Phosphate Regenerative Activity in the Muds of a Tropical Estuary

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Results of some laboratory experiments on the phosphate regenerative activity in the muds of Cochin backwater were presented. Muds, selected from three different sites of the estuary, reacted differently in their phosphate regenerative activity. Sediment from the marine zone appeared to be more stable and in near equilibrium state with the overlying water. Sediments of the brackish water zone showed marked differences in their chemical characteristics and phosphate regenerative activity. Sediment from the high saline brackish water released phosphate continuously to the overlying water during the experiment, whereas the sediment from the less saline brackish water showed a reverse trend by adsorbing phosphate from the overlying water. Associated variations in pH and Eh of the sediments along with the release or adsorption of phosphates were not very regular. Probable factors influencing the regenerative capacity of the sediments have been discussed.

Recent studies on the distribution of nutrients of the Cochin backwater have revealed large variations in space and time1. Since the system is a shallow one, it was thought that one of the major factors governing the distribution of nutrients may be the variations in the regenerative property of the bottom mud rich in organic matter due to biological and chemical oxidation. Several authors2-8 have emphasized the important role played by bacteria in the mineralization of organic matter in the sediments and release of the inorganic phosphates and nitrogen compounds into the overlying water. It has been recognized that the mud-water interface is an active zone wherein mineralization of organic matter occurs6,8. In shallow systems major recycling of nutrients is affected through the sediments8. It was, therefore, thought that some observations at the mud-water interface in the laboratory would be of value with reference to the phosphate regenerative activity of the muds of the estuary.

Methods

Fig. 1 shows a part of the backwater system and the positions of the stations from where collections of mud samples were made using a Van Veen grab during January and February 1968. Station 1 was predominantly marine whereas stations 2 and 3 were brackish with salinity values of 34.52, 32.67 and 30.90% respectively at the surface.

Mud samples thus collected were cleared from large organisms such as bivalves, gastropods and polychaetes. Each sample was then spread uniformly at the bottom of a rectangular glass trough (25 x 26.5 x 30 cm) to make a layer approximately 1 cm thick. The glass troughs were filled with water collected from the surface at the respective station, with a minimum disturbance to the mud. The troughs were covered with glass plates. Estimations of inorganic phosphate were made from the water just above the mud every 24 hr, for a week. Variations in the concentrations of inorganic phosphate in the water layer immediately above the mud-water interface were taken as an approximate measure of the regenerative capacity of the mud. Associated factors like Eh and pH of the mud and water as well as the changes in the dissolved oxygen content of the water were also measured.

Results and Discussion

It is seen from Fig. 2 that the sediments during the experiments behaved very differently. Table I gives the initial concentrations of organic carbon, chlorophyll a, total phosphorus and iron in the sediments, from which it is clear that the concentrations of these differ significantly. The physical characteristics of the sediment also show considerable variation at the 3 locations. The sediments of stations 1 and 3 contained high percentage of silt and clay (73 and 47% respectively) and at station 2 the silt and clay percentage was low (25%). The rest of the
fraction in all the sediments was mostly fine sand (Cherian, personal communication). The regeneration of phosphate from the sediment (Fig. 2) was very active. Continuous increase occurred in the phosphate concentration of the overlying water which after 7 days reached a value of 9.32 µg-at/l. Very little change occurred with sediment 1 and largely a reverse trend was observed with sediment 3. Associated variations in pH and Eh of the sediments along with the release or adsorption of phosphates were not very regular. Although it was not possible to establish a strictly quantitative relationship between pH and Eh and the release or adsorption of phosphates from or to the sediments, a general association of lowered pH and Eh with the regeneration of phosphates from the sediments was evident from a close examination of the data. Carrit and Goodgal10 reported that the bottom deposits under freshwater frequently become anaerobic and acidic during stagnation and under these conditions the phosphate release during the decomposition of organic debris favours solid-phosphorus complex, as maximum uptake was found to occur in the pH range 4 to 6. The return of phosphorus to solution from adsorption complex is favoured by an increase in pH. In the present experiments a definite relationship could not be found except in the sediment 3 where the adsorption of phosphorus from the overlying water occurred at a relatively lower pH. It is found that the pH of the sediments has been in the range 7.2-8.0 and within this range the influence of pH on adsorption or regeneration of the sediments was not quite appreciable. The natural pH buffering capacity of the sediments may also be rendering it difficult to realize the true correlation between the change in the pH of the sediment and its phosphate regenerative activity. It is possible that under controlled experimental condition of pH, the formation of sediment phosphate complex perhaps would be well realized at low pH conditions as observed by Carrit and Goodgal10 and Pomero Y et al.11. But during high bacterial decomposition the lowering of pH affected by the formation of carbon dioxide and organic acids results in the release of

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Sediment 1</th>
<th>Sediment 2</th>
<th>Sediment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic carbon</td>
<td>29.75</td>
<td>11.70</td>
<td>29.55</td>
</tr>
<tr>
<td>Chlorophyll a (µg/g dry mud)</td>
<td>12.04</td>
<td>4.72</td>
<td>11.32</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>1.32</td>
<td>0.61</td>
<td>1.44</td>
</tr>
<tr>
<td>Total iron</td>
<td>66.00</td>
<td>22.00</td>
<td>75.10</td>
</tr>
</tbody>
</table>
phosphates; the concentration of phosphates may sometimes far exceed the capacity of phosphate retention of the muds at that pH level, rendering the relation of pH with phosphate regeneration activity of the sediments complicated. Therefore, it is clear that the observed pH of the sediment alone, especially at lower levels, may not give definite indication of the adsorption or desorption of phosphate by the sediments.

The redox potential of the sediment 2 accompanied by very low oxygen content and continuous increase in the phosphate concentration of the overlying water indicate a possible high microbiological activity at the mud-water interface. Sediment 3 behaved quite differently, by depleting the phosphorus content of the overlying water. In this case there was no evidence of an intense microbial action as seen from the oxygen levels of the overlying water (Fig. 2). The redox potential of the mud largely remained positive during the experiment. Only on the 4th and 5th days the potential dropped suddenly to a level of anaerobiosis with quick recovery again to positive potential during the next two days. The apparent adsorption of phosphorus of the overlying water may be due to higher iron exchange capacity of the sediment, or fixation as ferric phosphate within the sediment to a considerable extent. The highest concentration of iron (Table 1) in the sediment 3 suggests the probability of phosphorus being fixed more as ferric phosphate. Sediment 1 displayed relatively little change during the experiment as compared with sediments 2 and 3. Even though the redox potential showed some variations, the potential remained positive throughout. pH of the sediment showed erratic variations. Phosphate concentration in the water remained more or less constant. A slow and progressive decrease in the dissolved oxygen of the water suggests controlled bacterial activity of the sediment. Carrit and Goodgal10 and Pomeroy et al.11 suggested that the sediments act as a buffer on the phosphate concentration of the overlying water. While it is tempting to conclude that the increase in dissolved oxygen of the sediment 2 is the result of the decomposition of organic matter, it may be more likely due to the increase in oxygen concentration of the overlying water, perhaps due to the bacterial activity and the physico-chemical composition of the sediments. It is also obvious from the experiments that since the aerobic bacteria are quite active in the freshwater portion of the estuary, the bacterial activity and the physico-chemical composition of the sediments are the major factors controlling the phosphate concentration of the overlying water.

The concentration of phosphorus was inversely related to the dissolved oxygen of the overlying water. In this case the concentration of phosphorus may have been fixed as ferric phosphate. The high concentration of iron (7.5%) in the sediment 3 may be responsible for the observed anomaly. In sediment 2 the observed lowest concentrations of iron, phosphorus and organic matter indicate an intense biochemical decomposition affecting a greater release of phosphate on to the overlying water. The initial concentration of phosphates of the overlying water which is high, seems consistent with the observed regeneration activity of the sediment. In the sediment 1 the initial concentrations of the chemical constituents mentioned above were more or less similar to those of sediment 3. From the phosphate data the remarkable stability of sediment 1 in maintaining near equilibrium condition with the overlying water, perhaps suggests a low activity of the sediment, with the adsorptive and desorptive processes occurring more or less simultaneously. This feature reflects on the nature of the sediment and the environment in general, where fluctuations in hydrographical conditions are minimum.

Despite the limitations in the results of present experiments, the interesting features on the phosphate regeneration capacity of the Cochin backwater sediments, especially in the brackish zone, are quite apparent. They seem to reflect the effects of variable hydrographical conditions on the muds. These conditions may cause changes in the bacterial activity and adsorptive desorptive processes occurring more or less simultaneously. The order of magnitude of the changes prevailing in the natural environmental conditions may not be as high as observed under experimental conditions.

It is, however, possible that the results presented here, based on experiments in the laboratory, may give an indication (although qualitative) of the types of changes taking place in the natural environment, subject, however, to modification by physical factors such as circulation and mixing processes.

During the investigation on nutrients of Cochin backwaters, Sankaranarayanan and Qasim1 could not find any direct evidence of phosphate regeneration activity of the estuarine sediments. They reported considerable depressant effect of organic carbon, chlorophyll a, total iron and total phosphorus in the sediments (Table 1) in relation to their phosphate regenerative capacities revealed some interesting features. These initial concentrations were found to be inversely related to the phosphate releasing capacity of the sediments. In sediment 3, wherein the apparent adsorption of phosphates was noticeable, the iron and phosphorus contents were also relatively high. This feature appears to remain consistent with the close affinity of iron and phosphorus, probably getting fixed more as ferric phosphate in the sediment. The high concentration of organic matter (in terms of organic carbon and chlorophyll) appears to have no noticeable depressant effect on the phosphate adsorption. Jitts13 observed considerable depressant effect of organic matter on the phosphate adsorption. He suggested that the organic matter may influence the phosphate adsorption of the sediment by a competitive combination with the active phosphate, adsorbing elements of the silt or by masking effect of the silt particles on phosphate ions. In the present study it is felt that the presence of high concentration of iron (7.5%) in the sediment 3 may be responsible for the observed anomaly. In sediment 2 the observed lowest concentrations of iron, phosphorus and organic matter indicate an intense biochemical decomposition affecting a greater release of phosphate on to the overlying water. The initial concentration of phosphates of the overlying water which is high, seems consistent with the observed regeneration activity of the sediment. In the sediment 1 the initial concentrations of the chemical constituents mentioned above were more or less similar to those of sediment 3. From the phosphate data the remarkable stability of sediment 1 in maintaining near equilibrium condition with the overlying water, perhaps suggests a low activity of the sediment, with the adsorptive and desorptive processes occurring more or less simultaneously. This feature reflects on the nature of the sediment and the environment in general, where fluctuations in hydrographical conditions are minimum.

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During the investigation on nutrients of Cochin backwaters, Sankaranarayanan and Qasim1...
explained the large scale variations in the nutrient content of the waters based on the seasonal hydrographical and meteorological conditions. However, they found it difficult to explain why such large variations in the nutrients occur within short distances in the backwater. In the light of present experiments it is suggested that the differences in the regenerative property of the muds of the estuary at different sites may be largely responsible for such variations.

Acknowledgement

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