CYCLING OF ELEMENTS IN ESTUARIES

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ABSTRACT

Meaningful evaluation of the ecological stresses imposed by man's release of heavy metals or radioisotopes into estuaries requires an improved understanding of the interactions between the waste materials and the functional components of the ecosystem. In this paper, we review and discuss the types of information required for the development of useful models for the cycling of contaminant metals (both radioactive and stable) in estuarine ecosystems. With particular reference to the coastal plain estuaries of the southeastern United States, we discuss the major reservoirs of those metals, the mechanisms and pathways of elemental transformation and rates of elemental turnover among reservoirs, and the responses of these processes and reservoirs to environmental change. A conceptual systems model is presented as the preliminary phase in the development of dynamic mathematical models of elemental cycling.

Estuaries form the interface between the open ocean and man's land base, which in the coastal zone undergoes intensive development to facilitate maximum use of the sea. This narrow interface is a highly productive environment used at some stage of development by most of the marine fishery organisms exploited by man. Waste products of man's expanding population and increasing industrialization are transported into and through this estuarine environment and may render the habitat unsuitable for desirable species, or may render certain species unfit for human consumption. Man's impingement upon estuaries has assumed many forms; estuarine habitats have already succumbed to industrial and municipal pollution, to landfill and dredging operations; and economic and population pressures demand that additional estuarine areas be challenged by an increasing multiplicity of additions and modifications whose combined ecological effects are yet unknown.

Meaningful evaluation of the ecological stresses imposed by man's activities requires an improved understanding of the interactions between the wastes and the functional components of the ecosystem. Such understanding entails knowledge of the general principles of ecosystem operation, and not merely a description of the ecosystem structure at one or more instants in time. Man's continued and expanding variety of demands on estuarine environments as producers of food, avenues of transportation, receptacles for wastes, and as sources of recreational and esthetic pleasure make it imperative that we understand the interactions of all the material imports, whether of human or natural origin; and all the outputs, including both tidal exports and human exploitation of resources, to ensure the continued viability of the resultant ecosystems. No estuarine ecosystem has yet been studied in sufficient detail to permit accurate prediction of ecosystem response to contaminative additions. Considerable insight may be gained, however, from attempts to synthesize adequate predictive systems models from fragmentary data already available from ecological studies, experimental biology, and experience with previous instances of pollution. In this paper, we examine and discuss briefly the nature of the information required for the development of useful models for the cycling of contaminant metals (both radioactive and stable isotopes) in estuarine ecosystems.

To understand the "cycling of elements" in a natural ecosystem necessitates identifying the major reservoirs of those elements, determining

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Manuscript accepted April 1972.

the mechanisms and pathways of elemental transformations and rates of elemental turnover among reservoirs, and determining the response of these processes and reservoirs to changes in the environment under study.

In aquatic ecosystems, nearly all of the metallic elemental content of the system resides in the sediments and in the water. The fraction residing in the biota is small—with phytoplankton and zooplankton constituting the most important living elemental reservoirs in terms of turnover and total physical transport and redistribution processes. The major commercial species harvested by man from estuaries have little effect on the overall distribution of metallic elements in the estuary, simply because most of these species are high in the trophic scheme and have relatively low biomass. Yet, in contaminated environments these same species may concentrate certain elements to levels potentially harmful to people consuming large quantities of seafood. Our consideration of elemental cycling must therefore be biased toward biological species of little importance to the overall elemental mass balance because these species form the major interface between man and the remainder of the ecosystem.

METALLIC ELEMENTS OF PRIMARY CONCERN

In the preceding and ensuing paragraphs we discuss the cycling of "metallic elements." Such a generalization is not entirely practical because chemical and physical characteristics of the different metals determine to some extent their behavior in the natural environment and their relative toxicity to biological systems influences the extent of our interest in the various metals. In addition, the relative abundance of various elements affects both their ecological behavior and human interest In terms of chemical and physical properties, we can categorize the metals into five groups: alkali metals, alkaline earths, transition elements, rare earths, and actinide elements. The transition elements may be further subdivided into "family groups" on the basis of the electronic configurations of the atoms. The term "heavy metal" usually refers to all those metals with atomic numbers higher than 20 (Ca), i.e., beginning with the first transition series: Sc, Ti, V, Cr, etc. In the popular literature "heavy metal" frequently also carries the connotations of pollution and/or toxicity. Table 1 categorizes metallic elements according to biological function and abundance and shows elemental abundances for seawater and the crust of the earth. Not all the elements listed in Table 1 as "essential" are required by every animal and plant—only a few higher plants may require aluminum or vanadium, silicon is an essential bulk component of diatoms not required by other forms, and molybdenum appears to be essential only to organisms that derive their nitrogen by nitrate reduction or fixation of free nitrogen (Underwood, 1962; Epstein, 1965). Similarly, the designation of toxicity is arbitrary, since most of the essential elements are toxic at unusually high concentrations. The nonessential elements include a few (cesium, rubidium, strontium) which consistently occur in organisms and can replace to a large degree the biological functions of essential elements (Rb and Cs for K, Sr for Ca). To a much lesser extent, the metals Cr, Ni, and Cd may fulfill the biological functions of Zn, Mn, or Cu. It should be noted that the metals which are essential or relatively nontoxic to biological systems generally have a low atomic number (only Rb, Sr, Mo, and Cs exceed 30) and are relatively abundant in the biosphere. The toxic metals generally have high atomic numbers (an outstanding exception is Be with an atomic number of 5) and low abundances (notable exceptions include As, Ba, and Pb, all of which occur consistently in living organisms, and Be and Th, which are extremely variable in their biological distribution).

In addition to the elements in Table 1, certain other metals are of concern because of radiation from radioisotopes, whether naturally occurring or introduced from man's nuclear activities. The abundances and composition of radionuclides in the marine environment are summarized elsewhere (Rice and Wolfe, 1971; Joseph et al., 1971). Most of the significant radionuclides are isotopes of certain elements in Table 1 such as chromium, iron, manganese, zinc, cesium, and strontium. To this list we should add cerium,

TABLE 1.—Metallic elements of biological significance.

	Seawater abundance[1]	Crust abundance[2]
	mg/liter	*ppm*
"Essential bulk" elements		
Calcium	400	36,300
Magnesium	1,350	20,900
Potassium	380	25,900
Sodium	10,500	28,300
"Essential trace" elements		
Cobalt	0.0005	23
Copper	0.003	45
Iron	0.01	50,000
Manganese	0.002	1,000
Zinc	0.01	65
Aluminum	0.01	81,300
Molybdenum	0.01	1
Silicon	3	277,200
Vanadium	0.002	110
"Nonessential trace" elements		
Cesium	0.0005	1
Chromium	0.00005	200
Nickel	0.002	80
Rubidium	0.12	120
Strontium	8	450
Tin	0.003	3
"Toxic" elements		
Antimony	0.0005	0.2
Arsenic	0.003	2
Barium	0.03	400
Beryllium	0.0000006	2
Bismuth	0.00002	0.2
Cadmium	0.00011	0.2
Lead	0.00003	15
Mercury	0.00003	0.5
Selenium	0.004	0.09
Silver	0.0003	0.1
Thorium	0.00005	10

[1] Goldberg, 1963.
[2] Mason, 1958.

zirconium, niobium, ruthenium, scandium, and plutonium—all of which occur in only trace amounts in the biosphere, but have radioisotopes which are produced in significant quantities by man and accumulated by animals and plants. In the following discussions "metallic elements" will be used to refer generally to all of the elements mentioned above and in Table 1. Space will not permit separate discussion of each element; instead we will attempt to discuss those general aspects of ecosystem structure and function likely to be most significant in governing the flux of elements within and through estuaries and to identify those elements known to be valid examples or exceptions.

Although an estuarine ecosystem is very complex and difficult to model mathematically, we will take the approach of defining the variables which should be considered in a mathematical model of the dynamic cycling of metals in estuaries, with particular emphasis on the coastal plain estuaries of the southeastern United States.

MAJOR RESERVOIRS IN THE CYCLING OF ELEMENTS

In marine and estuarine environments, nearly all of any given metallic element occurs in the sediments and water (Duke, Willis, and Price, 1966; Duke et al., 1969; Pomeroy et al., 1969; Lowman, Rice, and Richards, 1971). Both sediment and water contain several individual reservoirs for elements, with some components much more important than others to cycling in the system. The "water components" include dissolved ionic forms, dissolved organic complexes, and suspended particulate matter—all of which interact with sediment compartments via adsorption, ion-exchange or sedimentation-resuspension processes. In tracer studies with ^{65}Zn, the rapid instantaneous uptake of radioisotope by estuarine sediments indicated a high rate of continuous exchange of zinc across the sediment-water interface (Duke, Willis, and Wolfe, 1968). In sedimentary deposits, elements may become "trapped" in deeper sediments and be effectively removed from further exchange with the system. In salt marsh, however, *Spartina* recycles phosphorus and zinc from deep subsurface sediments (Pomeroy et al., 1969), and burrowing animals such as crabs, polychaetes, and clams rework shallow and surface deposits, thereby prolonging contact with overlying waters (Gordon, 1966; Rhoads, 1967; Rhoads and Young, 1971). In preliminary studies on the exchange of zinc between estuarine sediments and water, the resuspension of sediments by the burrowing and feeding activity of polychaetes markedly increased the rate of loss of tracer ^{65}Zn from the water overlying the experimental cores (Duke et al., 1968, and unpublished observations). Surface silt layers of high organic content may be a major source of elements to deposit feeders in detritus-based food webs (Cross, Duke, and Willis, 1970; Lowman et al., 1966). In turbulent estuaries, these surface deposits may become suspended and be ingested by filter-feeding organisms such as menhaden, bivalve molluscs, and zooplankton. Suspended particulate matter may arise also from the ultimate flocculation and precipitation of dissolved ionic species, such as Fe and Al, which are readily hydrated to form colloidal hydroxides at the pH of seawater (Riley and Chester, 1971). Other sources of suspended particulate matter include feces excreted directly into the water column by pelagic animals, castoff exuviae from zooplankton, and dead planktonic organisms.

Different dissolved chemical species in the water undoubtedly represent discrete and significant reservoirs in the cycling of elements. Organic metallic complexes or chelates may equilibrate slowly with the ionic forms and have been shown or suggested to have drastically different availabilities to organisms. For example, EDTA (ethylenediaminetetraacetic acid) reduced the accumulation of ^{59}Fe by crabs (*Panopeus*), clams (*Mercenaria*), and oysters (*Crassostrea*) (Rice, 1965). Goldberg (1952) demonstrated that the marine diatom *Asterionella japonica* also could utilize iron if particulate or colloidal but not when complexed with citrate, ascorbate, or artificial humate. On the other hand, accumulation of cobalamin by clams (*Donax*) was much enhanced over accumulation of ionic cobalt (Lowman and Ting, in press); and it has been suggested that natural organic chelators may enhance the growth of phytoplankton (Barber and Ryther, 1969), thereby implying that organic complexes might constitute an important avenue for accumulation of metallic nutrients by marine organisms. Unfortunately, technology for the separation and identification of organic ligand-metal complexes from natural waters is in its early infancy, and one can only speculate on the significance of the various chemical forms present in estuarine waters. Regardless of the relative biological availabilities of metals from different organic complexes or from uncomplexed forms, the formation of soluble organic-metal complexes increases the holding capacity of estuarine water for a particular metallic element. Soluble organic complexes therefore probably decrease the net adsorption of metals onto sedimenting particulate materials, thereby increasing the metals' susceptibility to export via tidal flushing. The nonliving elemental reservoirs designated in Table 2 are thought to be of greatest significance in determining the distribution and flux of metallic elements in estuaries.

The estuarine biota consists of many species in a complex and interwoven network of feeding relationships. From a practical viewpoint, all species cannot be considered major elemental reservoirs for modeling purposes. One approach would be to group species by trophic position and consider each trophic level as a single reservoir. Many species, however, are opportunistic feeders with omnivorous habits which complicates their ready assignment to a particular trophic level and necessitates the use of fractional trophic levels. In addition, some species of comparable trophic position and abundances must be considered separately because one is desired as human food and another not. For example, oysters, clams, and scallops should be considered separately from other filter-feeding bivalve molluscs. Another example might be the primary carnivores, flounders and skates, of which only the flounder is harvested for human food. It is more feasible to group species wherever possible and consider individual species only where necessary. Preliminary surveys of the estuarine flora and fauna in the vicinity of Beaufort, N.C., suggest that the organisms in Table 2 should be considered as separate reservoirs or components. Some of the species are identified because of their commercial importance; others only because of their abundance and probable significance as forage. Organisms not identified to species have been lumped arbitrarily into "other" categories according to their feeding habits and trophic position.

The reservoirs identified in Table 2 as being "significant" or "important" in the cycling of elements in estuaries obviously are not all of equal importance. The list is probably incomplete, but at the same time may include some unnecessary designations. Most of the reservoirs identified to species have been considered in the development of a static model of annual energy flow in these estuaries (Williams and

Murdoch, 1970).[2] Quantification of the biomass in each of the major biological components is a primary objective of ecological research at the Atlantic Estuarine Fisheries Center, and preliminary estimates are currently available for the dominant macroorganisms (Williams, Thayer, Price, Kjelson, and Turner, Unpublished data). Analytical data on the concentrations of iron, manganese, zinc, and copper in these organisms and in sediments and water are also available or forthcoming (Cross et al., 1970; Cross and Brooks, in press; Wolfe, 1970a; Cross, Lewis, and Hardy[3]). Meaningful quantification of reservoir size for any element in certain components, however, will be extremely difficult to achieve (especially for the "other" categories, e.g., filter-feeding bivalves, deposit-feeding bivalves, carnivorous benthos, etc.). It may be practical to evaluate the importance of these "catch-all reservoirs" only by manipulating trial values for biomass and elemental concentrations during early phases of model development.

Pathways of elemental flux between reservoirs also are tentatively identified in Table 2. Individual transfer processes are designated in the matrix of Table 2 by an "I", indicating an influx of a metallic element from the reservoir at the top of the table to the reservoir on the left. Fluxes between biological reservoirs represent food chain transfers of elements. Such transfers usually involve one-way cyclic net flows (with internal loops) through the food web of the ecosystem. At this time the feeding habits of many of the listed species are incompletely known, and the food web of Table 2 must be regarded partly as the product of intuition and speculation.

The flux of elements between the organisms and the nonliving reservoirs is less readily identified, however, than the food web, because of uncertainty about the relative abundance and importance of different physical-chemical states, e.g., the ionic forms versus organic complexes. Physical-adsorption and ion-exchange processes, operative on biological (and nonbiological) surfaces, obviously would contribute to the total flux of an element; but since these processes are generally reversible, their importance to net transfers (especially at higher trophic levels) remains unknown. There must be a net influx of most elements from the soluble ionic phase to most organisms during their life span, however, simply because the surface area for adsorption increases during growth.

The significance of organic-metal complexes is unknown. We suspect that dissolved organic compounds constitute a mechanism for internal feedback loops involving all organisms at all trophic levels, except perhaps man. Thus, an organism may accumulate specific organic-metal complexes which undergo metabolic transformation, and the metals may in part be excreted as different organic complexes which reenter the cycle as nutrients for phytoplankton or heterotrophic microbes. We can only speculate now on whether there is net production or net utilization of metal-organic complexes by organisms. This ambiguity is indicated in Table 2 by a "double I" (i.e., by I's at both relevant intersects of the matrix), representing ingestion or absorption of organic-metal complexes by most organisms with simultaneous excretion of other organic complexes which might be quite different chemically.

Fluxes between nonliving reservoirs are more dependent upon reversible physical processes, such as adsorption, ion-exchange, and sedimentation-resuspension. The net direction of flux may therefore depend on such variables as salinity, pH, and turbulence. The association of heterotrophic microbes with suspended particulate material probably results in a net influx of most metals into this reservoir from soluble sources with subsequent passage into detritus-based food chains. The extent of reversibility for the transfers (identified by "R" in Table 2) varies also from element to element. Thus, ^{137}Cs may be transported into estuaries on bed-load sediment and desorbed at higher salinities

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[2] Williams, R. B., and M. B. Murdoch. 1970. A general evaluation of fishery production and trophic structure in estuaries near Beaufort, N.C. *In* Center for Estuarine and Menhaden Research Annual Report to the Atomic Energy Commission. Filed at NMFS Atlantic Estuarine Fisheries Center, Beaufort, N.C. 28516. [Processed.]

[3] Cross, F. A., J. M. Lewis, and L. H. Hardy. Concentrations of Mn, Fe, Cu, and Zn in four species of filter-feeding bivalve molluscs. Unpublished manuscript filed at NMFS Atlantic Estuarine Fisheries Center, Beaufort, N.C. 28516.

TABLE 2.—Major reservoirs and pathways of elemental flux in an estuarine ecosystem. I = influx from top to left; R = reversibility (see text)

	Soluble ionic	Soluble organic	Interstitial soluble	Subsurface sediments	Bed-load sediment	Surface sediment deposits and microflora	Suspended particulate detritus and microflora	Salt grass	Benthic algae and epiphytes	Eelgrass and epiphytes	Phytoplankton	Zooplankton	Heterotrophic microbes	Meiofauna	American oyster	Hard clam	Bay scallop	Shrimp *(Penaeus)*	Shrimp *(Palaemonetes)*	Atlantic menhaden	Striped mullet	Bay anchovy	Other filter feeders	Other deposit feeders	Blue crabs	Snails	Larval/postlarval fish	Atlantic silverside	Atlantic croaker	Spot	Pinfish	Flounder	Bluefish	Spotted seatrout and weakfish	Other carnivores	Water fowl	Other birds	Import from watershed or precipitation or human effluents	Import via immigration
Nonliving reservoirs																																							
Soluble ionic													I																									I	
Soluble organic	R					I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	
Interstitial soluble	R	R																																					
Subsurface sediments			R			I																																	
Bed-load sediment	R		R																																			I	
Surface sediment, detrital deposits and microflora	R	R	R		I			I	I	I					I	I	I						I		I	I													
Suspended particulate, detritus and microflora	R	R			R	R		I	I	I	I	I								I	I	I					I	I	I	I	I	I	I	I	I	I	I	I	
Primary producers																																							
Salt grass *(Spartina)*	I	I	I																																				
Benthic algae and epiphytes	I	I																																					
Eelgrass and epiphytes	I	I		I		I																																	
Phytoplankton	I	I																																					
Herbivores																																							
Zooplankton	I	I					I				I																												
Heterotrophic microbes	I	I				I	I	I	I	I				I	I	I	I																						
Meiofauna	I	I	I			I																																	
American oyster *(Crassostrea)*	I	I					I				I																												
Hard clam *(Mercenaria)*	I	I					I				I																												
Bay scallop *(Argopecten)*	I	I					I				I																												
Shrimp *(Penaeus)*	I	I				I					I																											I	
Shrimp *(Palaemonetes)*	I	I				I																																	
Atlantic menhaden	I	I					I				I	I																										I	
Striped mullet	I	I				I	I				I	I		I																								I	
Bay anchovy	I	I					I				I	I																											
Other filter feeders	I	I	I				I				I																												
Other deposit feeders	I	I	I			I			I	I				I																									

Carnivores																																							
Blue crab (*Callinectes*)	–	–													–	–	–	–	–	–	–	–	–	–															
Snails (*Busycon, Urosalpinx, Odostomia*, etc.)	–	–													–	–	–						–				–												–
Larval/postlarval fish	–	–					–					–																											
Atlantic silverside	–	–										–																											–
Atlantic croaker	–	–																–	–				–	–															
Spot	–	–																–	–																				
Pinfish	–	–				–			–	–		–						–	–				–	–															
Flounder (*Paralichthys*)	–	–																–	–	–	–	–					–												
Bluefish	–	–																–		–	–	–			–		–	–	–	–	–				–				–
Spotted seatrout and weakfish	–	–																–		–	–	–						–	–	–	–				–				–
Other aquatic carnivores	–	–													–	–	–	–	–	–	–	–	–	–	–			–	–	–	–				–				–
Waterfowl (ducks, geese, etc.)									–	–													–	–	–	–	–	–	–	–	–	–	–	–					–
Other birds (gulls, terns, herons, etc.)															–	–	–			–	–	–	–				–	–	–										–
Man—commercial catch															–	–	–	–		–	–				–	–			–	–		–	–	–					
Man—sports and recreation															–	–	–	–			–				–				–	–	–	–	–	–	–	–			
Exports																																							
Tidal flushing	–	–			–		–				–	–																											
Emigration																		–		–	–				–							–	–	–	–	–			

(Wolfe, 1971); whereas ^{65}Zn may be irreversibly adsorbed onto estuarine sediments (Johnson, Cutshall, and Osterberg, 1967). The actual flux of any given element through the complex interwoven network of pathways tentatively identified in Table 2 is in a state of dynamic equilibrium affected by system imports and exports and by a number of environmental variables, to be discussed in the following sections.

INPUTS AND OUTPUTS OF ELEMENTS TO AND FROM ESTUARIES

System inputs and outputs consist of the physical translocation of elemental reservoirs (sediment, water, and biotic components) across the boundaries of the estuarine system (Table 2), and fluxes of other materials (nonreservoirs) which influence the distribution or movement of elements among the system reservoirs. Rainfall is a dominating system input, which introduces small amounts of some elements directly as aerosols (Gorham, 1961), but exerts its greatest influence in the form of runoff. The volume and flow rate of runoff in turn determine the amount and composition of elements leached from the land and the size of the bed load of eroded sediment transported into the estuary. The volume and flow of runoff also interact with the tidal volume to affect the flushing rate for the estuary. Tidal flushing continuously removes from the estuary a fraction of the dissolved and suspended materials, including the planktonic reservoirs. The tidal volume also represents an input of ocean water, but since seawater contains less of most metallic elements than estuarine waters, net loss from the estuary probably results. If, on the other hand, the coastal or estuarine waters contained an excess of uncomplexed organic material, seawater might represent an input of soluble ionic metallic elements which could accumulate in the estuary through sedimentation, or be removed from the estuary as organic complexes, either by flushing or bioaccumulation.

Variable wind speed and direction affect water circulation patterns particularly in shallow estuaries and thereby vary the "normal" flushing characteristics of an estuary. Circulation within the estuary obviously determines also the physical distribution of certain reservoirs within the system, and this aspect of cycling compounds the difficulties of developing a realistic model. Application of the term "ecosystem" to an estuary, however, implies that an estuary behaves as a discrete, identifiable unit and, despite the clumped distributional patterns exhibited by organisms in the environment, spatial distribution of reservoirs within the system is assumed insignificant; i.e., the system model is homogeneous.

In addition to tidal flushing of planktonic organisms, biotic inputs and outputs include the contribution of terrestrial primary productivity, brought into estuaries as dissolved organic material and particulate organic detritus in runoff, and the seasonal migrations of larger invertebrates and fish into and from estuarine waters.

A final input which must be considered consists of human waste materials. Organic waste materials affect productivity and biological species structure of the ecosystem and probably also affect the availability of metallic elements through organic complexing. In addition, large amounts of certain metallic elements are introduced into many estuaries directly in industrial and municipal effluents.

FACTORS INFLUENCING DISTRIBUTIONS AND TRANSFERS OF ELEMENTS AMONG THE VARIOUS RESERVOIRS IN ESTUARIES

The various groups of biota, the dissolved and particulate components in the water column, and sediment compartments, represent the major reservoirs per se for metallic elements, but the interaction of these compartments and regulation of their sizes are influenced greatly by other variable characteristics or components of estuarine ecosystems including inputs of energy and auxiliary materials or factors which affect reservoir sizes or transfer rates within the system. These factors represent "nondynamic state variables" in the modeling terminology of Kowal (1971). These characteristics may be categorized as: (1) those that affect productivity in the trophic web and (2) those that affect the physical state or rates of exchange between components for the specific elements of interest. The influences of major nondynamic state variables are summarized briefly in Table 3.

Solar energy is perhaps the best example of the first type of input. Solar energy drives the primary productivity supporting all the biotic reservoirs and establishes the basic temperature regime for the entire system, which is a dominant factor influencing the rate of material transfer processes, biological and nonbiological. The seasonal variability of temperature can readily be incorporated into systems models according to a sinusoidal function. This general approach has been described and applied by Williams (1969). In the first category also are dissolved gases, e.g., CO_2 and O_2, and inorganic nutrients, especially the various forms of P and N. Certain dissolved organics may also be included here, although absolute requirements for these have not been demonstrated in the nutrition of estuarine organisms, and dissolved organic-metal complexes constitute a major reservoir already considered. Acidity, or pH, is an important factor in that it acts with temperature to control CO_2 solubility and thereby affects primary productivity, but pH also falls into the second category because it determines the equilibrium distribution of metals in adsorption reactions, i.e., exchange between water and sediments, or between water and biological surfaces; and in chelation reactions, including metal-organic complexes in the dissolved phase.

Wind is another significant energy input in shallow estuaries. Wind increases turbulence and suspension of particulate matter which promotes exchange of elements between water and sediments and affects the size of the suspended particulate reservoir subject to flushing.

Salinity is also a determinant in the distribution and cycling of elements. Salinity, as a measure of ionic strength, affects the adsorption equilibria established between sediments and water and biological surfaces and water, and probably also influences the configuration of proteins and other biological polymers which form complexes with metals. This mechanism may be the basis of salinity effects on active transport processes in ionic and osmotic regulation in es-

TABLE 3.—Role of nondynamic state variables.

Factor	Compartment and sign (+ or —) of correlation	
Fe, Al, Mn, etc.	Suspended particulate	+
Nutrients (nitrate, nitrite, ammonia, phosphate, and silicate)	All primary producers and microbial heterotrophs	+
Solar insolation	All primary producers	+
Temperature	Exchange rates	+
	Adsorption	—
	Respiration	+
Season of year	Inputs and outputs via migrations	±
Wind speed and wind direction	Suspended particulate	+
	Flushing export rate	±
Dissolved carbon dioxide	All primary producers	+
Dissolved oxygen	Respiration	+
pH	Surface adsorption	+
Salinity	Surface adsorption	—
	Ion-exchange rates	+
Precipitation	Inputs of sediment bed-load	+
	Suspended particulate	+
	Dissolved ionic	+
	Dissolved organic	+

tuarine organisms. In addition, salinity provides a measure of bulk components of seawater, e.g., Ca and K, which may compete directly with trace components for adsorption sites of biological accumulation, e.g., Sr and Cs. For example, increasing salinity decreases the accumulation rate and concentration factor for ^{137}Cs in estuarine clams (Wolfe and Coburn, 1970). Salinity is correlated also with the concentration of ^{137}Cs in lower-salinity estuarine water, possibly as a result of mass action on the sediment-water exchange equilibrium (Wolfe, 1971). Important dissolved trace components include Fe, Al, and Mn, whose concentrations depend less on salinity than on watershed characteristics and runoff. At the pH, Eh, and ionic strength characteristic of seawater, these elements form insoluble hydroxides which flocculate and provide adsorptive surfaces for other elements. Such a coprecipitation process may be an important determinant in the distribution of fallout ^{106}Ru in estuaries (Wolfe and Jennings, in press).

For any given estuary the chemical environment and flushing characteristics are affected greatly by the geological and chemical characteristics of the watershed area, the type of estuary (stratified vs. well-mixed, etc.), and the physical size, shape, and orientation of the estuarine basin. Such characteristics must be considered when different estuaries are compared.

A set of biological processes accompanies each trophic interaction and determines the efficiencies for transfers of biomass between components. These are feeding or ingestion rate, digestion rate, assimilation efficiency, respiration, and growth efficiency. Each of these characteristics may be influenced in turn by various environmental factors, such as temperature and salinity (Peters and Boyd, in press; Peters and Angelovic, in press).

Assimilation and respiration maintain the biomass of the biological reservoirs for elements, but the accumulation and retention of most metallic elements are probably not directly correlated with the assimilation and respiration of carbon. For dynamic modeling of the cycling of metallic elements in the estuarine biota, however, it is essential to consider the changes in biomass as well as changes in concentration of the element of interest. The interrelation of ^{65}Zn-excretion and respiration has been examined directly for pinfish, *Lagodon rhomboides*, (Hoss, 1971). Lowman et al. (1971) computed assimilation efficiencies ("conversion factors") for the transfer of several metallic elements from oceanic phytoplankton to zooplankton, based upon relative concentration factors in zoo- and phytoplankton and a mean carbon assimilation of 50%. On this basis, assimilations for 24 elements ranged from 1 to 85%—indicating nonparallelism with carbon assimilation—but Lowman went on to say: "The major weakness in this method of calculating conversion factors for a variety of elements is the uncertainty of the accuracy of the concentration factors for phytoplankton and zooplankton." Similar uncertainty exists for published concentration factors for various elements in estuarine organisms, especially since environmental conditions (and therefore elemental concentrations in estuarine water) are subject to such wide variation. A further complication is the uncertainty concerning the proportion of total elemental intake represented by food sources. According to Polikarpov (1966), marine animals satisfy their requirements for most elements by direct absorption from the surrounding water. Considerable experimental evidence, however, supports the importance of food as a source of elements for many organisms (Rice, 1963; Hoss, 1964; Baptist and Lewis, 1969). Atoms adsorbed directly from the water onto body surfaces, whether internal or external, do contribute to the concentration factor but have no relevance to assimilation of food. Surface adsorption frequently results in assimilation, however, as in phytoplankton (Goldberg, 1952) and the mantle epithelium of Pelecypoda (Nakahara and Bevelander, 1967). For organisms with well-defined and easily analyzed internal tissues, e.g., crustacean and fish muscle, internal concentrations of elements probably represent the assimilated fraction, but for many smaller or less differentiated organisms, internal tissues cannot readily be separated from adsorptive surfaces. Assimilation efficiency may depend also on biochemical composition of the food—at least at certain trophic levels. For example, the assimilation of ^{65}Zn by human subjects was 35% from a diet of whitefish (Honstead and Brady, 1967) and 13.5% from oysters (Honstead and Hildebrandt, 1967), showing a high (though perhaps coincidental) positive correlation with the protein content of the foodstuff (Wolfe and Rice, 1968).

The concentration of an element in representatives of a population of organisms is a function of the turnover time for the element and the average life span of the organism. Long-lived organisms probably achieve a steady state for the turnover of most elements after the cessation of growth—and if the availability of the element from the organism's environment is stable. In organisms with rapid growth and high population turnover, net accumulation probably proceeds for most metallic elements throughout the entire short life span of the organism, and steady state is not reached before the organism is consumed by the next trophic level. The environmental and physiological factors determining the steady state conditions are not known, however. Many organisms may accumulate metallic elements far in excess of their biological requirements (Wolfe, 1970b; Pequegnat, Fowler, and Small, 1969), and accumulation of metals may continue independent of the biological necessity in some cases until available reaction sites (e.g., between metal and proteins or tissue surfaces) are saturated. This process is suggested also by the increasing concentration of mercury with age (or size) in various fish (Westö, 1969; Bache, Gutenmann, and Lisk, 1971).

In a dynamic estuarine system, where environmental levels of metallic elements are subject to rapid fluctuations, the organismic response to environmental change must be identified. Information of this nature is sorely lacking in the literature. Pringle et al. (1968) tested the response of oysters to various increased experimental levels of lead, and after 49 days exposure, accumulation had proceeded in direct relation to availability of lead in the environment. Other data (Chipman, Rice, and Price, 1958; Preston, 1967; Wolfe, 1970a) suggest that concentration factors for Zn in oysters are inversely related to zinc content of water, implying that net accumulation would diminish or cease at some high environmental concentration (low concentration factor in oyster) and steady state would be established. In these cases, however, the variability of instantaneous uptake of the element can only be inferred from the amounts contained after a long period of accumulation. In natural ecosystems, fallout radioisotopes appear in estuarine organisms very quickly after initial entry of the isotopes into the ecosystem (Wolfe and Schelske, 1969; Wolfe and Jennings, in press). A high rate of instantaneous uptake has also been demonstrated for many organisms and many elements in experiments on radioisotope accumulation, but, in most cases, concentrations of stable element counterparts for the radioisotopes were undetermined so that rates of flux for the stable element could not be computed from the observed flux of radioactivity. Although the accumulation and turnover of a radioisotope in a single component can be modeled mathematically independent of the stable element chemistry (Reichle, Dunaway, and Nelson, 1970), it is the flux of stable elements which determines the movement of radionuclides among the various components of an ecosystem and investigators should routinely collect data on the stable element composition of the compartments involved in their accumulation studies. In this way, experimentally observed radioisotopic accumulation rates can be used in conjunction with the specific activity, i.e., the concentration ratio of radioisotope to total element, to determine rates of elemental turnover. It seems probable that instantaneous uptake of an element is a direct function of available environmental levels whereas instantaneous loss is a direct function of accumulated amounts. The instantaneous uptake rate is also a function of other environmental variables. For example, in the estuarine clam *Rangia cuneata*, the instantaneous uptake rate and the equilibrium concentration of ^{137}Cs increase with temperature and decrease with salinity (Wolfe and Coburn, 1970). Salinity, temperature, pH, and total Zn also influenced the accumulation of ^{65}Zn by various estuarine organisms under experimental conditions (Duke et al., 1969).

Net accumulation (or net loss) results when instantaneous uptake exceeds (or is less than) instantaneous loss, and the physiology and metabolism of the organism determine the residence times required for passage through its many alternate internal compartments and pathways. Retention times are usually discussed in terms of biological half-life. (See for example Baptist, Hoss, and Lewis, 1970.) Since organisms have several compartments simultaneously interacting with the environment, retention typically consists of several components with different rates. One might expect the faster rates to be associated with surface adsorption reactions, intermediate rates with excretion of unassimilated material as feces, and slow rates with the turnover of the assimilated and metabolized fraction of the elemental content. Although the relative amounts of an accumulated radioisotope involved with different retention components can be determined for the particular conditions and time period of accumulation and loss used in the experiment, these amounts will not be representative of stable element pools unless all of the internal compartments are equally labeled, i.e., to a uniform specific activity. Thus, long-term accumulation experiments under conditions of constant specific activity are required (Cross, Willis, and Baptist, 1971). The individual retention components for an element probably will have to be considered for each important reservoir in modeling the overall flux of that element in the ecosystem.

We have discussed several aspects of elemental cycling in estuaries and have demonstrated the incompleteness of man's knowledge of how an estuary operates as a system with many integral, smoothly functioning components. We believe, however, that many of the unsolved problems which have presented themselves will be realistically resolved only by a holistic approach to ecological research. The foregoing discussion represents an effort to conceptualize the elemental cycling system that operates in our southeastern coastal zone estuaries. Prior recognition of the complexity and integrity of the system as a whole provides an improved basis for planning meaningful research on the transfer processes between individual components of an estuary. Considerable research is required before we can actually quantify the reservoirs, routes, and rates of elemental flux involved in this preliminary model of these ecosystems. The complexity of the ecosystem defies precise quantification of all the reservoirs and all the transfer rates under any set of environmental conditions. In such a system, however, the predictability of the magnitude and variability of any elemental reservoir depends upon recognition of all the interactions impinging upon that reservoir. Research now in progress at the Atlantic Estuarine Fisheries Center will enable us to estimate the size ranges for most reservoirs of manganese, iron, and zinc in our local estuarine system. The major gaps in our present knowledge lie in:

1. Determining the relative amounts of different physico-chemical forms of an element or radioisotope in natural waters, their relative stabilities, and the ease of interconversion between the various forms.
2. Determining the relative biological availabilities of these different physico-chemical forms to various types of biota.
3. Determining trophic structure of the entire ecosystem. The role of microorganisms—as sources of metallic elements to consumers in detritus-based food chains, as producers of organic-metal complexes, and as remineralizers of metals previously incorporated into plant or animal tissues—is particularly poorly understood.
4. Determining feeding rates and assimilation efficiencies for carbon and metallic elements at each major trophic interaction.
5. Determining biological retention of metallic elements in the major organisms consumed by man.
6. Determining the interactions of variable environmental parameters on reservoir size and transfer rates at each step in the overall system.

As further information becomes available, this preliminary systems model will be refined and tested as to its adequacy for describing the flux of manganese, iron, and zinc in our local estuarine system. Maintenance of this sort of holistic viewpoint toward ecological function and continuous updating of existing conceptual models will provide the most reliable basis for rational management of man's releases of toxic heavy metals and radionuclides—or indeed, of any contaminant additions to the environment.

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