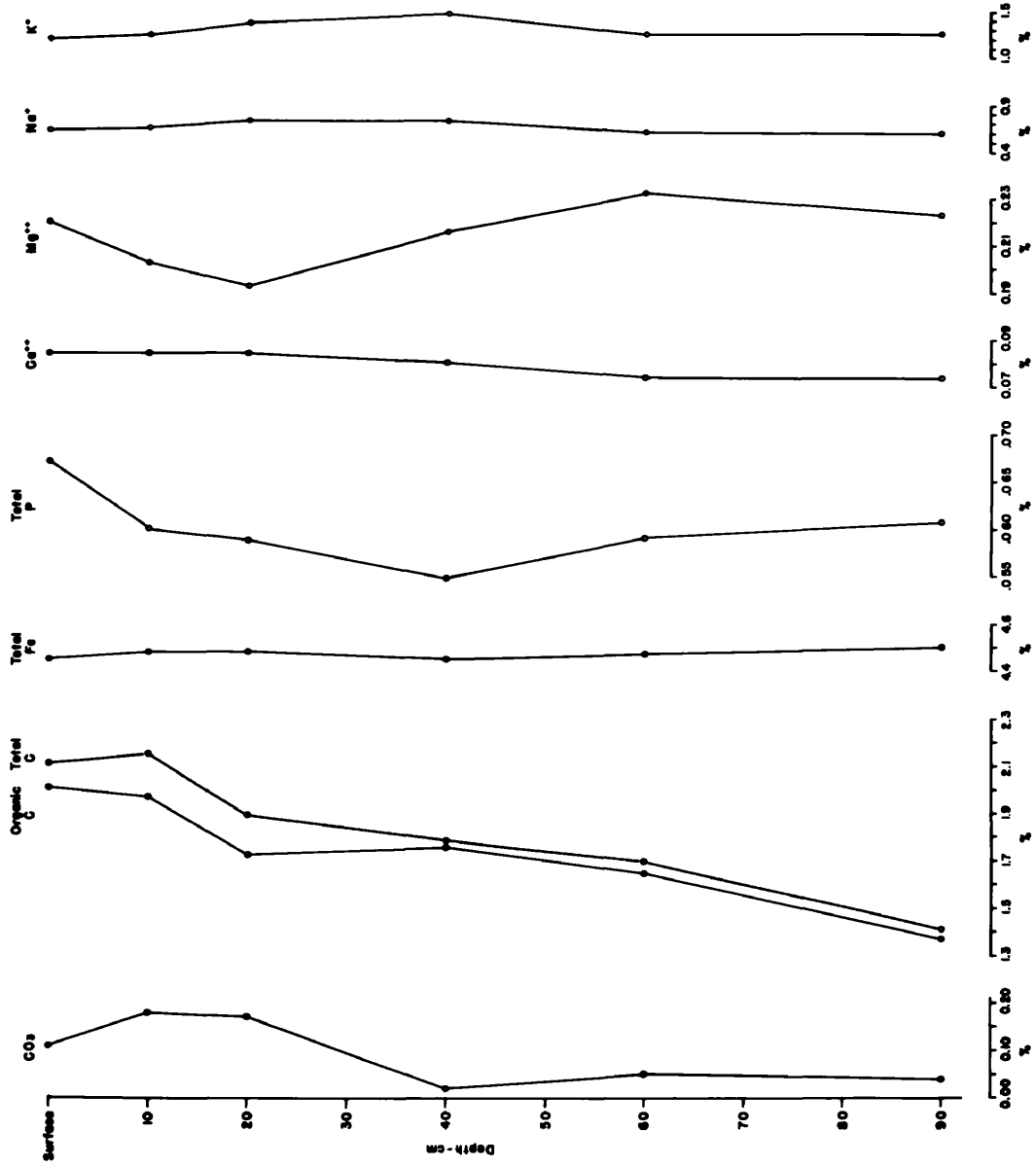


Figure 9

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at station Z2 of a clayey silt sediment type

STATION Z2

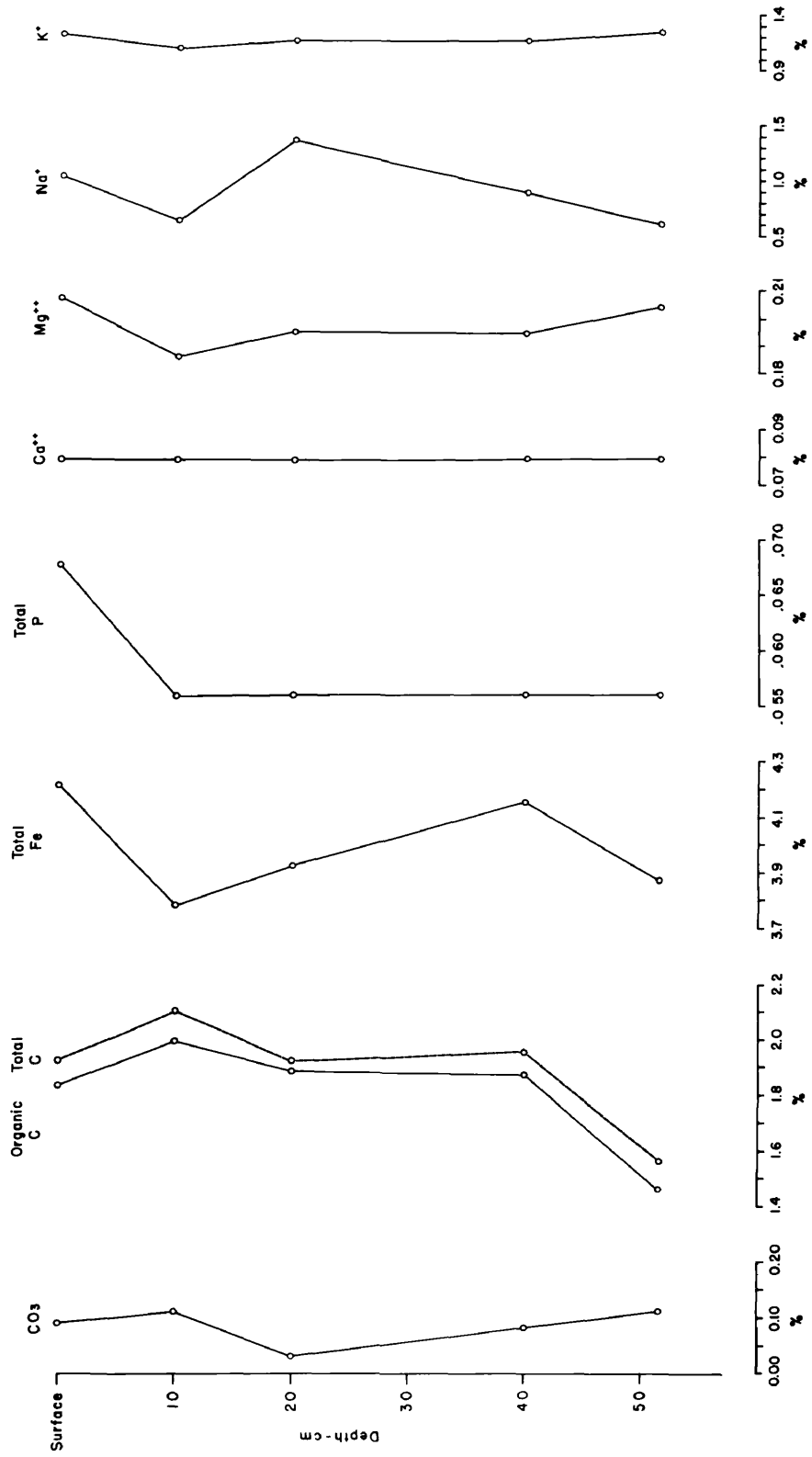
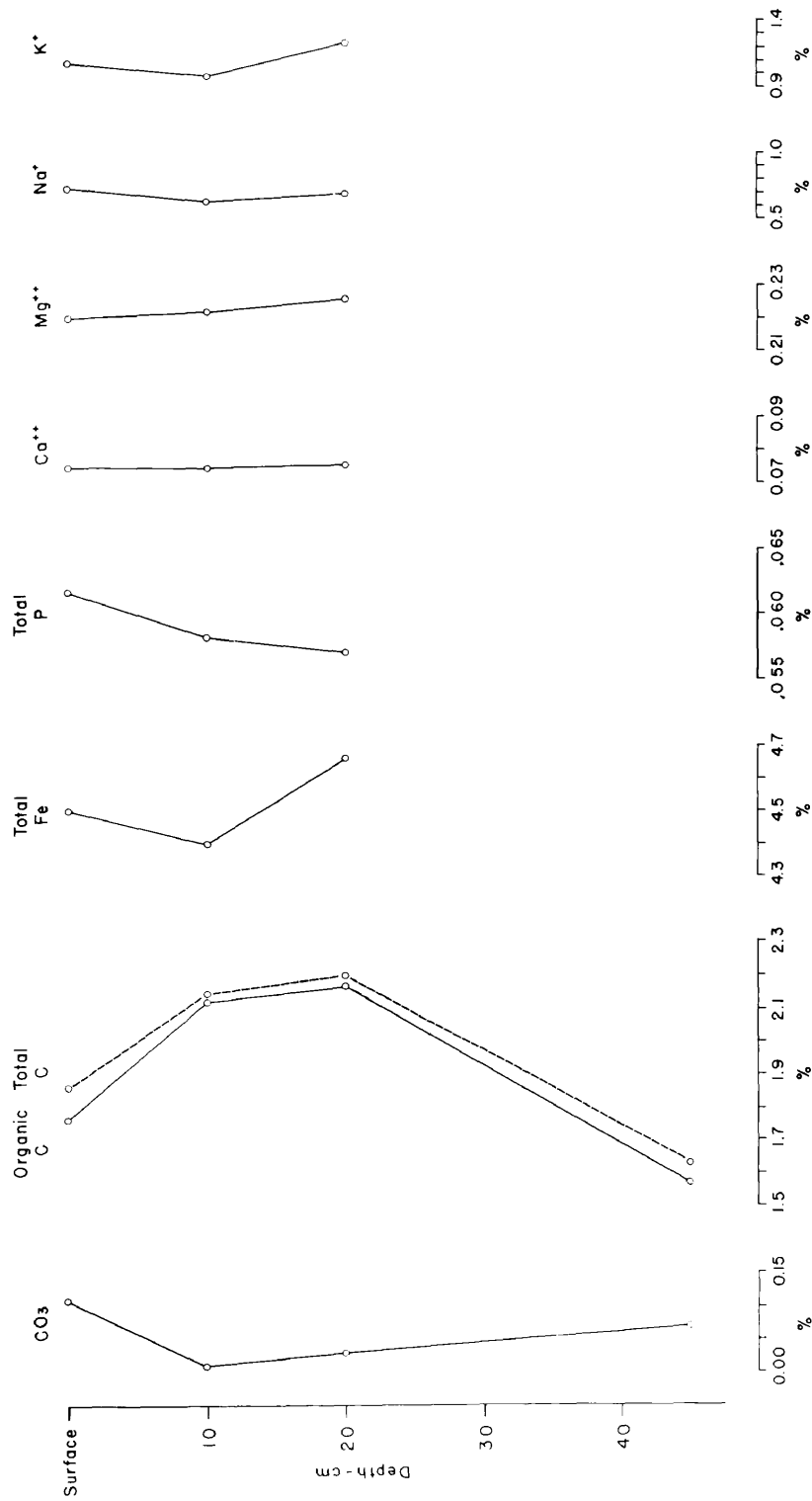


Figure 10

Variations in carbonate, organic carbon, total carbon, total iron, total phosphorus, calcium, magnesium, sodium, and potassium with depth of sediment at station 200 of a clayey silt sediment type

STATION ZOO



organic carbon below 20 cm. The highly variable inorganic carbon content of all sediments was probably due to shell depositions.

The highest organic carbon values were found in the cores (Z00, Z2, F0, and G6) from the deep water area near the spoil disposal site. Organic carbon content was lowest in the cores of sand (X0, E7, and G8). The range of inorganic carbon content in the surface sediments was from 0.02% in a sand sample (X0) to 0.39% in a clayey silt sample (A0). Organic carbon content in the surface sediments varied from 0.15% in a sand sample (E7) to 2.01% in a clayey silt sample (G6).

A poor relationship existed between organic carbon content of the sediments and depth of water. In general, a relationship between median diameter of the sediment and the amount of included organic carbon existed at the extremes of sediments sizes. Clay-sized sediments had large amounts of organic carbon and sand-sized sediments had smaller amounts. Organic carbon content of the sediments seemed to be most closely related to an areal distributional factor.

Iron.--Eleven cores were examined for changes in total iron content with depth. Only two cores (H0 and Z2) showed a higher total iron content at the surface than at greater depths.

The distribution of iron with depth in the cores was similar to the distribution of organic carbon in many instances. A relationship between total iron and organic carbon was suggested by a comparison of similar sediment types (Fig. 11). Total iron content in the surface sediments varied from 1.118% in a sand sample (E7) to 4.500% in clayey silt and silt samples (Z00 and H0).

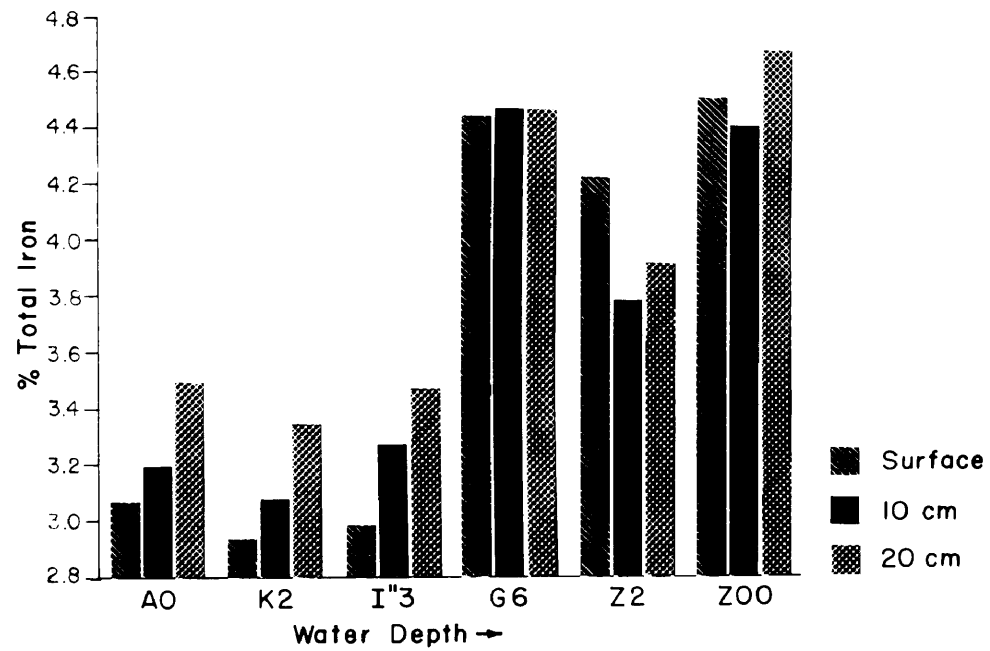
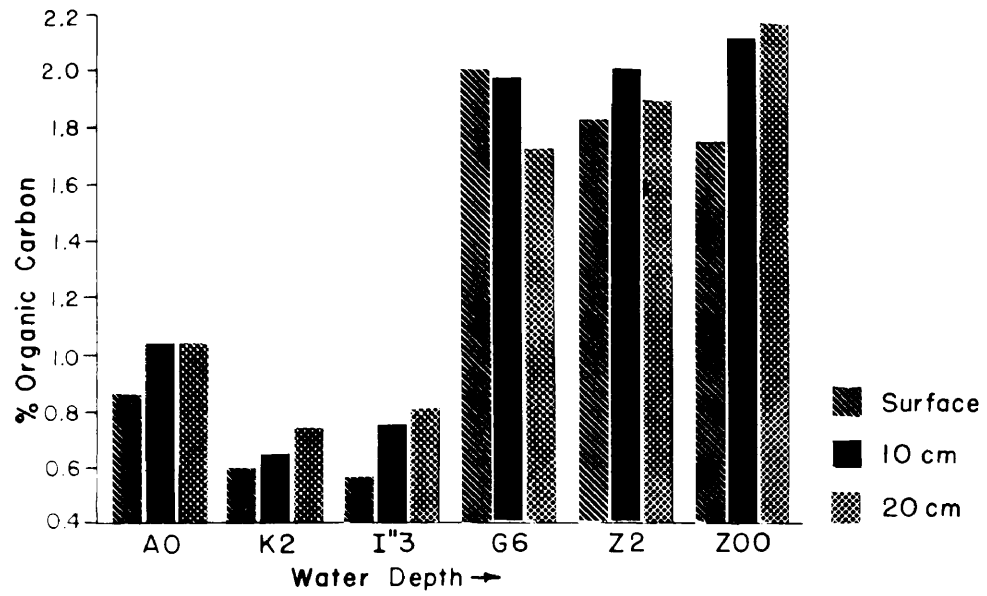
Phosphorus.--Only the core from the dredged area (K2) contained highest phosphorus values at 10 and 20 cm depths. The other ten cores showed phosphorus contents to be higher in the surface sediments.

No consistent relationship was found between total phosphorus content and depth of water, sediment type, or median size diameter of sediment. The sand samples (X0, E7, and G8) had the lowest phosphorus contents. The range of phosphorus content in the surface sediments was from 0.012% in a sand sample (E7) to 0.075% in a silt sample (H0).

Calcium and Magnesium.--The calcium content decreased at 10 and 20 cm depths in only two (H0 and A12) of the eleven cores analyzed. The magnesium content of the sediments did not reflect consistent trends with increasing core depth.

Figure 11

**Comparison of total iron and organic carbon with
depth of water and depth of core in sample sta-
tions A0, K2, I*3, G6, Z2, and Z00 of a clayey
silt sediment type**

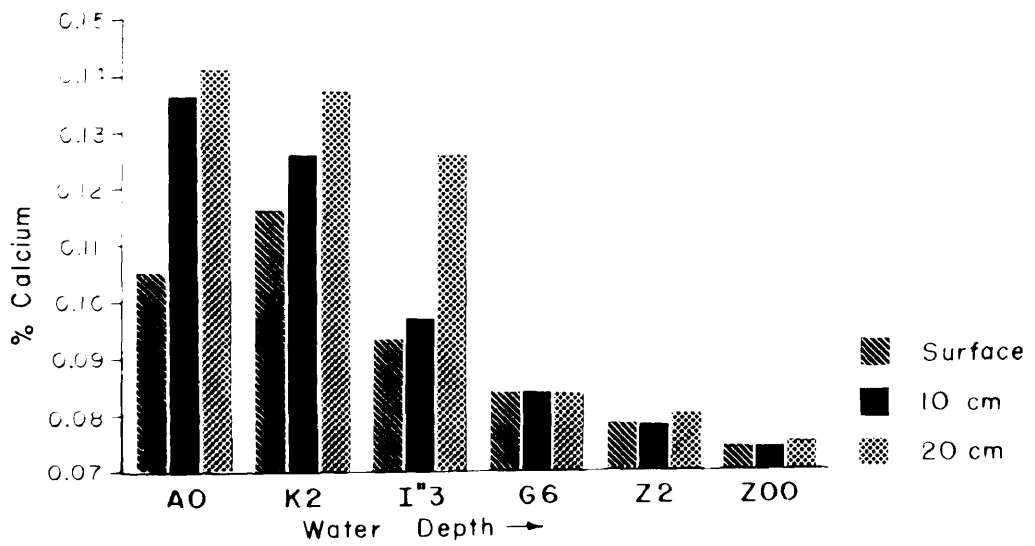
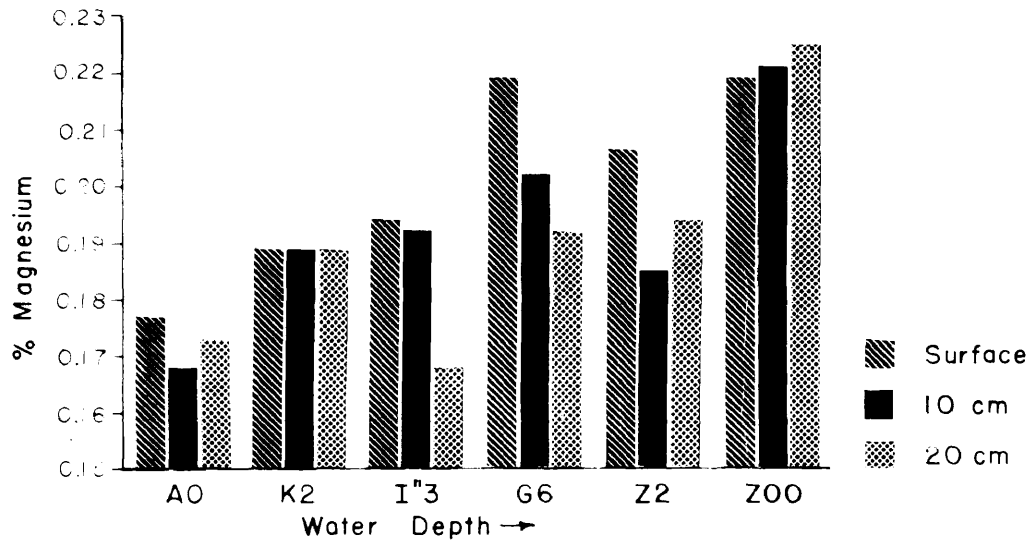


Magnesium was higher than calcium in all cores. An inverse relationship was indicated to exist between calcium and magnesium with increasing water depth (Fig. 12). The sand samples (X0, E7, and G8) exhibited the lowest calcium and magnesium contents. Calcium content in the surface sediments varied from 0.011% in a sand sample (G8) to 0.125% in a sand-silt-clay sample (A4). The range of magnesium content in the surface sediments was from 0.046% in a sand sample (E7) to 0.219% in a silty clay sample (Z00).

Sodium and Potassium.--No definite trends were indicated in the sodium or potassium content of the sediments with either increasing core depth, water depth, sediment type, or median size diameter of sediment. Neither sodium nor potassium was consistently predominant. Potassium generally showed less variation within or between cores than sodium. Sodium content in the surface sediments varied from 0.220% in a sand sample (E7) to 2.745% in a clayey silt sample (A0). The range of potassium content in the surface sediments was from 0.384% in a sand sample (E7) to 1.175% in a silty clay sample (Z2).

Figure 12

Comparison of calcium and magnesium with depth of water and depth of core in sample stations A0, K2, I"3, G6, Z2, and Z00 of a clayey silt sediment type.



DISCUSSION

Homogeneity of sediment texture and the absence of laminations in the sampled sediments is probably indicative of a reworking of the materials and a consolidation of fine mud particles into faecal pellets by burrowing and detritus-feeding invertebrate animals. Large benthic invertebrate populations were found over the entire survey area (VIMS, 1962).

There was an indication that the largest populations of the clam, Mulinia, were found at those stations with the highest organic content in the sediment. Bader (1954) demonstrated a similar relationship between the numbers of marine pelecypod mollusks and the amount of organic carbon in the sediment.

Like settling characteristics of organic constituents and fine clay particles could account for the organic carbon content being highest in the surface sediments from the deeper water area of the survey. According to Powers (1954), differential size settling of clay particles in Chesapeake Bay has been found to be limited to deep water areas. Greater preservation of organic carbon is more likely in the clay sediments than in the coarse-grained sediments. Oppenheimer

(1960) has suggested that organic matter adsorbed in the clay lattices may be unavailable for oxidation by bacteria.

A high deposition of organic matter and a rapid accumulation rate of fine-grained inorganic material could account for the high amounts of organic carbon below the surface in the majority of the survey sediments. The reducing conditions (as indicated by Eh) within several centimeters of the surface in the deeper water sediments would stop aerobic oxidation of the organic carbon. Therefore, once buried, there would be a greater likelihood of the preservation of organic carbon in these sediments.

After finding organic matter contents ranging from 6 to 15% in middle bay sediments, Ryan (1953) stated that the organic content of Chesapeake Bay muds is considerably greater than the worldwide average for estuarine sediments. It is likely that the sediments from the study area contain no more than about 4% organic matter, as carbon forms 50 to 60 % of organic matter (Trask, 1939). This diversity in organic matter content of Chesapeake Bay sediments may be due to differences in analyses or anaerobic conditions existing throughout the summer in the sediments where Ryan sampled.

During the summer an increasing oxygen depletion has been observed in the inflowing ocean water as it proceeds up the bay (Carpenter and Cargo, 1957). The movement of oceanic water up the deeper channels of Chesapeake Bay has been explained by Pritchard (1952). Oxygen measurements of the bottom waters in the survey area taken during July 1949 and 1950 (CBI, 1949, 1950) did not show anaerobic conditions to exist, but a low oxygen measurement of 1.90 ml/l was obtained during July 1950. Similar measurements taken of the bottom water in the middle bay area showed extremely low oxygen conditions consistently during the same period. Therefore, the differences of organic carbon content in the sediments of Chesapeake Bay may reflect the degree of oxygenation of the overlying waters.

The correlation found in this study between iron and organic carbon content with depth of sediment and with areal distribution reflects a similar finding by Rochford (1951) in Australian estuaries. Bass Becking and Moore (1959) also have shown direct relationships between iron and organic matter content in sediments and have theorized the existence of an "organo-iron" complex. The iron in the deep clayey sediments probably existed in the reduced or ferrous state, as indicated by the greenish-gray coloration of the cores.

An indication of a typical aerobic hydrosol condition is shown by the high phosphorus content in the surface sediments of the undisturbed stations. The oxygenated water overlying the sediments in this area probably acts as a barrier to the removal of phosphorus ions into solution. The phosphorus may be evidence of either a large contribution by plankton detritus from the overlying water or a concentration by microbial activities in the sediment itself. The condition of phosphorus decreasing with increasing sediment depth, as found in this study, has been found in many marine, estuarine, and lacustrine studies (Moore, 1930; Rochford, 1951; Shepard and Moore, 1955; Mortimer, 1941, 1942).

The cation content of the survey sediments may reflect the relative amounts of each cation adsorbed onto the mineral particles. In this study it is assumed in the comparison of similar sediment types that the differences in cation contents would be primarily due to the adsorbed ions.

The greater percentage of magnesium in the survey sediments may be attributed to the higher amount of available magnesium cations than of available calcium cations in sea water. Carpenter (1957) found a mean calcium-magnesium ratio of four to one in the lower Chesapeake Bay tributaries.

This ratio is reversed in sea water, with the proportion of magnesium being approximately three times greater than calcium (Sverdrup et al., 1960).

The increase in salinity with depth of water in the bay may explain the decrease of calcium and the increase of magnesium in the sediments with increasing water depth. Salinities of the bottom water in the area of the survey have been shown to be twice that of the surface water (CBI, 1951).

The higher bonding energy of potassium with respect to sodium may explain the nearly equal ratio of sodium and potassium in the survey sediments. The ability of clay to take up potassium has been used as an explanation of the increase of sodium over potassium in the water from rivers to the ocean (Clarke, 1924).

SUMMARY

The chemistry of the sediments from the area of the Rappahannock Shoal and the spoil disposal site reflects the depositional environment. Vertical variations in physical and chemical properties of the sediments seem to be indicative of the diagenetic environment. The more significant chemical findings noted in this study are the following.

1. There is an indication of incomplete decomposition and oxidation of organic carbon by the high amounts of organic carbon found deep in the sediment.
2. The amounts of organic carbon in the sediments of the study area seem to refute previous high estimates of organic matter for Chesapeake Bay sediments. There is probably a much greater range in organic carbon content in Chesapeake Bay muds than previously assumed.
3. Inorganic carbon in the sediments shows a highly variable content which is possibly due to shell accumulations.
4. Organic carbon and total iron data suggest that there is no uniform distribution of these compounds in the sediments and that their quantities are closely determined by the environmental characteristics of the area. The highest amounts of organic carbon and total iron are present in the deepest water area of the survey. Direct relationships are

suggested between the quantities of organic carbon and total iron with depth of sediment and with areal distribution.

5. An aerobic hydrosol condition is indicated by the high content of phosphorus in the surface sediments of all the undisturbed sediments not affected by dredging.

6. Cation variations in the sediments suggest exchange processes between sediments and water to be dependent upon the cation composition of the water, bonding energy of the cations, and the sorptive capacity of the sediment. Sand samples, by containing the least amounts of all cations, indicate a lesser sorptive capacity than the smaller-size fractions of the sediments. The inverse relationship between calcium and magnesium content in sediments with increasing water depth suggests a greater amount of available magnesium cations than of available calcium cations due to a salinity increase.

7. The ranges of the chemical components analyzed for the surface sediments in this study are as follows:

Organic carbon	0.15% - 2.01%
Inorganic carbon	0.02% - 0.39%
Total iron	1.118% - 4.500%
Total phosphorus	0.012% - 0.075%
Calcium	0.011% - 0.125%
Magnesium	0.046% - 0.219%

Sodium 0.220% - 2.745%
Potassium 0.384% - 1.175%

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