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# Cycling of Nutrients in Estuaries<sup>1</sup>

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The cycling of nutrients required for the growth and reproduction of estuarine organisms must be understood if we are to manipulate the estuarine environment to obtain maximum production of fish and shellfish. When the cycling of nutrients is interrupted, or when the supply of nutrients is limited, the growth of estuarine primary producers such as phytoplankton and marsh grass is reduced. This reduction can adversely affect the flow of energy through the estuary and the production of fish and shellfish. If levels of nutrients are increased in certain phases of the cycle, however, production is increased. The use of radioisotopes has advanced our understanding of the cycling of nutrient elements. The cycling of carbon, phosphorus, and certain trace metals has been studied with this technique. For example, the movement of zinc, a trace nutrient, has been investigated at the Radiobiological Laboratory. Radioactive zinc was used to follow the movement of this nutrient through the water, biota, and sediments of experimental environments in the laboratory and in tidal ponds. Also, the exchange of this element between water and sediments was measured in an estuary. Sediments act as a reservoir for zinc, which exchanges rapidly between sediments and sea water. It is therefore unlikely that zinc limits estuarine production. Techniques used in this study can be applied easily to investigations of other trace nutrients.

#### INTRODUCTION

A BASIC UNDERSTANDING of the cycling nutrients will contribute greatly to man's capability of manipulating estuaries to increase the yield of seafood. Already, estuaries are among the most productive areas in the world and their importance continues to grow with the world's growing populations. As the need for food continues to increase, however, estuarine acreage suitable for aquatic life continues to decrease as a result of pollution, filling, dredging, and other activities of man. Since new estuaries cannot be created, except at great expense, it is urgent that further destruction be stopped and that better utilization of existing estuaries be initiated. The farmer already has experienced a reduction in acreage of his farmland as a result of industrialization and of government crop control. To counteract this reduction, farmers have used good management techniques to increase their total yields despite the decreased

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acreage. If we are to obtain more seafood from our estuaries we must also use good techniques in managing them.

It has been demonstrated repeatedly that small enclosed bodies of water can be manipulated to insure increased yields of fishery organisms. This approach has been exploited successfully in Japan and elsewhere. Many times production has been increased by simply increasing the level of certain inorganic nutrients in the water. Some thought currently is being directed toward increasing production of oceanic waters, but this undertaking would be difficult and expensive because of their enormous size. Nature, however, has provided man with an environment, ranging in size between ponds and the open ocean, which may prove to be adaptable to the techniques of aquaculture — the estuary. In other words, we may be able, in the not too distant future, to manipulate this environment to obtain greater yields of seafood.

Estuarine ecosystems including marshes, tidal creeks, and bays differ from fresh water and marine ecosystems in their relatively high concentrations of nutrients. In contrast to other ecosystems, estuaries can act as nutrient "traps" (Schelske and Odum, 1961). Nutrients entering the estuary from fresh water drainage systems and originating from the decay of marsh plants within the estuary are trapped by physical, chemical, and biological processes. For instance, the mixing of waters of different salinities produces vertical currents which move the nutrients rapidly throughout the water, biota, and sediments and reduce the amounts swept out to sea. Biodeposition is another mechanism by which nutrients are retained. The ribbed mussel, *Modiolus demissus*, deposits great quantities of organic particles as pseudofeces that sink to the bottom (Kuenzler, 1961). Nutrient materials in these particles thus become available to other organisms. Biological processes may be most important, therefore, in retaining nutrients in the estuary.

The large quantities of nutrients trapped in the estuary promote a high rate of plant production. This production is of utmost importance since all animals in the estuary are either directly or indirectly dependent upon the photosynthetic capability of plants. Shallow estuaries, such as those along the Atlantic Coast, have three main groups of primary producers: microscopic algae, seaweeds, and salt marsh phanerogams. These plants supply the organic material that flows through the biota of the estuarine ecosystem. Much of this material never reaches carnivores or the animals used as food by man and thus can be considered "wasted." For example, some organic material is eaten by organisms which are not used as seafood. Frequently, these organisms prey on or parasitize the organisms harvested for food. Thus, two problems confront those concerned with increasing the yield of fishery organisms: (1) increasing the production of organic matter, with which this paper is concerned, and (2) channeling the organic material into food webs that support fishery organisms.

Estuarine water at least part of the time contains inorganic nutrients necessary for high production of organic matter. These nutrients, however, are not always present in the water in proportion to the requirements of the plants, and a lack of sufficient quantities of one or another nutrient often is limiting to the production of organic matter. Further, all of a nutrient present in the water is not always available to plants,

since nutrients may occur in complex molecules or coupled to soluble organic compounds which cannot be metabolized. Finally, the level of a nutrient in the water at any given time represents only the net difference between all factors tending to increase the concentration and all factors tending to decrease the concentration. Data on the levels of nutrient present at one particular time give no information on the most important factor — the rate of turnover of the element in the estuary.

# STUDY OF NUTRIENT CYCLING WITH RADIOISOTOPIC TECHNIQUES

Determining the rates of flow of nutrients through the estuary is difficult since many nutrients occur in trace amounts. With radioisotopic techniques it is possible to determine not only the rates of movement of nutrients but also their routes of movement. By coupling chemical analysis of the stable element with radioisotopic measurements it is possible to determine if the radioisotope is being distributed in proportion to the abundance of the stable element. This procedure makes it possible to observe the rate of flow and the cycle the element takes in moving throughout the estuary. Information on the rates of movement of several nutrients have been obtained with the radioactive-tracer technique. For example, carbon 14 has been used to determine the rate of production of organic material and the movement of this material through the ecosystem. Other radioisotopes, such as phosphorus 32 and zinc 65, have been used also as tracers in nutrient studies in the laboratory and in the field.

Nutritive elements are cycled continuously through water, sediments, and biota — the three phases of the estuarine environment. Water is the medium of transport for these elements as they move in the environment and the chemical composition of the water influences the physical state of certain elements. Thus, the composition of the water affects the availability of these elements to the biota. Although the concentrations of many elements in estuarine water are small, they are in equilibrium with large reservoirs in the sediment and suspended material in the water. The ease with which shallow water can be stirred and mixed increases the importance of exchange of elements between estuarine sediments and water to such an extent that the sediments may have a major influence on the routes and rates of movement of nutrients. Nutrients sorbed onto sediment particles under certain conditions are available to the biota. Sediment-sorbed nutrients can occur again in the water and be accumulated by the biota by absorption and adsorption. Although animals accumulate nutrient elements from the water, most of their nutrient requirements are obtained from food. A portion of the nutrients accumulated by the biota is returned to the environment through excretion and through decomposition of organisms after death. The nutrient cycle in an estuary can be described as the movement of nutrients through the three phases superimposed upon the movements of these phases. For example, the sorption of a nutrient onto a sediment particle suspended in the water represents the movement of a nutrient, but the injestion of the particle containing the nutrient by an organism represents the movement of one of the three phases. A simplified schematic diagram of a typical nutrient cycle in an estuary is shown in Fig. 1.

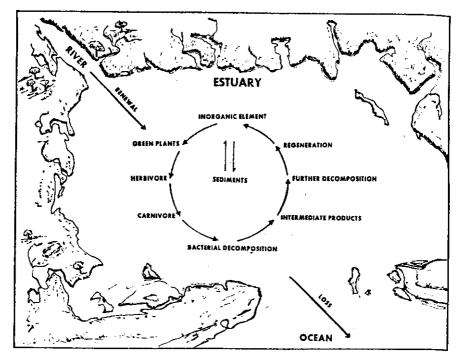


Fig. 1. Simplified schematic diagram of a nutrient cycle in an estuary.

#### Carbon Cycle

The carbon cycle is one of the better known nutrient cycles in the aquatic environment. Carbon, which occurs in sea water as CO2, HCO, and covalently bound in certain soluble compounds, is converted into organic material by photosynthetic plants. Plant materials are transferred to herbivores that graze upon them. These herbivorous animals are then preyed upon by carnivorous animals. Plants and animals which are not eaten release their contained carbon to the environment upon death. Carbon accumulated by animals also is returned to the water by respiration and excretion. The release of carbon by living and dead plants and animals accounts for a large portion of the total organic carbon present in sea water. Expressed on a relative scale with 100 equaling the amount of soluble organic matter in sea water, the total organic matter approximates the following distribution: soluble organic 100; particulate detritus 10; phytoplankton 2; zooplankton 0.2; and fish 0.002 (Parsons, 1963). This distribution is for the oceanic environment and probably would differ somewhat from the distribution in estuaries. No similar data, however, are available for the estuary. Relatively little is known about the rate at which carbon is produced in an estuary and even less about the movement of soluble and particulate carbon. Carbon 14 has been used as a tracer to investigate these problems in the oceans.

Carbon 14 has been used to observe the influence of bacteria on

the movement of organic material between sediments and sea water (Duke, Ibert, and Rae, 1961). A naturally occurring spectrum of carbon 14-labeled organic material was sorbed onto montmorillonite clay and the loss of the carbon 14 from the clay in the presence and absence of marine bacteria was compared. The organic material was prepared by growing phytoplankton in synthetic sea water containing BaC"0, and then extracting the labeled organics from the cells. Flasks containing clay slurry labeled with the carbon 14 organics were inoculated with marine bacteria and placed on a rotary shaker. After 7 days, the carbon 14 of inoculated clay was compared with that of the clay in flasks containing no bacteria (control). Some of the bacteria increased the removal rate in the 7-day period by a factor of about two (Table 1). Occurrence of such a phenomenon in nature would make sediment-sorbed materials more available to the biota.

TABLE I

EFFECT OF BACTERIA ON THE MOVEMENT OF CARBON 14-LABELED
ORGANICS FROM CLAY TO SEA WATER AFTER INCUBATION FOR 7 DAYS'

Bacteria strains	Carbon 142 cpm/ml	Amount removed (percent)
No bacteria (control)	1,089	0
10 BGP (Pseudomonadaceae)	469	51
14 TA (Pseudomonadaceae)	536	51
18 TGA (Brevibacteriaceae)	<b>639</b>	41
19 TG (Pseudomonadaceae)	668	39
16 TG (Achromobacteriaceae)	753	31
16 TGB (Achromobacteriaceae)	831	24

Data taken from Duke, Ibert, and Rae (1961). Average carbon 14 content of clay from three experiments.

A sensitive method for measuring primary productivity became available with the production of radioisotopes (Steemann Nielsen, 1952). By this method the rate at which energy is accumulated in the form of organic matter can be calculated from the net mass of carbon fixed per unit of time per unit volume of water. An adaptation of this method has been used to estimate benthic productivity (Grontved, 1960). Core samples, suspended in filtered sea water containing HC"O<sub>1</sub>, are maintained in sunlight and shaken periodically. After 2 hours, a sample is filtered. From the proportion of carbon 14 on the filter, Grontved calculates "potential production" and suggests that real production is about one-half this amount. This method for measuring benthic production is sensitive and relatively simple to apply. Application of these methods to estuarine waters will provide estimates of total organic production which is potentially available to fishery organisms through the carbon cycle.

#### Phosphorus Cycle

Phosphorus and carbon are related with respect to the regeneration and assimilation of nutrients. These elements and nitrogen occur in sea water in a nearly constant ratio (C:N:P=41:7:1 grams). Also, the ratios of the three elements in plankton are very nearly the same. For

many years the low concentration of phosphorus has been known to be a factor limiting the growth of phytoplankton in the sea. Studies in the laboratory with pure cultures, as well as work in the field, have shown that phosphorus often is deficient where blooms of phytoplankton do not occur or are short-lived. That the phosphorus concentration of the medium decreases following an increase in the phytoplankton population has been relatively easy to demonstrate in the laboratory. Detection of phosphorus exchange, however, was not possible until tracer techniques for radioactive phosphorus were developed. Using these techniques, Rice (1953) investigated the exchange of this important nutrient between sea water and phytoplankton. Phytoplankton cells which had accumulated phosphorous 32 were placed in a medium which was continually renewed and contained only stable phosphorus. The appearance of radioactive phosphorus in this medium indicated that phosphorus exchange had occurred. When the cells were maintained in the light the rate of movement of the radioactivity was rapid at first and then decreased with time; after 14 days, 6.97% of the total radioactivity contained in the cells had been exchanged to the medium. When the radioactive cells were maintained in the dark, only 3.26% of the phosphorus 32 in the cells exchanged with the medium in 14 days.

The exchange of phosphate between estuarine water and sediment also has been studied experimentally with phosphorus 32 (Pomeroy, Smith, and Grant, 1965). This exchange consisted of a two-step ion exchange between clay minerals and water, plus an exchange between interstitial microorganisms and water. Biological exchange was insignificant in undisturbed sediments but in suspended sediments biological exchange moved nearly as much phosphate as was exchanged with clay minerals. These results confirm the suggestion that sediments act as a buffer on the phosphate content of estuarine water. Rates of exchange and the exchange capacity of the sediments appeared to be large enough to maintain phosphate at a level favorable to plant production, even though phytoplankton blooms and tidal flows tended to decrease the concentration of phosphorus in the water.

## Zinc Cycle

Of the three nutrient cycles discussed in this paper, least is known about the zinc cycle. It is known, however, that zinc does occur in all three phases of the estuarine environment. In water, this element is postulated to exist mostly in the ionic state but some zinc also occurs in a complexed form. In the sediment phase, zinc probably occupies spaces in the lattice structure of clays or is sorbed onto surfaces or interfaces of other sediment particles. Zinc is relatively abundant in several species of marine organisms and is essential for their growth and reproduction. This element is sorbed onto mucous surfaces and is specifically bound to enzymes, such as carbonic anhydrase and alcohol dehydrogenase. Although zinc occurs in minute quantities in sea water, observations have been made on its movement through estuarine communities maintained in experimental ponds and in the laboratory.

The movement of zinc through the water, sediments, and macrobiota of two experimental estuarine ponds was followed with zinc 65 as

a tracer (Duke, Willis, and Price, 1966). One pond was essentially a closed system, whereas the other was connected to an adjoining estuary. In the closed system, zinc 65 introduced into the water of the pond moved rapidly from the water to other components of the ecosystem. After 1 day only 66% of the zinc 65 remained in the water. In the open system, 82% of the zinc 65 was flushed out of the pond within 1 day by tidal exchange of water. Of the zinc 65 remaining, 36% was in the bottom sediments, 59% in the water, and 5% in the macrobiota. The filter feeding mollusks-oysters, clams, and scallops-in both ponds accumulated more zinc 65 and contained more stable zinc per unit weight than did blue crabs, mud crabs, snails, croakers, and cord grass-the other organisms in the pond. After 100 days, the bulk of the zinc 65 and stable zinc was in the sediment in both ponds. Analysis of the ratio of zinc 65 to stable zinc (specific activity) in components of the ecosystem indicated that the exchange of zinc between sediments and water controlled the movement of this element in the ponds. Evidently, sediments may act as a reservoir for zinc in the estuarine environment.

Movement of a nutrient, such as zinc, through the estuarine ecosystem and its availability to the biota depends in part on the chemical state of the nutrient in the water. Therefore, if zinc were complexed with organic material in sea water, organisms might accumulate it at different rates and to different levels than if the zinc were not complexed. To test this possibility, communities of organisms and sediments were exposed to zinc 65 in sea water in a complexed and uncomplexed state (Annual Report, Radiobiological Laboratory for fiscal year ending June 30, 1963; Circular 204). Zinc 65 in the form of ionic zinc in HC1 was added to sea water containing EDTA (ethylene diamine tetraacetic acid) and the water was flowed through a tank containing oysters, clams, and samples of montmorillonite clay. Water containing an equal amount of zinc 65 but without the chelating material was flowed through another tank that contained the same species of organisms and same type of sediment. After 21 days, sea water without zinc 65 was flowed through both tanks so that the loss of the isotope from the organisms and clay could be observed. There was a difference in the rates and levels of accumulation of zinc 65 by organisms and clay in the two tanks (Fig. 2). For example, oysters maintained in water without chelate (tank 1) accumulated 24 times as much zinc 65 in 21 days as did those maintained in water containing the chelate (tank 2). The loss of the isotope from the organisms in the two tanks also was different. After 21 days in the loss phase of the experiment, oysters in tank 2 lost twice as much of their zinc 65 content as oysters in tank 1. Evidently, biological uptake and loss of zinc was affected by the chemical state of the element in the sea water.

#### SUMMARY

Fishery production in the estuarine environment can be increased by increasing primary production of organic material. If methods can be developed for channeling the organic material into food chains of commercially important species, then fishery production can be increased to the maximum. Primary production is frequently limited by a lack of sufficient quantities of a particular nutrient. In these situations, simply supplying this nutrient in adequate amounts will increase production to

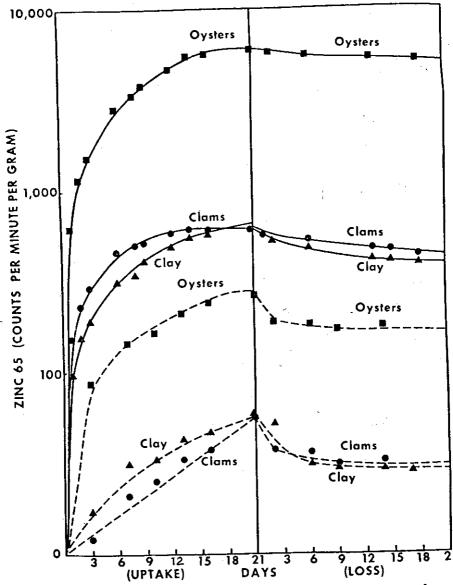


Fig. 2. Effect of EDTA on uptake and loss of zinc 65 by oysters, clams, and clay samples. Broken lines represent uptake by animals and clay maintained in water containing the chelate.

a level where some other factor becomes limiting. To be able to supply the right nutrients in proper amounts will require more data on their availability to plants, the rates of turnover of the nutrients in each reservoir, and the routes taken by nutrients as they move through the ecosystem. Nutrient cycles in the estuary must be understood—and understanding of the cycling of a nutrient will require an extensive investigation into the various dynamic aspects of estuarine ecology. Once this information is available, more effort can be directed toward channeling organic material into seafood organisms.

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