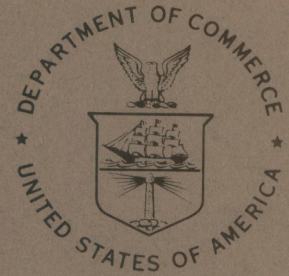


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NOAA Technical Memorandum ERL MESA-14



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DETERMINATION OF PHOSPHATE FLUXES ACROSS  
THE SEDIMENT-WATER SURFACE OF THE NEW YORK BIGHT

John W. Morse  
John de Kanel

Marine Ecosystems Analysis Program  
Boulder, Colorado  
April 1977

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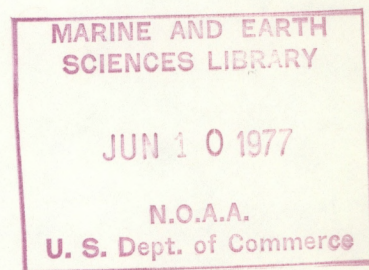
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# DETERMINATION OF PHOSPHATE FLUXES ACROSS THE SEDIMENT-WATER INTERFACE OF THE NEW YORK BIGHT

John W. Morse and John de Kanel

## 1. INTRODUCTION

Among the goals of the MESA New York Bight Project are understanding nutrient transport systems responsible for sustaining New York Bight phytoplankton, and fractionation of contaminants between water and solid phases. This research was carried out to:

1. Investigate speciation of phosphatic compounds and the reliability of present analytical methods.
2. Investigate the concentration of dissolved phosphatic compounds as a function of depth within New York Bight sediments.
3. Provide interpretation of the results in terms of probable dominant transport processes and estimates of possible phosphorus fluxes from the sediments to overlying water.
4. Provide interstitial water samples for trace metal and organic analysis.

This investigation was of a preliminary nature with only one site being visited once. The results should not be used for generalization over the New York Bight area, but should be useful in planning a more comprehensive program.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Shipboard Procedures

On October 7, 1974, samples were taken using the NOAA Ship *Ferrel*. The sampling site (40° 29'N, 73° 46'W) was on the northern edge of the Chriaensen Amphetheater 10 km north of the sewage sludge dump site. The water depth was approximately 13 m. Sampling was accomplished by a diver hand coring with plastic core liners (5 cm diameter), which were sealed with rubber stoppers immediately following withdrawal from the sediment. Eight cores were obtained from an area of approximately 1 square meter. The diver is to be commended for his careful work which allowed the cores to be recovered with little disturbance of the easily suspended flocculant top layer.



In order to obtain sufficient volumes of interstitial water from small sampling intervals, samples from two cores were homogenized prior to extraction. Although the limited number of cores did not allow a statistically meaningful analysis of local heterogeneity to be made, the extraction procedure was carried out twice in order to get some idea of the variability. Extraction in an oxygen-free atmosphere had originally been planned. However, the consistency of the sediment made extrusion from the core barrel extremely difficult and it was necessary to extrude in air. There is a possibility that some of the orthophosphate could have precipitated as a result of this procedure. Pore water was extracted by use of a bank of gas-powered nylon squeezers. Within the squeezer the water passed first through a glass fiber filter and then through a 0.4 micron Nuclepore after filter from which it entered a syringe. Approximately 25 ml of water from each sample was generally obtained. Pore water samples were poisoned with 1 ml of chloroform and sealed in glass vials.

Shipboard analysis of dissolved sulfide had been planned, but preliminary results indicated that it was not present in sufficient quantities. Samples were analyzed at Yale University within 24 hours of collection.

## 2.2 Analytical Methods

1. Reactive phosphate was determined by the standard "molybdate blue" method (Strickland and Parsons, 1972).
2. The amount of total dissolved phosphate was determined by the method of Strickland and Parsons (1972).
3. Inorganic polyphosphate was determined by the method presented by Strickland and Parsons (1972).
4. The method of Rigler (1968) was used to determine the portion of the reactive phosphate which was orthophosphate.
5. Oxidizable organic phosphate ( $UV + H_2O_2$ ) was determined by the method of Strickland and Parsons (1972).
6. Weight percent water in the sediment was determined by weight loss after drying at  $100^\circ C$  for 24 hours.

## 3. RESULTS

### 3.1 Speciation of Phosphatic Compounds

Analytic result of the phosphorus speciation study are presented in Table 1. It is the opinion of the investigators that these results illustrate the general unreliability of the presently available analytic techniques. The oxidizable organic phosphate was found to make up such a small



proportion of the phosphate that the values for it are probably within analytical error. This is emphasized by the observation that in one case a negative concentration was found. Polyphosphates were found to make up generally less than 5% of the total phosphate present (see Table 2). Reactive phosphate made up from 15 to 30 percent of the total phosphate present except for sample II, 2 to 4 cm, which yielded anomalously low total phosphate concentrations. Duplicate runs on this sample for total phosphate gave similar results (see Table 1). We have recently been involved in studying dissolved phosphate in continental slope and deep sea sediments. The data (as yet unpublished) frequently indicate total dissolved phosphate concentrations which are less than reactive phosphate concentrations. Since this is by definition impossible, we strongly suspect that there is a problem with the total phosphate method. The hydrous zirconium oxide columns that were used in the determination of the portion of reactive phosphate which is orthophosphate did not give reproducible results. It is our opinion, that while the method may work well in fresh waters, it will not work well in sea water due to competition for exchange sites by sea salts. The results probably reflect only minimum amounts of reactive phosphate in organic matter.

Data on the relative proportions of phosphatic species in solution are presented in Table 2. A point of primary importance is that all the techniques for the study of phosphatic species generally fail to account for more than a quarter of the total phosphate present (which may be underestimated). Also of importance is the data which indicate that, even with the limitations of the column technique which probably overestimates the amount of orthophosphate present, substantial proportions of the reactive phosphate are not orthophosphate.

### 3.2 Depth Trends

The two pairs of cores exhibit similar trends with depth in the sediment for total phosphate, but not for reactive phosphate. Both cores have a marked increase in total phosphate in the top 8 cm. Reactive phosphate is relatively constant in core pair I, but shows an increase by approximately a factor of 3 in core pair II. Oxidizable organic phosphate and polyphosphate show no significant trends with depth in the top 8 cm. The proportion of orthophosphate in the reactive phosphate fraction increases with depth in the sediment. Since the results are for two sets of core pairs from the same immediate area, a degree of lateral heterogeneity must exist.

### 3.3 Estimation of Fluxes Across the Sediment-Water Interface

Visual inspection of the cores indicated that there was intense in-faunal activity. Worms and living crabs were observed in the cores. It is consequently our opinion that bioturbation not diffusion is the dominant transport mechanism at the sediment-water interface. Data are not available on bioturbation rates which are probably variable both laterally and seasonally. Consequently, a flux rate cannot be calculated. Significant fluxes are possible. If 2 ml/cm<sup>2</sup> of interstitial water are exchanged per



Table 1. Analytic Results-Dissolved Phosphatic Speciation In New York Bight Sediments

Core Pair	Depth (cm)	Reactive $\text{PO}_4$	Total $\text{PO}_4$	Oxidizable Organic $\text{PO}_4$	Inorganic Polyphosphate	Reactive Orthophosphate	Weight % $\text{H}_2\text{O}$
I	0-2	36.8	124	-4.1	3.3	19.9	34.7
I	2-4	30.8	181	3.6	9.0	11.2	37.6
I	4-8	34.9	232	8.2	7.7	12.2	31.8
II	0-2	19.1	109	3.6	4.7	7.78	
II	2-4	37.8	32.9 44.7	0.2	7.7	7.78	
II	4-8	60.5	343	6.7	3.5	6.80	

Concentrations are in micromoles/liter



Table 2. Comparative Results

Core Pair	Depth (cm)	Percent of Total Phosphorous				Maximum % Reactive $\text{PO}_4$ as Ortho-
		Reactive $\text{PO}_4$	Oxidizable Organic $\text{PO}_4$	Inorganic Polyphosphate		
I	0-2	30	--	3		45
I	2-4	17	2	5		64
I	4-8	15	4	3		65
II	0-2	18	3	4		59
II	2-4	--	--	--		79
II	4-8	18	2	1		89



day, the *total* phosphate added to a stagnant column of overlying water 15 meters deep would be enough to raise the concentration by approximately 0.6 micromoles/liter.

#### 4. RECOMMENDATIONS FOR FUTURE RESEARCH

1. Development of better analytical techniques.
2. Much more intensive sampling, with a good laboratory immediately available.
3. Development of techniques for directly measuring fluxes across the sediment-water interface.
4. Study of bioturbation rates.

#### 5. CONCLUSIONS

Only a small portion of the total dissolved phosphate can be accounted for as distinct species in the interstitial waters of the site which was investigated. Although there is no direct evidence it appears probable that the dominant mode of exchange of dissolved species across the sediment-water interface is bioturbation. Small scale lateral heterogeneities exist which indicate that much more intensive sampling is necessary to understand the distribution of phosphate in New York Bight sediments.

#### 6. REFERENCES

- F. H. Rigler (1968), *Limnol. Oceanog.*, 13:7-13.
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