DIVISION of FISHERIES and OCEANOGRAPHY

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SEDIMENT TRAPPING OF NUTRIENTS IN AUSTRALIAN ESTUARIES

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COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION

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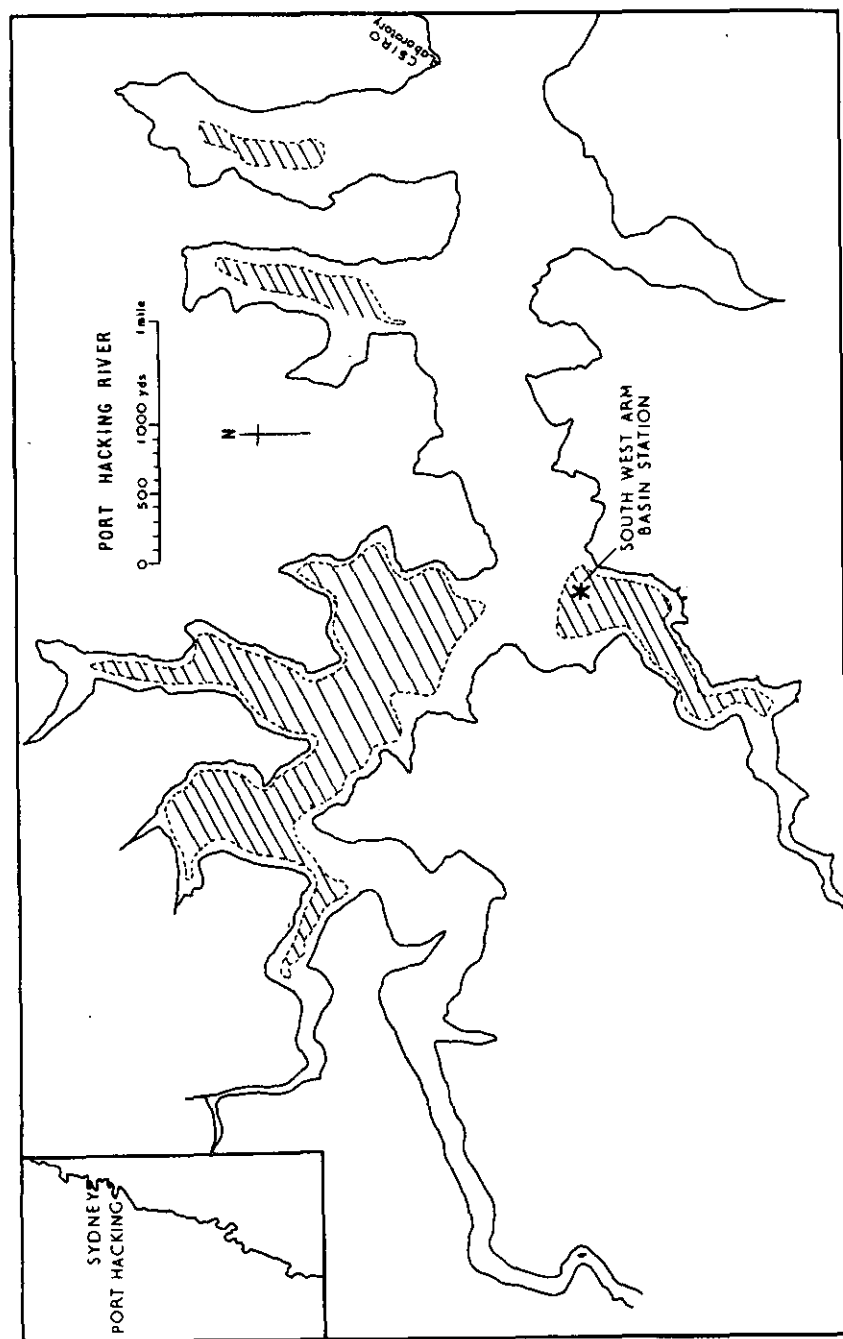
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Fig. 1. Map of Pt Hacking estuary showing depths greater than 40 feet and location of South West Arm station.

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Abstract

In general the concentration of nutrients, particularly phosphates and nitrates, in the waters of each Australian estuarine system, is quite low. During run-off there is a contribution of nutrients from leaching of the hinterland soils but this is rather spasmodic and irregular and does not seem to alter the more typical low nutrient situation. Australian coastal marine waters are correspondingly low in nutrients and it is unlikely therefore that the marine contribution to the nutrient budget of an Australian estuary is very large. However this paper shows that, during conditions of high stratification and correspondingly lowered oxygen content in the bottom waters of many Australian estuarine systems, the nutrients quite dramatically increase in concentration. Analysis of these estuarine bottom sediments shows, that particularly in the very fine high organic silt fraction, the phosphate concentrations are quite high. However the manner in which this accumulation has occurred with time, and the mechanism by which these entrapped nutrients are released during anoxic conditions is not clearly established. A number of possibilities for such an entrapment and release mechanism are examined in this paper. The implication of this mechanism for the use of oxygen and nutrients as water quality parameters in estuarine management is also discussed.

INTRODUCTION

Earlier studies (Rochford 1951, Spencer 1956) have shown that in Australian estuarine systems large increases in bottom orthophosphate concentration occur invariably during lowered oxygen concentration following upon stratification caused generally by salinity dilution during periods of vertical thermal stability. However although the relationship between intensity of stratification and the degree of deoxygenation was established in these earlier studies, no explanation of the mechanism was proven.

In 1955 and 1956 Spencer examined in much greater detail the time sequence of the deoxygenation cycle in South West Arm, Port Hacking, but was unable to write up these data before leaving the Division of
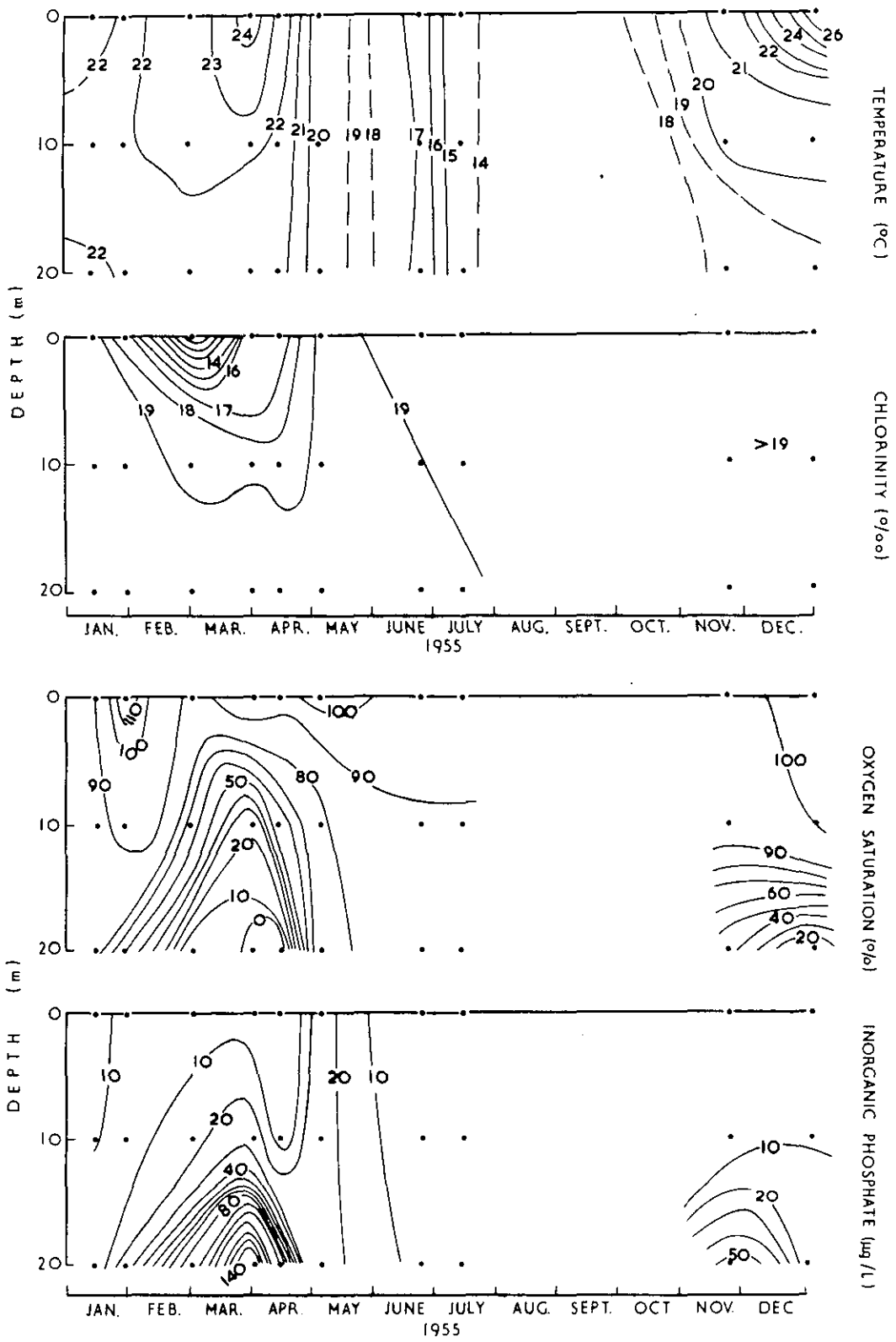
Fig. 2.   The changes with time and depth of temperature, chlorinity, % oxygen saturation and phosphates during 1955 at the South West Arm station (Fig. 1).

Fisheries and Oceanography.   It is these data that are examined in
this paper.   They provide some further evidence of the possible
mechanism responsible for nutrient trapping and release in estuaries,
but indicate also the need for further more exact sampling and in
particular the need for interdisciplinary investigations by both
biologists, physicists and chemists to provide the final solution.

DATA

The data of this paper for 1955 have been published (CSIRO 1957).
Those for 1956 however have not been published but would be made avail-
able on request by CSIRO Fisheries and Oceanography.

Since January 1974 sampling of the Pt Hacking estuary has been
carried out by CSIRO.   These data have also been used in this paper.

Figure 1 shows the location of the South West Arm station within
the Pt Hacking estuary.

ESTUARINE NUTRIENT CYCLES

Figure 2 illustrates the sequence of events during the annual
development, and disappearance of stratification in South West Arm.
During February-April the effect of stratification upon the oxygen and
phosphate content of bottom waters becomes maximal only after chlorinity
is well diluted at the surface.   It is clear also that on this occasion
the direct contribution of runoff to the orthophosphate concentration of
the surface layers is negligible.   In November and December thermal
stratification in the absence of chlorinity stratification was associated
with a decrease in bottom oxygen and a rise in phosphate but to a lesser
degree than in the previous autumn when chlorinity stratification was
also present.   The phosphates released into the bottom waters could
originate:

(a)   in the pre-stratified overall content of phosphorus in
non-soluble forms, e.g. organic phosphorus, in plant and animal
tissues;

(b)   in a detrital load containing phosphorus flushed into the
South West Arm basin during runoff;

(c)   in a sediment reservoir of phosphates released into the
water column only during near anoxic conditions.

Figure 3 shows that during the development of $Cl‰$ stratification
(A-B) relatively little change in phosphate occurred until the oxygen
concentration was around (0.28 ml/l) at point B of the cycle.   From B
to C very large increases in bottom phosphate occurred although the
breakdown in the $Cl‰$ stratification was well advanced by point C.   The
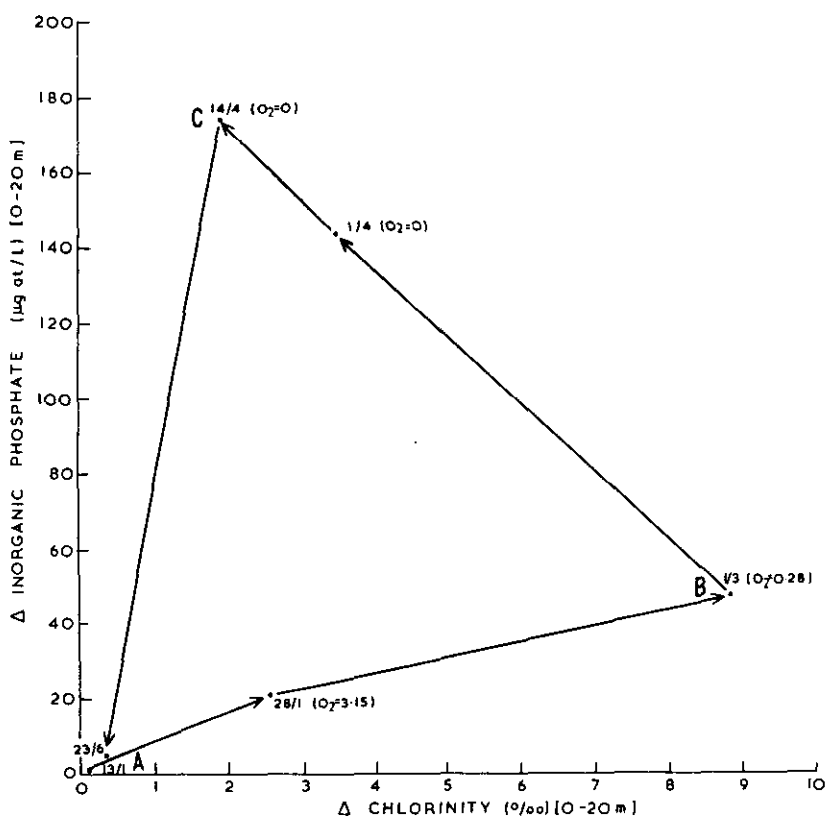bottom oxygen concentration fell to zero during B to C and was associated

Fig. 3. The sequence of changes in the Cl‰ gradient, phosphate
gradient, and bottom oxygen values at the South West Arm
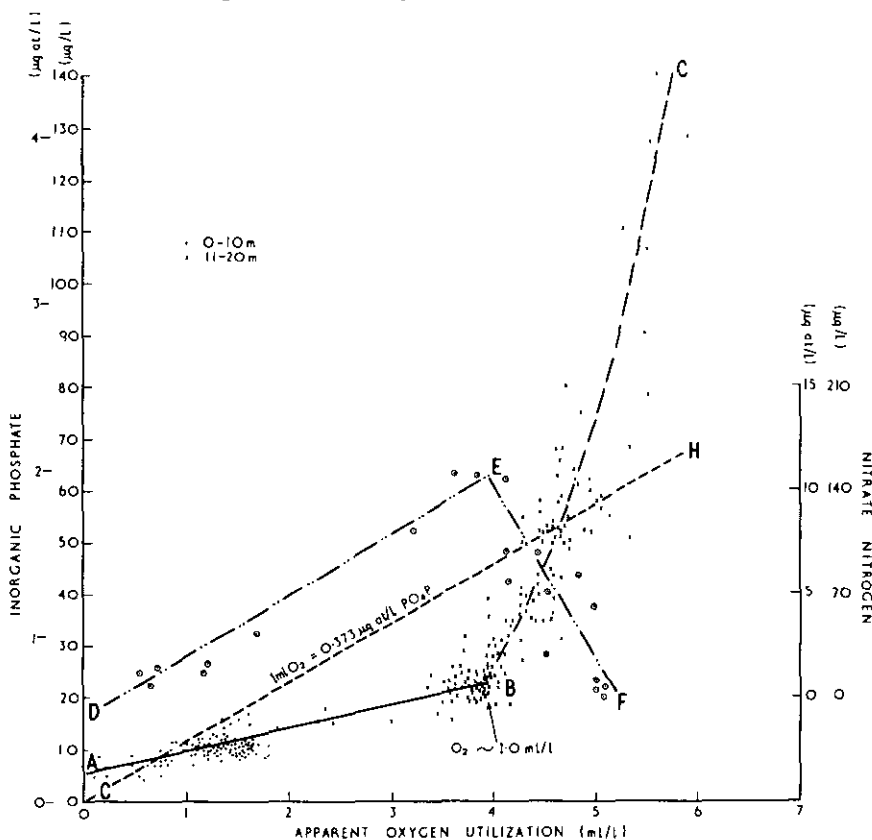station (Fig. 1) during the first half of 1955.

Fig. 4. The relationships between Apparent Oxygen Utilization (AOU) and
phosphate (line ABC) during January-April 1956 at the South West
Arm station (Fig. 1). Line GH shows the relationship between AOU
and phosphate during the biological breakdown of open sea plankton
detritus (Richards 1965). Line DEF showing the relationship
between AOU and nitrate is based upon 1974 data from South West
Arm.

with the large increase in phosphate.   However the terminal point of
the phosphate cycle (c) must have been the result of other than physical
mixing.   Most probably it represented the point of exhaustion in the
cycle of perhaps organic matter required for biological processes.   From
point C onwards however physical mixing caused bottom reoxygenation and
presumably reduction in the mean column phosphate.   The very low
phosphates at the culmination of the cycle (point A) however must have
been the result of one or other of the following:

(a) biological fixation and loss from the basin by advection;

(b) biological fixation and incorporation as detritus into the
bottom sediment;

(c) ferrous to ferric iron phosphate transformation and its
flocculation onto the bottom sediments.

INTER RELATIONSHIPS BETWEEN PHOSPHATE, NITRATE AND OXYGEN CONCENTRATION

Figure 4 shows the relationships observed during the development of
the stratification cycle in the South West Arm basin of Pt Hacking (data
mainly from 1956).

During the initial phase of reduction in oxygen concentration
phosphates in both the upper 10 and lower 10 m of the water column
increased at much the same rate (5µg/1 or 0.15 µg-at/1 per 1 ml O_2/1).
Nitrates during this same phase increased at the rate of 42 µg/1 or
3µg-at/1 per 1 ml O_2/1 decrease.   The average N/P ratio during this
phase is 8.4:1 by weight or 20:1 by atoms.   Beyond an apparent oxygen
utilization (AOU) value of 3.75-4.00 ml however phosphates increased at
a much faster rate (50 µg/1 or 1.56 µg-at/1 per 1 ml O_2/1) whilst
nitrates decreased reaching zero concentration at an AOU of 5 ml/1.   At
an AOU of 4.00 ml/1 the actual oxygen concentrations were around 1.00 ml/1
whilst at the 5.00 ml/1 they were around 0.00 ml/1.

All of the measurements of Figure 4 were no closer than 1 m to the
sea bed.   Recent precision sampling by diving has shown that when measur-
able concentrations of oxygen were found at 1 m above the bottom, no oxygen
was found within 10-20 cm of the bottom.   Thus the change in the rate of
phosphate accumulation and the change in sign of the nitrate counterpart
around 1 ml/1 of oxygen might be the result of anoxic conditions develop-
ing immediately above the bottom of the basin.

In the open ocean the increase in phosphate by biological degradation
of planktonic matter, is accompanied by a decrease in oxygen in the ratio
0.373 µg-at/1 of phosphate : 1 ml/1 of oxygen.   In South West Arm the
organic matter involved in the initial phase of the phosphate-oxygen cycle
must be poorer in phosphorus relative to carbon (the major oxygen accept-
or) than that of the plankton organic matter of the open ocean.   Moreover
this organic matter of South West Arm is also much richer in nitrogen
relative to phosphorus than that of the open sea.   It is likely therefore
that the organic matter principally involved in the initial phase of the
nutrient-oxygen cycle in South West Arm is of plant rather than animal
origin.

Beyond the AOU value of 4 ml/1 however we must be dealing with an organic system that is much richer in phosphate than even the open ocean plankton, if the only source of phosphates continues to be organic detritus. It is thought more likely however that here we are dealing with the sedimentary system in which phosphates having been trapped from all sources for lengthy periods of time are released by microbiological activity during anoxic conditions. The decrease in nitrate during this second phase of the nutrient-oxygen cycle would be the result of bacterial reduction of nitrate, to provide a secondary source of oxygen. However nitrates are fully reduced before the phosphate enrichment cycle has finished and presumably bacterial reduction of sulphates provides the oxygen for the final stages of the cycle. The highest phosphate recorded during this cycle was around 4 μg-at/1 which would be the equivalent of the biological degradation of 160 μg/1 of carbon if the organic matter involved was planktonic in origin. This carbon equivalent is some 5-8 times greater than observed by Newell (1967) in the eastern Indian Ocean. However these South West Arm carbon equivalent values are similar to those (100-200 μg/1) found in the most productive regions of the world oceans, e.g. north-eastern Pacific (Parsons and Strickland 1962). Unfortunately no values for the carbon content of Australian estuarine waters are available.

However Rochford (1951) analysed estuarine bottom sediments of South West Arm for their phosphorus content and found during a two year period a mean total phosphorus value of 646 μg/g (SD 146) and a mean adsorbed phosphate value of 45 μg/g (SD 31.5). Thus the total phosphorus content of only 1 cm depth of sediment if completely solubilized through a 10 x 10 cm square, and mixed into a 1 m water column of the same dimension could increase the phosphate concentration to 500 μg-at/1. Less than 1% solubilization would therefore be required to build up the maximum observed value of 4 μg-at/1 of phosphate. Provided the microbiological or other mechanisms for their release therefore exist the relatively large increases in bottom phosphates in South West Arm could easily be derived from the phosphates stored in the sediments.

Bass Becking and Mackay (1956) examined the biological effects of the sulphate reduction systems in a number of Australian estuaries. They have shown that under stressed conditions *Enteromorpha* can release phosphates from an outer pellicle. Perhaps the initial phosphate release in South West Arm is attributable to the effects of dilution upon *Enteromorpha* and other sea grasses.

DISCUSSION AND CONCLUSIONS

In South West Arm (Pt Hacking estuary) the inter-relationships between P, N and O at varying concentrations can be interpreted as follows:-

(a) During runoff large quantities of plant organic matter are swept into the basin and gradually settle to the bottom.

(b) The biological decomposition of this plant organic matter, reduces the oxygen concentration to around 1 ml/l at 1 m above the sediment surface. On this surface however it is highly likely that anoxic conditions would develop when the 1 m oxygen concentration is 1 ml/l or less.

(c) Microbiological reduction of nitrates, and eventually sulphates in these anoxic conditions, enables the final biological breakdown of the plant tissue to be completed. Phosphates are released at the same time into the water column.

(d) However most of the phosphates accumulated in the bottom basin waters under anoxic conditions are released from the bottom sediments largely by changes in pH and Eh caused by microbiological activity. The system involved is most probably a ferric-ferrous iron phosphate one.

(e) Phosphates continue to increase in bottom waters during the period of breakdown of Cl‰ stratification. The oxygen demand (BOD?) is apparently greater than the inflow of oxygen from the surface by mixing. At some stage however the BOD becomes very small and from then on in the cycle reoxygenation is rapid. Presumably the BOD becomes quite small when the organic matter added during runoff is fully degraded.

(f) The rapid loss of phosphate from the deep basin waters after reoxygenation begins is attributable to the oxidation of ferrous phosphate to various forms of ferric phosphate. The latter in seawater flocculates and settles to the sediments, thus completing the entrapment process.

REFERENCES

Baas Becking, L.G.M. and Mackay, M. (1956).- Biological processes in the estuarine environment. V. The influence of *Enteromorpha* upon its environment. *Proc. K. ned. Akad. Wet.* Ser. B, 59: 109-123.

CSIRO (1957).- Estuarine hydrological investigations in eastern and south-western Australia 1955. *CSIRO Aust. Oceanog. Stn. List* 29.

Newell, B.S. (1967).- Seasonal variation in the Indian Ocean along 110°E. II. Particulate carbon. *Aust. J. mar. Freshwat. Res.* 20: 51-54.

Parsons, T.R. and Strickland, J.D. (1962).- Oceanic detritus. *Science N.Y.* 136: 313-14.

Richards, F.A. (1965).- Chemical observations in some anoxic sulphide-bearing basins and fiords. Proc. 2nd International Water Poll. Res. Conference Tokyo 1964.

Rochford, D.J. (1951).- Studies in Australian estuarine hydrology. I. Introductory and comparative features. *Aust. J. mar. Freshwat. Res.* 2: 1-116.

Spencer, R. (1956).- Studies in Australian estuarine hydrology. II. The Swan River. *Aust. J. mar. Freshwat. Res.* 7: 193-253.