

AN ABSTRACT OF THE THESIS OF

DAVID WILLIAM EVANS for the degree of DOCTOR OF PHILOSOPHY

in Oceanography presented on September 8, 1976

Title: EXCHANGE OF MANGANESE, IRON, COPPER, AND ZINC
BETWEEN DISSOLVED AND PARTICULATE FORMS IN THE
NEWPORT RIVER ESTUARY, NORTH CAROLINA

Abstract approved: _____

Redacted for Privacy

Norman H. Cutshall

Exchange of manganese, iron, copper, and zinc between solution and particulate phases was studied in the Newport River estuary, North Carolina. Metal analyses were by flameless atomic absorption spectrophotometry, those in solution after concentration by Chelex-100 resin. Longitudinal sampling transects in the estuary in October, 1974, and February and April, 1975 showed trends of dissolved metal concentrations versus salinity interpretable in terms of exchange of the metals between solution and particulate phases. A simple mixing model explained variations of dissolved metal concentrations within the estuary by river and seawater inputs and outputs and internal sources and sinks reflecting the exchange processes. Metal concentrations on suspended particulate matter provided corollary evidence of metal exchanges.

Dissolved Mn concentrations within this estuary at intermediate salinities were consistently in excess of those predicted by conservative mixing of Newport River water and seawater. Variations in river concentrations of dissolved Mn could not explain these nonlinearities in dissolved Mn:salinity trends, which therefore, must have been caused by additions of Mn to solution in the upper estuary. Nor could desorption of river-derived particulate Mn have supplied the added dissolved Mn, which seemed to originate from anoxic, organic rich bottom sediments in the upper estuary. Experimental disturbance of sediments from here released dissolved Mn to the overlying water. Reduction of oxidized particulate Mn to dissolved Mn^{2+} in sediment pore waters seemed the likely mechanism.

Because the flux of added dissolved Mn which was observed could not be supplied at steady-state by total dissolution of river-derived particulate matter deposited in the upper estuary, a recycling model was proposed. Evidence was found in the dissolved and particulate distributions of Mn supporting this model in which solubilized Mn^{2+} was carried downstream in the estuary by the net water flow, oxidized to MnO_2 and removed from solution in the lower estuary and carried back upstream to the upper estuary on Mn rich particles to renew the reduction-solubilization cycle. Because not all added dissolved Mn was recycled upstream, consideration was given to alternative non-steady-state hypotheses in which the sampling

transects fortuitously coincided with short-term dissolved Mn input processes.

Iron was lost from solution in Newport River water when it entered the estuary. The apparent cause was seawater-induced flocculation of micro-colloidal $\text{Fe}(\text{OH})_3$, which was maintained in a filter-passing state in river water by dissolved organics. No evidence was found of reduction-solubilization or other particulate to solution transfers of Fe.

Both Cu and Zn were lost from solution in the estuary. On the February, 1975 transects, however, high river flows disturbed bottom sediments in the upper estuary, releasing both metals to solution in the overlying waters, presumably from sediment pore waters. These added metals were quickly removed from solution in the lower estuary.

This estuary seemed to be a sink for river derived dissolved Fe, Cu, and Zn. Dissolved Mn, however, was added to the ocean in excess of that supplied to the estuary by the river. If the loss mechanisms of dissolved Mn observed in the lower estuary continued seaward, the estuary might also be a sink for dissolved Mn, as suggested by mass balance considerations.

The Newport is a shallow estuary of low river input, and the fluxes of metal exchange observed might not extrapolate to larger rivers and their estuaries, which are the main determinants of the

dissolved trace metal flux to the oceans. But the linear mixing model approach to metal exchange could be extended to their study and that of adjacent coastal waters.

Exchange of Manganese, Iron, Copper, and
Zinc Between Dissolved and Particulate
Forms in the Newport River Estuary,
North Carolina

by

David William Evans

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

June 1977

APPROVED:

Redacted for Privacy

Research Associate School of Oceanography

Redacted for Privacy

Dean of School of Oceanography

Redacted for Privacy

Dean of Graduate School

Date thesis is presented September 8, 1976

Typed by A & S Bookkeeping/Typing for David William Evans

ACKNOWLEDGMENTS

Acknowledgments tend to the maudlin, and the temptation is strong to resort to parody. But to do so would be both an injustice to those who helped me and a distortion of my true feelings. A dissertation is certainly the most intense and personal piece of scientific work most researchers undertake, but also the work which calls most upon the help of others. I would like to thank them.

Special thanks are due Ted Rice, Doug Wolfe, and Bud Cross whose invitation to work at the Atlantic Estuarine Fisheries Center, Beaufort, North Carolina initiated a unique and very special thesis research program. They are also thanked for the support, financial, scientific and personal, which sustained me there. Of the many friends in Beaufort who made my stay there so rewarding, I would like to single out Ann Hall, Neysa Jones, Don Hoss, Don McCrimmon, Ron Mollick, Polly Penhale, and Jim Thorp. Bud Cross who acted as surrogate thesis advisor was more than that in his friendship, concern, and encouragement.

Norm Cutshall's help, suggestions, encouragement and friendship went beyond what anyone could expect of his major professor. I thank him for the many efforts he made on my behalf under often difficult conditions of long distance communication and for steering me through some murky waters.

My fellow graduate students at Oregon State, Russ Flegal, Katsuo Nishikawa, Fritz Riedel and Steve Davis tolerated my moodiness, provided needed encouragement, and offered many useful insights in writing my thesis. Thanks to them also. To Vern Johnson, acknowledged almost universally in theses of the Marine Radioecology Group, I add my thanks for his common sense criticisms of my many half-baked ideas, for his interest in ideas of all kinds, and his special sense of humor. To this perennial bridesmaid, I now throw the bouquet. To all others who aspire to be Doctors of Philosophy, I leave an inspirational quote from that esteemed contemporary philosopher, Alfred E. Neuman, "What me--worry?"

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
BACKGROUND	5
Theoretical Considerations of Trace Metal	
Exchanges in Estuaries	6
Adsorbed Trace Metals	8
Electrostatic (non-specific) Adsorption	11
Specific Adsorption	13
The Irving-Williams Order in the	
Adsorption of Trace Metals	14
Competition of Major Seawater Cations	
with Trace Metals for Adsorption Sites	17
Insoluble Precipitates	23
Zinc	24
Copper	27
Iron	28
Manganese	31
Biogenic Components of Trace Metal Fixation	34
Mineral Lattice Fixed Metals	35
Recapitulation	36
Experimental Approaches in Studying Dissolved-	
Particulate Exchanges in Estuaries	37
Selective Leaching of Sediments	38
Desorbable Trace Metals in River	
Sediments	41
Laboratory Mimicry of Estuarine Chemical	
Processes	42
Radiotracer Experiments	43
Other Experimental Studies	46
Recapitulation	47
Estuarine Field Observation Studies	49
Input-Output Studies	49
Distributional Studies	51
Sediment and Suspended Particulate	
Trace Metal Distributions	52
Dissolved Trace Metal Distributions	56
Summary	60
Mixing Models	63
ENVIRONMENTAL SETTING OF THE NEWPORT RIVER	
ESTUARY	75

	<u>Page</u>
METHODS AND MATERIALS	82
Sample Collection	83
Dissolved Trace Metal Analysis	85
Particulate Analysis	90
RESULTS AND DISCUSSION	91
Manganese	91
Statistical Tests of Non-Linearity	95
Variations in River Input Concentrations as	
Possible Causes of the Observed Non-Linearities	99
Desorption of River-Derived Suspended	
Particulate Matter as the Source of Dissolved	
Mn Maximum	103
Bottom Sediments as a Source of Added	
Dissolved Mn	107
Flux of Dissolved Mn from Cross Rock	
Sediments	113
Replenishment of Exported Excess Dissolved Mn	117
Recycling Hypothesis	120
Upstream Movement of Estuarine	
Particulate Matter	121
Particulate Fixation of Dissolved Mn	122
Removal of Mn from Solution in the	
Lower Estuary	127
Oxidation of Mn^{2+} as the Removal	
Mechanism	129
Alternatives to the Steady-State	131
Iron	134
Dissolved Iron	134
Lack of Fe Mobilization in Sediments	140
Particulate Fe	141
UV Absorbance and Possible Third Water	
Type in the Estuary	144
Copper	147
Dissolved Copper	147
Particulate Copper	150
Zinc	155
Dissolved Zinc	155
Particulate Zinc	158
Summary	160
CONCLUSIONS	164
Cycling of Metals in Newport River Estuary	164
Flux of River Derived Mn, Fe, Cu, and Zn to	
the Open Ocean	170

BIBLIOGRAPHY	173
APPENDIX A	192
APPENDIX B	204
APPENDIX C	216

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Simplified conceptual model of the electrical double layer showing both specifically adsorbed and electrostatically adsorbed metal ions.	10
2.	Stability constants (K_1) of some metal ions with organic ligands showing the Irving-Williams order of complex stability. Also shown are the solubility products (K_{so}) with sulfide and hydroxide anions.	16
3.	Oxidation potential-pH diagrams for Fe (a) and Mn (b) at 25°C and activity $10^{-5}M$ (Redrawn from Morgan and Stumm, 1965).	29
4.	Hypothetical relationships between micronutrient concentrations and salinity in estuaries showing conservative behavior and internal sources and sinks of the micronutrient (Redrawn from Peterson et al., 1975).	66
5.	Coastal North Carolina.	76
6.	Newport River estuary.	77
7.	Dissolved Mn relationship with salinity in the Newport River estuary during five sampling transects.	93
8.	Dissolved Mn relationships with salinity in the Newport River estuary during five sampling transects, with effects of river MN variations.	101
9.	Excess dissolved Mn concentrations in relation to salinity during five sampling transects in the Newport River estuary.	105
10.	Concentrations of suspended particulate Mn per liter of water in relation to salinity during five sampling transects in the Newport River estuary.	106

<u>Figure</u>		<u>Page</u>
11.	Dissolved Mn concentrations plotted versus longitudinal location in the Newport River estuary during five sampling transects.	108
12.	Excess dissolved Mn accumulated in the Newport River estuary during five sampling transects.	114
13.	Concentrations of Mn on suspended particulate matter in relation to salinity during five sampling transects in the Newport River estuary.	123
14.	Excess particulate Mn in the Newport River estuary in relation to salinity during five sampling transects.	128
15.	Dissolved Fe concentrations in relation to salinity in the Newport River estuary during three sampling transects.	135
16.	Concentrations of Fe on suspended particulate matter in relation to salinity during three sampling transects in the Newport River estuary.	142
17.	Ultraviolet (UV) absorbance in relation to salinity during five sampling transects in the Newport River estuary.	145
18.	Dissolved Cu concentrations in relation to salinity in the Newport River estuary during five sampling transects.	148
19.	Concentration of Cu on suspended particulate matter in relation to salinity during five sampling transects in the Newport River estuary.	152
20.	Dissolved Zn concentrations in relation to salinity in the Newport River estuary during five sampling transects.	156

<u>Figure</u>		<u>Page</u>
21.	Concentration of Zn on suspended particulate matter in relation to salinity during five sampling transects in the Newport River estuary.	159
22.	Analysis of Chelex-100 extracts of Mn standards by flameless graphite furnace-atomic absorption spectrophotometry compared to the direct analysis of the same standards in deionized distilled water by the same method.	193
23.	Relationship of "apparent" Mn recovery to the concentration of coextracted Na, Ca, and Mg in the Chelex-100 extracts at various salinities.	195
24.	Coastal North Carolina showing sample locations during R/V Eastward cruise, December 3-6, 1974.	218

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Concentrations of Na, Ca, Mg, Mn, Fe, Cu, and Zn in average river water and seawater (from Goldberg et al., 1971).	12
2. Compounds of zinc (a) and copper (b) possibly limiting their solubility in seawater at 25°C (from Wedepohl, 1969).	25
3. Previous studies using linear mixing models and salinity trends in estuaries to infer sources and sinks of chemical substances.	69
4. Reservoirs of Mn, Fe, and Zn in the Newport River estuary (from Wolfe et al., 1973).	80
5. Instrument settings used in trace metal analysis using the Perkin Elmer Model HGA 2000 Graphite Furnace and Model 403 atomic absorption spectrophotometer.	89
6. Summary statistics of dissolved and suspended particulate Mn, Fe, Cu, and Zn in Newport River and at AEFC dock during three weeks prior to October, 1974 and February, 1975 estuary transects.	94
7. Analysis of variance testing for non-linearity in dissolved Mn-salinity trends of October, 1974.	97
8. Summary of statistical tests of non-linearity of dissolved trace metal-salinity trends in Newport River estuary.	98
9. Dissolved and suspended trace metal concentrations in water overlying sediment cores from Cross Rock, April 17, 1975.	111
10. Fluxes of dissolved Mn added in the Newport River estuary calculated from the excess dissolved Mn and estimated flushing time.	115

<u>Table</u>		<u>Page</u>
11.	Mn, Fe, Cu, and Zn concentrations in four size fractions of sediments from the Newport River and its estuary (Cross Rock) collected April 20, 1975.	125
12.	Summary of trace metal concentrations in suspended particulate matter and $< 2\mu\text{m}$ fraction of bottom sediments in the Newport River, estuary, and adjacent ocean.	153
13.	Annual budget of Mn, Fe, and Zn (kg/yr) in the Newport River estuary (From Wolfe et al., 1973).	165
14.	Analysis of Newport River water for dissolved Mn, Fe, and Cu by Chelex-100 extraction with and without $\text{K}_2\text{S}_2\text{O}_8$ oxidation of organic matter.	197
15.	Reproducibility of dissolved and suspended particulate analyses of seawater from AEFC dock for Mn, Fe, Cu, and Zn.	199
16.	Concentrations of Mn, Fe, Cu, and Zn in water samples from a trace metal intercalibration analyzed by Chelex-100 extraction and graphite furnace-atomic absorption spectrophotometry.	200
17.	Analytical blanks of dissolved and suspended particulate Mn, Fe, Cu and Zn: means \pm one standard deviation in units of ng/sample.	201
18.	Analyses of NBS bovine liver standards after HNO_3 -HF digestions.	202
19.	Reproducibility of analyses of kaolinite suspensions collected on Nuclepore filters and analyzed for Mn, Fe, Cu, and Zn after HNO_3 -HF digestion.	203
20.	Complete trace metal and environmental data from the Newport River and estuary, October, 1974, February, 1975, and April, 1975.	206
21.	Trace metal concentrations in offshore water samples collected from R/V Eastward, December 3-6, 1974.	217

EXCHANGE OF MANGANESE, IRON, COPPER, AND
ZINC BETWEEN DISSOLVED AND PARTICULATE
FORMS IN THE NEWPORT RIVER ESTUARY,
NORTH CAROLINA

INTRODUCTION

It is widely recognized that estuaries are not merely passive conduits nor simple transition zones through which river-derived material passes on its way to the sea. They are complex and dynamic systems with unique characteristics not found in either their freshwater or marine neighbors. This unique character exists largely as the result of the extended residence time of materials (chemical, biological, and geological) carried in from both the parent river and from the ocean, and from the periodic change in the inputs.

On a geological time scale, specific estuaries are transient features. Of those now existing, most have been formed since the end of the last ice age and most will disappear within the next ten or twenty thousand years. On a much shorter time scale, estuaries also change minute by minute and hour by hour in response to tidal and meteorological forces and the daily light cycle. But at intermediate time scales, days to years, many estuaries show remarkable stability and constancy. This stability results from a balance of

inputs and outputs, internal recycling, and a complex array of negative feedbacks.

The high productivity of many estuaries results only in part from high inputs of nutrients from the parent river. More generally, high productivity is made possible by efficient recycling of nutrients among sediments, water, and biota in a system in which the residence time of both nutrients and primary and secondary producers is long enough to allow efficient conversion from inorganic to organic forms.

But the same homeostatic processes which make possible the generally beneficial high productivity can also cause the retention of pollutant substances in estuaries. There they can be a danger to estuarine biota and also to man through his consumption of that biota or his use of other estuarine resources. This is of special concern when one realizes that estuaries are principal sites of human habitation and industries with their accompanying wastes.

The trace metals, manganese (Mn), iron (Fe), copper (Cu), and zinc (Zn) are of special interest because they are not only essential nutrients, but also potential toxic pollutants. This dual role implies that both upper and lower limits on their acceptable concentrations exist in estuarine ecosystems. Sunda (1976) found for some algae that the difference between concentrations of ionic Cu where nutrient deficiency begins and toxic effects are first seen

may be nearly zero. Optimal concentration ranges of trace metals may be very small. The homeostatic character of estuaries will damp out fluctuations in trace metal concentrations to a limited degree, but extraordinary inputs or unwise manipulation of estuarine processes can cause dangerous concentration transgressions. It is therefore necessary to understand the magnitude, direction, and sensitivity to outside influence of the competing processes which determine the concentrations of Mn, Fe, Cu, and Zn in estuaries.

The exchange of trace metals between sediments and solution largely controls their translocations in estuarine ecosystems. Sediments generally contain the overwhelming reservoir of trace metals in estuaries. Dissolved trace metals are more mobile, however, because of the shorter residence time of water in estuaries in comparison to that of sediments. Dissolved trace metals are more readily available to many forms of biota as well. Therefore, the interchange of trace metals between sediments and water determines in large part whether trace metals remain in estuaries or are flushed out to sea, and whether they are taken up by biota.

I am concerned with two aspects of the trace metal exchange between sediments and water in estuaries. First, I would like to determine in a typical small coastal plain estuary of the southeastern U.S. if there is a net transfer of the trace metals, Mn, Fe, Cu, and Zn from sediments to solution or in the opposite direction.

This amounts to determining whether the estuary is a source or sink as dissolved river-derived trace metals are carried to the ocean. Currently this is a matter of some dispute with important consequences for the mass balance of trace metals in the ocean. Second, I would like to determine something of the nature of the transformations within the estuary resulting in this exchange. The Newport River estuary provides a useful site for such a study because it is representative of many shallow estuaries on the Atlantic coast, and because related studies of the estuarine behavior and distribution of Mn, Fe, Cu and Zn have been undertaken there.

To this end I have focused on the distribution of the trace metals in solution, because they are subject to more noticeable changes in concentration reflecting exchanges than are particulate forms, and because they are more amenable to numerical modeling and hypothesis testing. The approach taken is one of mass balance, an attempt to account for dissolved trace metals in solution in the Newport River estuary in terms of inputs, outputs, and internal sources and sinks. Dissolved trace metal distributions in relation to salinity provide the means of applying a simple mixing model to distinguish variations due to inputs and outputs from those due to internal exchange processes with sediments. The overall approach is largely observational rather than theoretical or experimental, and reflects the belief that observation is the most direct means of studying what actually happens in the natural environment.

BACKGROUND

The chemical environment in estuaries and oceans differs from that in rivers. The concentrations of many substances such as dissolved salts are higher in estuaries and oceans, and other properties such as pH and redox potential are likely to differ too. As a result, the distribution of trace metals between dissolved and particulate phases will readjust itself in the direction of a new equilibrium when rivers mix with seawater in estuaries.

Suggestions of the extent and direction of this readjustment can be derived from chemical theory, from laboratory experiments, and from field observation. These three approaches have been used by other investigators to predict the behavior of trace metals carried by rivers into the estuarine and marine environments. The predictions derived from these approaches are often contradictory. The contradiction is often the product of the complexity of estuarine chemistry; many different chemical reactions are going on simultaneously. Theoretical and experimental approaches are not capable of completely imitating this complexity. On the other hand, observational studies reveal the net result of all interacting reactions but often hide the individual reactions in so doing. But beyond these understandable sources of contradiction which are imposed by the limitations of the approaches, there are others resulting from

faulty application of these approaches. Failure to recognize assumptions and to determine if they are actually fulfilled is one fault. At other times the desire to find a single simple cause for observed behavior patterns biases interpretation.

The following sections describe some attempts to predict and explain estuarine trace metal exchanges between solution and particulate phases using these three approaches. The contradictions and complexity will become self-evident, and certain limitations will be pointed out. In the end, however, a general qualitative picture should emerge of how river-derived Mn, Fe, Cu, and Zn behave upon entering and traversing estuarine environments. This will provide a basis for comparison with the behavior of these metals in the Newport River estuary reported subsequently.

Theoretical Considerations of Trace Metal Exchanges in Estuaries

The distribution of trace metals between solution and solid phases in estuaries is determined by the relative affinities of the metals for each of the various phases present. In closed systems and under equilibrium conditions, chemical thermodynamics provides a means of predicting the composition and distribution of trace metal species among these phases. Unfortunately, estuaries are neither closed nor in equilibrium. Nevertheless,

equilibrium can be approached in some subsystems of estuaries (e.g. sediment pore waters). In non-equilibrium subsystems, the discrepancies from equilibrium conditions can be used to predict the direction of spontaneous chemical reactions (Stumm and Morgan, 1970).

The estuarine distribution of trace metals is further complicated by the existence of many heterogeneous components in the solid phases and complex speciations in the dissolved phase. Metals can be bound on particulate surfaces by various mechanisms of adsorption. They can also be bound within the solid phases as insoluble precipitates or coprecipitates, as biogenic components, or bound within the crystalline lattices of mineral fragments. In the dissolved phase, trace metals can exist as free cations (hydrated), as oxyanions, as ion pairs, and as charged and uncharged complexes with both inorganic and organic ligands (Stumm and Brauner, 1975). Parks (1975) has pointed out the complexity of the situation:

Clearly, the partition between the various phases will vary with the identity of the trace component and of the solids, the chemical environment (e.g. pH and salinity) and the suite of inorganic and organic ligands present.

It is convenient to consider in turn each of the four listed components of trace metal fixation in the solid phases (adsorbed,

precipitated, biogenic, and lattice bound) and their potential roles in exchange with the dissolved phase.

Adsorbed Trace Metals

In many marine and estuarine systems, the concentration of some trace metals in solution is very much less than that predicted by simple considerations of the solubility of the least soluble compound of the metal thought to be present. Adsorption onto solid surfaces is usually invoked as the process that maintains the metal concentrations in solution at less than saturation (Krauskopf, 1956). Substances adsorbed in one environment may be desorbed from the solid substrate if transferred to another environment. Conversely, a change in environment might increase adsorption. The transition from rivers to estuaries is such a change which could affect the adsorption of trace metals. The following discussion considers some of the possible effects the river to estuarine transition could have on trace metal adsorption and desorption.

From a thermodynamic point of view, adsorption of trace constituents from solution onto solid surfaces is the result of a decrease in the free energy of the whole solid-solution system by the free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$. The free energy of adsorption can be broken down into contributions from the various chemical bonding processes accompanying adsorption. These bonds

may be electrostatic (Coulombic), covalent, Van der Waals, hydrophobic, solvation, etc., Parks (1975). Thus $\Delta G_{\text{ads.}}^{\circ}$ is composed of $\Delta G_{\text{elec.}}^{\circ}$, $\Delta G_{\text{cov.}}^{\circ}$, $\Delta G_{\text{VW}}^{\circ}$, $\Delta G_{\text{sol.}}^{\circ}$, etc. It is convenient to distinguish $\Delta G_{\text{elec.}}^{\circ}$ from all the others which are lumped as $\Delta G_{\text{chem.}}^{\circ}$. Inadequate information presently exists on the free energy changes of these bonding mechanisms during adsorption, and the development of a comprehensive predictive theory lies in the future. The discussion of adsorption must be, of necessity, general and largely qualitative.

Figure 1 shows a conceptual picture of the electrical double layer model used to describe most adsorption processes. A solid substrate carrying an inherent charge (in this case negative) has specifically adsorbed a layer of positively charged ions. The inherent charge results most commonly from isomorphous substitutions within the substrate mineral lattice (e.g. Al^{3+} for Si^{4+} in clay minerals) causing charge deficiencies or surpluses, or from edge effects where crystalline layers terminate in broken or unsatisfied bonds (e.g. $-\text{Si}-\text{O}^-$) (Parks, 1975). Specifically adsorbed ions (or neutral species as well) are held by non-electrostatic chemical bonds (e.g. covalent). These specifically adsorbed substances can partially neutralize the inherent charge of the substrate. In frequent cases they can be adsorbed to such an extent that the net charge of the substrate is reversed. For example, Neihof and Loeb

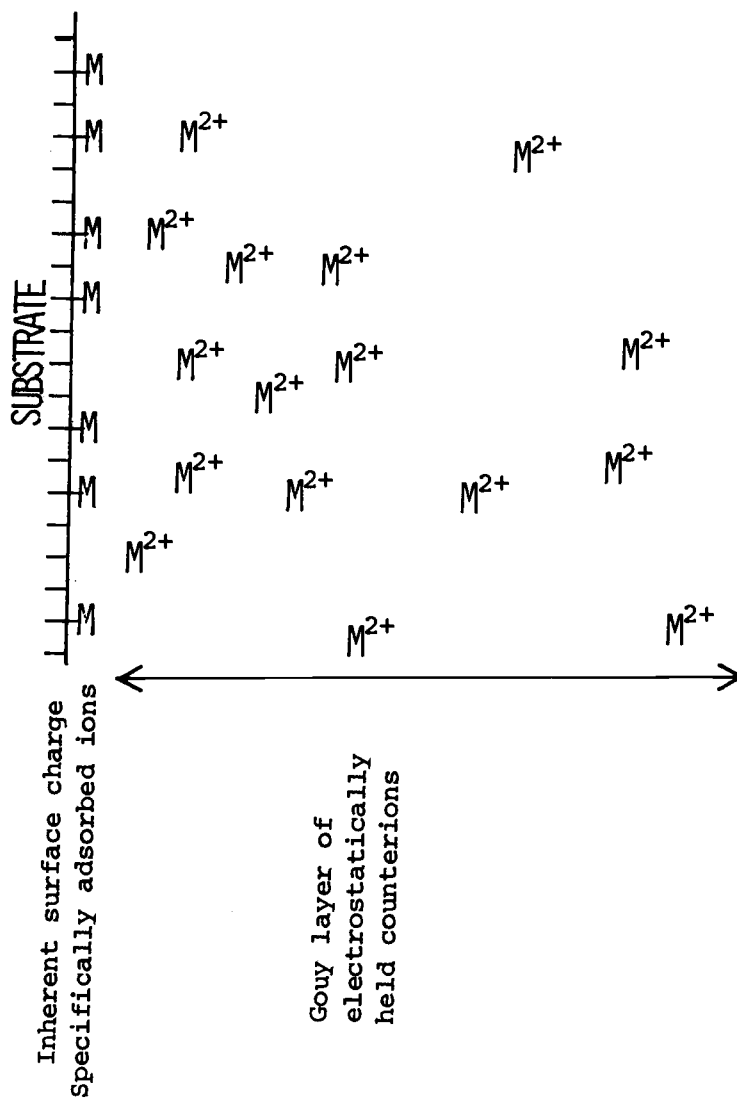


Figure 1. Simplified conceptual model of the electrical double layer, showing both specifically adsorbed and electrostatically adsorbed metal ions.

(1972) found that all solids they studied acquired negative surface charges when placed in natural seawater because anionic organic solutes in the seawater became specifically adsorbed to the solids.

Electrostatic (non-specific) adsorption

The net surface charge of the substrate and specifically adsorbed substrates attracts ions of the opposite charge into a diffuse layer of counterions that lies outside the layer of specifically adsorbed ions. These counterions are held by electrostatic forces rather than by the stronger chemical forces that hold the specifically adsorbed ions. Because the bonding is electrostatic, it is not chemically specific. In principle, ions of the same charge, such as Na^+ and K^+ , should be held in this so called Gouy layer in the same ratio as in the surrounding bulk solution. In reality, some slight specificity exists among ions of the same charge because of differences in the hydrated ionic radii (Stumm and Morgan, 1970). Divalent and trivalent ions will be more strongly held than monovalent ones in the Gouy layer because of their higher charge densities.

The important point concerning this layer of counterions is that its composition will change in response to changes in the bulk solution composition. Specifically, the transition from river water to seawater is likely to cause displacement of electrostatically

adsorbed ions such as Ca^{2+} , which predominates in river water, by the abundant Na^+ and Mg^{2+} ions in seawater. Any trace metal ions (e.g. Mn^{2+} , Fe^{3+} , Cu^{2+} , and Zn^{2+}) held in such sites would be similarly desorbed. (Table 1 shows concentrations of Ca, Mg, Na, Mn, Fe, Cu, and Zn in average river water and seawater, and points out their different bulk compositions and relative elemental proportions.) Such processes of displacement are frequently termed "ion exchange", which implies a stoichiometry fixed by charge balance. However, the term, "ion exchange", is frequently used to describe an array of reversible, stoichiometric processes in which one ion replaces another on the solid substrate, whether the latter is held electrostatically, specifically adsorbed, or held between the lattice structure of the crystalline substrate. The term is mistakenly used at times for non-stoichiometric and irreversible processes.

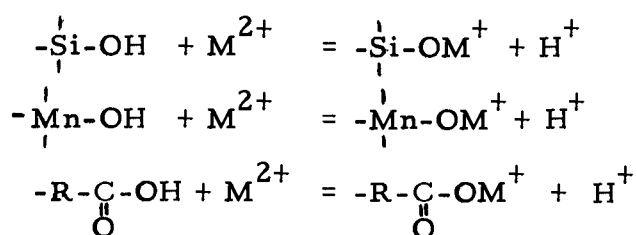
Table 1. Concentrations of Na, Ca, Mg, Mn, Fe, Cu, and Zn in average river water and seawater (from Goldberg et al., 1971). Also included are the elemental ratios to that of Mg.

Element	River Concentration		Seawater Concentration	
	$\mu\text{mole/liter}$	mole/mole Mg	$\mu\text{mole/liter}$	mole/mole Mg
Na	2.7×10^2	1.6	4.8×10^5	9.0
Ca	3.7×10^2	2.2	1.0×10^4	.19
Mg	1.7×10^2	1.0	5.4×10^4	1.0
Mn	1.3×10^{-1}	8×10^{-4}	3.6×10^{-2}	7×10^{-7}
Fe	1.2×10^1	7×10^{-2}	5.4×10^{-2}	1×10^{-6}
Cu	1.1×10^{-1}	7×10^{-4}	4.7×10^{-2}	9×10^{-7}
Zn	3.1×10^{-1}	2×10^{-3}	1.5×10^{-1}	3×10^{-6}

Specific Adsorption

Specific adsorption includes all those processes of fixation of solutes on solid surfaces which are not electrostatic. Specificity is the result of the varying strength of the chemical bonds between the solutes and the functional groups on the solid surface.

The predominant and most commonly considered adsorption substrates in aquatic environments are clay minerals, hydrous oxides of Fe and Mn, and organics (either as living or detrital particles or as coatings on other substrates). In aqueous environments, these substrates usually have hydrated oxygen groups at their surfaces which can form complexes with metal ions. One can visualize the process of complexation for the three substrate types below, using a carboxylic acid as a representative organic material.



Many other reactions with other substrate functional groups are possible, but the exchange with hydrogen bound to the exposed oxygen atom is common. The amine and sulfhydryl groups of amino acids and proteins are commonly occurring organic functional

groups on solid substrates which also have exchangeable hydrogen ions. Chelate formation in which multidentate bonding occurs is another frequently cited possibility.

This is but a simplistic view of adsorption and ignores many other reactions and substrate sites. A more thorough discussion can be found in Parks (1975) who discusses the role of adsorption in the marine environment in a clear and cogent manner. It is worth quoting him again on an important and particularly relevant point:

"The same forces responsible for complexation or compound formation are responsible for [specific] adsorption. There are no others available. This observation provides a means of comparing the expected magnitudes of $\Delta G^{\circ}_{\text{chem}}$ among various systems. Solute species which are capable of forming strong complexes or insoluble compounds with some component of the solid are likely to adsorb more strongly than those which are not."

This suggests a way to consider how readily trace metals might be adsorbed or desorbed in estuaries.

The Irving-Williams order in the adsorption of trace metals

For transition metals such as Mn, Fe, Cu, and Zn, there exists a general trend of complex stability largely independent of the nature of the ligand. Usually called the Irving-Williams order (Irving and Williams, 1953), the order is qualitatively explainable

in terms of the ionization potential of the cation and crystal field stabilization of the cation-ligand complex (Stumm and Morgan, 1970). The order of complex stability is usually given by $\text{Zn}^{2+} < \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$ for divalent cations. Figure 2 shows the log stability constants and the log solubility products of a group of potential ligands with some divalent transition metal ions as well as Fe^{3+} and Mg^{2+} . It has been modified from similar diagrams of Irving and Williams (1953) and Stumm and Brauner (1975), showing the metal ions in the order of increasing stability constants rather than the normal order of increasing atomic number. The Irving-Williams order is apparent for the ligands chosen, although other ligands can exist, in natural systems, that have metal ion specificities outside this order. This is especially true where biological processes are involved since several highly specific ligands are known (e. g. vitamin B-12 preferentially binds Co^{2+}).

Where laboratory experiments have been carried out on clay minerals, hydrous metal oxides, and organic substrates, the Irving-Williams order of metal adsorption has been generally confirmed. Hodgson (1960) found Co displaced from montmorillonite by the transition metals in the order: $\text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$. In the reverse direction, Mitchell (1964) lists the following order of difficulty of displacement from clay minerals: $\text{Cu} > \text{Pb} > \text{Ni} > \text{Co} > \text{Zn} > \text{Mg} > \text{Na}$. Where adsorption on hydrous oxides of Fe

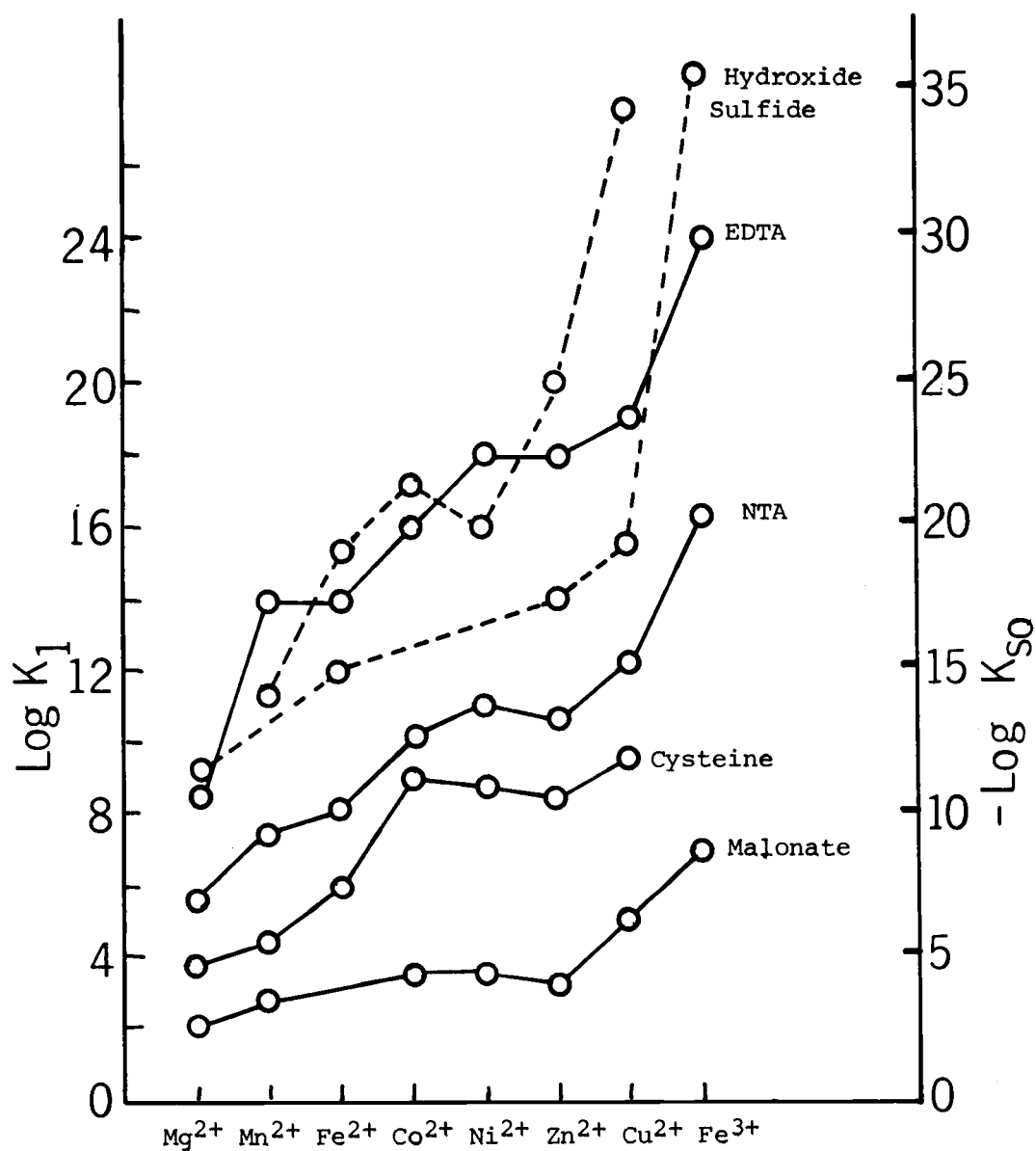


Figure 2. Stability constants (K_1) of some metal ions with organic ligands showing the Irving-Williams order of complex stability. Also shown are the solubility products (K_{so}) with sulfide and hydroxide anions.

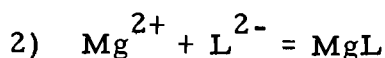
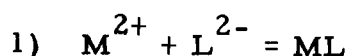
and Mn has been observed, similar but not identical orders have been found (Krauskopf, 1956). Gadde and Laitinen (1974) found the adsorption order on hydrous Fe and Mn oxides to be $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The Irving-Williams order has also been observed on hydrous metal oxides by Morgan and Stumm (1965), although Mn^{2+} was preferentially adsorbed on MnO_2 . For organics, Rashid (1974) found that sedimentary and peat humic acids adsorbed trace metals in the order $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$.

Competition of major seawater cations with trace metals for adsorption sites

The Irving-Williams order of binding strength is important because ions in the bulk solution will compete for adsorption sites with previously adsorbed trace metals and could displace them preferentially according to this order. The ions, Mg^{2+} , Ca^{2+} , and Na^+ , which are abundant in seawater should compete with trace metals for adsorption sites and could displace them from river-derived particulate substrates carried into the estuary. The most easily displaced trace metal should be that most weakly bound, Mn (Figure 2).

Competition of major seawater cations with trace metal ions for complexes with dissolved organic ligands has been studied in natural waters. Stumm and Brauner (1975), Duursma (1970), Stumm

and Morgan (1970), and Spencer (1958) all discussed the competition of Mg^{2+} and Ca^{2+} with Fe and other trace metals in the formation of soluble organic complexes. Although Mg^{2+} , Ca^{2+} , and Na^+ complexes are all weaker than the corresponding trace metal complexes, their very much higher concentrations in seawater would make them effective competitors, to the extent that little of the dissolved trace metals would be complexed to organics. Thus, the competitive reactions with an arbitrary ligand, L^{2-} , in solution might be:



With,

$$3) \quad K_{\text{ML}} = \frac{a_{\text{ML}}}{(a_{\text{M}}^{2+}) (a_{\text{L}}^{2-})}$$

$$4) \quad K_{\text{MgL}} = \frac{a_{\text{MgL}}}{(a_{\text{Mg}}^{2+}) (a_{\text{L}}^{2-})}$$

Thus,

$$5) \quad \frac{a_{\text{MgL}}}{a_{\text{ML}}} = \frac{a_{\text{Mg}}^{2+}}{a_{\text{M}}^{2+}} \frac{K_{\text{MgL}}}{K_{\text{ML}}}$$

where the a 's are activities and M^{2+} is an arbitrary divalent metal ion.

In seawater, Mg concentrations are about 0.1 molar, whereas the metals, Mn, Fe, Cu, and Zn are all about 10^{-7} molar (Table 1). For purposes of crude argument, one can substitute concentrations for activities in equation 5. Then, competition of Mg with the trace metal for ligand complexing becomes important only when the ratio of the stability constants, $(K_{ML})/(K_{MgL})$, is less than 10^6 . Using such an argument, Kester et al. (1975) concluded that organic complexation of Fe^{2+} and Fe^{3+} is not important in estuarine and marine waters. Competition by Mg^{2+} would displace Fe from the dissolved organic ligands.

Since many specific adsorption bonds can be thought of as complexes between the trace metal ion and substrate surface functional groups, Mg^{2+} can also compete with trace metals for adsorption sites. Mixing river water into seawater might then result in the displacement of specifically adsorbed trace metals by Mg^{2+} , if the stability constants of the substrate functional groups for the trace metal did not exceed that for Mg^{2+} in a ratio much larger than the inverse of their concentrations in seawater. For many trace metal:ligand complexes, the ratios of the stability constants to that of Mg are less than the approximate concentration ratio of 10^{-6} (Figure 2). For weaker ligands such as malonate or cysteine, Mg^{2+} might be expected to displace (i.e. desorb) all of the trace metals held to the solid substrate as such complexes. As the

strength of specific adsorption bonds approaches those to stronger ligands, such as EDTA, only the less stable metal complexes would be affected by Mg^{2+} competition. The ease of displacement would probably follow the inverse of the Irving-Williams order, with Mn being the most readily displaced. It seems likely that for specifically adsorbed trace metals carried into an estuary from freshwater, some Mn would be desorbed by the abundant cations in seawater, the other trace metals following to a lesser extent and in a characteristic order.

One might also expect adsorption sites on clay minerals and hydrous metal oxides to show this same displacement order since they seem to specifically adsorb trace metals to the exposed OH functional groups shown earlier, and these also show an Irving-Williams order of stability.

This argument, although an oversimplification, is qualitatively useful. Several shortcomings need to be pointed out, however. First, it is based on the total dissolved concentrations of Mg and the trace metals rather than their free ionic activities. These activities will change in response to the changing ionic strength encountered in the estuary and in response to changing solution complexation. However, Mg is likely to remain largely uncomplexed in seawater, whereas most trace metals will be complexed almost entirely, with little free trace metal ion in seawater (Millero, 1975). Thus the ratio of

Mg^{2+} to trace metal ion will be greater than 10^6 , which ought to drive reactions toward more complete desorption by Mg^{2+} in the estuary.

Second, problems arise in the desorption argument because trace metals are not absorbed solely as their divalent (or trivalent for Fe^{3+}) cations, but also as charged or uncharged complexes.

Stumm and Brauner (1975) have said:

"Hydroxo, sulphato, carbonato and especially uncharged inorganic complexes, tend to be sorbed much more at an interface than are [hydrated] free metal ions. This enhancement of adsorption by complex formation is caused primarily by the reduction in the solvation energy resulting from the lowering of the ionic charge . . ."

The effect of Mg^{2+} ions on trace metals adsorbed in this manner is not obvious.

Third, the prediction of selective trace metal desorption in estuaries ignores the increase in pH that usually accompanies the river to seawater transition. Because hydrogen ions are involved in so many solubility and absorption determining reactions, such as dissociation of ligand forming acids and the formation of hydroxy complexes, the effect of pH changes might dominate adsorption processes to the exclusion of all other ion effects. Stumm and Brauner (1975) pointed out the dependence on pH of the adsorption of metal ions on substrates with surface OH groups, presumably owing

to the degree of protonation of the surface oxide ions. They also pointed out the increase in formation of the more readily adsorbed hydroxo complexes with increasing pH. The similar pH dependence of the two processes makes it "difficult to distinguish between coordinate bonding of metal ions and the adsorption of hydroxo metal complexes." (Stumm and Brauner, 1975). This makes it difficult to foresee the effect of pH on the relative binding strength of the different metals.

Estuaries are giant titration systems in which river-derived material is titrated with a multicomponent titrant (seawater). To consider the titrants such as Mg^{2+} or OH^- separately is naive and almost certain to produce wrong conclusions. As has been pointed out repeatedly (Millero, 1975; Morel et al., 1973), one must consider all reactants and simultaneous interactions in making predictions about complex systems, because the effect of a critical reaction may be buried in the complex matrix of multiple interactions.

Nevertheless, with respect to adsorption, there are two main gradients in estuaries which seem likely to affect adsorption equilibria. The increase in cation concentrations seaward seems capable of desorbing specifically adsorbed metals, preferentially removing them in the inverse of the Irving-Williams order of complex stability (i.e., $\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$). Second, the usually increasing gradient of pH would favor an increasing

adsorption of trace metals as their more readily adsorbed complexes with OH^- and other pH dependent ligands increased in concentration seaward. The complexity of estuarine chemistry limits our ability to be quantitative about the overall effect of these competing trends, despite the efforts of many skilled investigators. The overall effect might be better studied using experimental or observational approaches.

Insoluble Precipitates

Insoluble compounds are a second component of trace metal immobilization in sediments. Through the competing processes of dissolution and precipitation or coprecipitation they can affect the exchange of trace metals between solution and particulate phases. The trace metals, Mn, Fe, Cu, and Zn share a limited similarity in their chemical behavior as transition or post transition elements. In particular, they form very sparingly soluble compounds with the common naturally occurring anions, OH^- , CO_3^{2-} , PO_4^{3-} , and S^{2-} . Where the product of the activities of the metal ion and an anion exceeds their solubility product in a particular aqueous medium, they would be expected to precipitate as an insoluble compound until the ion concentrations were reduced to that in equilibrium with the insoluble compound. Conversely, if the solution were undersaturated with respect to the metal ion and the anion, the solid compound of

the two, if present, should dissolve. Kinetic inertia and the existence of metastable phases, however, often prevent the establishment of equilibrium in natural systems.

The simplest approach to predicting solubility is to assume no complexed species (e. g. all are hydrated free ions) and to calculate solubilities from the solubility products of the least soluble compounds thought to be present. Frequently the observation that the dissolved metal concentration exceeds that predicted by such calculation is taken to indicate the existence of the previously neglected dissolved metal complexes. Conversely, measurement of dissolved metal concentration less than predicted from the solubility product is taken to mean that a less soluble compound is controlling the metal concentration in solution or some process other than simple solubility (e. g. adsorption) is in operation.

Zinc

Zinc has perhaps the simplest chemistry of the four trace metals under consideration because it has only one stable valence state (II) in aquatic systems. A number of studies since Krauskopf's (1956) early work have considered what possible insoluble compounds of Zn might control its dissolved concentration in seawater (Sillén, 1961; Brewer and Spencer, 1975). Table 2a from Wedepohl (1969) shows a recent compilation of compounds possibly limiting Zn concentrations in seawater. In oxygenated seawater, the limiting

Table 2. Compounds of zinc (a) and copper (b) possibly limiting their solubility in seawater at 25°C (from Wedepohl, 1969).

a. Zinc Compound	Solubility Product	Zn ²⁺ activity (mg/l) at saturation
ZnS	1.2×10^{-23}	10^{-8}
ZnCO ₃	$10^{-10.8}$ to $10^{-9.8}$	2 to 16
Zn(OH) ₂	$10^{-16.7}$	18
Zn ₃ (PO ₄) ₂	10^{-32}	20
Zn ₃ (PO ₄) ₂ × 4H ₂ O	$10^{-47.5}$	8

b. Copper Compound	Solubility Product	Cu ²⁺ activity (μg/l) at saturation
Cu ₂ S(chalcocite)	$10^{-48.35}$	1.2×10^{-11}
CuS(covellite)	$10^{-36.13}$	6×10^{-19}
Cu(OH) ₂	$10^{-19.25}$	22
Cu(CO ₃) ₂ (OH) ₂ (azurite)	$10^{-48.96}$	6
Cu ₂ (CO ₃)(OH) ₂ (malachite)	$10^{-33.78}$	2.3
Cu ₅ (H ₂ PO ₄)(OH) ₆	$10^{-92.5}$	11
Cu ₅ (PO ₄) ₂ (OH) ₄ (pseudomalachite)	$10^{-92.5}$?	0.08 ?
Cu ₂ (OH) ₃ Cl (atacamite)	$10^{-34.54}$	3.6
Cu ₄ (OH) ₆ (SO ₄) (brochantite)	$10^{-68.48}$	12

solubility of any of these postulated compounds is far greater than the 1.5 $\mu\text{g/l}$ reported as an oceanic average (Chester and Stoner, 1974). Making similar calculations for freshwater, Hem (1972) concluded that most rivers are also undersaturated with dissolved Zn. On this basis, it seems unlikely that the river to ocean transition will result in Zn supersaturation and precipitation under oxygenated conditions.

The argument against Zn precipitation in estuaries under oxygenated conditions is strengthened by the dominance of soluble inorganic complexes over the simple hydrated free ion in the chemical speciation of Zn in both river water and seawater. Millero (1975) recently calculated the expected chemical speciation of Zn in world average river water and seawater from basic thermodynamic constants. Zirino and Yamamoto (1972) and Dyrssen and Wedborg (1974) also calculated Zn speciation in seawater. Carbonate complexes dominate in river water, with a shift to hydroxy complexes in seawater. Little Zn^{2+} is present. Nevertheless, Millero (1975) refrained from speculating on the possible precipitation of Zn compounds in estuaries, saying, "Further work is necessary to examine how the state of ionic solutes influences chemical processes (such as solubility and ion exchange) that occur in estuaries."

Zinc sulfide is the one compound of Zn which might limit its solubility in estuaries because of its low solubility product. Free

sulfide ion and its hydrolysis products, HS^- and H_2S are not thermodynamically stable in oxygenated environments, although the slowness of the oxidation to SO_4^{2-} may permit their temporary existence in oxygenated estuarine waters to which they have diffused from anoxic sediments where they are stable (Bella, 1975). Free sulfide exists where the decay of organic matter proceeds beyond exhaustion of free oxygen, and where dissolved sulfate ion (which is abundant in seawater) becomes the electron acceptor. The reactions are mediated by specialized strains of bacteria. Thus the solubility of Zn is indirectly sensitive to the redox potential of the environment through its direct dependence on sulfide production in anoxic conditions.

Anoxic conditions are likely to exist in estuaries in the interstitial waters of bottom sediments where restricted diffusion of dissolved oxygen occurs and in fjords and some restricted marine basins where density stratification of the water column prevents mixing of oxygen into the bottom waters. In these regions ZnS can precipitate and limit Zn solubility. This is apparently the case in the anoxic bottom waters of the Black Sea (Spencer and Brewer, 1971).

Copper

Copper has two valence states in aqueous solution, Cu(I) and Cu(II), but the monovalent form is rarely found in natural aquatic

systems. As a result, Cu behaves very much like Zn, although its compounds are often less soluble. In river water, the dominant species in solution seems to be a carbonate complex which shifts to the hydroxyl complex in seawater (Millero, 1975). Little free ion, Cu^{2+} , should exist in either, as was the case for Zn. Table 2b shows possible solubility limiting compounds of Cu in seawater. Many are insoluble enough to nearly limit dissolved Cu concentrations in seawater to the $0.8 \mu\text{g/l}$ reported in average seawater (Chester and Stoner, 1974), if one ignores the soluble complexes of Cu. With the exception of phosphate, the anions forming the possible insoluble compounds are all much more abundant in seawater than in river water. River water with high dissolved Cu concentrations might precipitate one of these compounds upon entering an oxygenated estuarine environment.

Copper, like Zn, has a very insoluble sulfide which can precipitate under anoxic conditions where free sulfide ion is present.

Iron

Iron has two stable valence states in aquatic systems, Fe(II) and Fe(III). Its solution chemistry is dominated by oxidation-reduction reactions, complexation reactions, and pH dependent solubility reactions. Figure 3a from Morgan and Stumm (1965) shows the stability field diagram of Fe in equilibrium with O, H, and

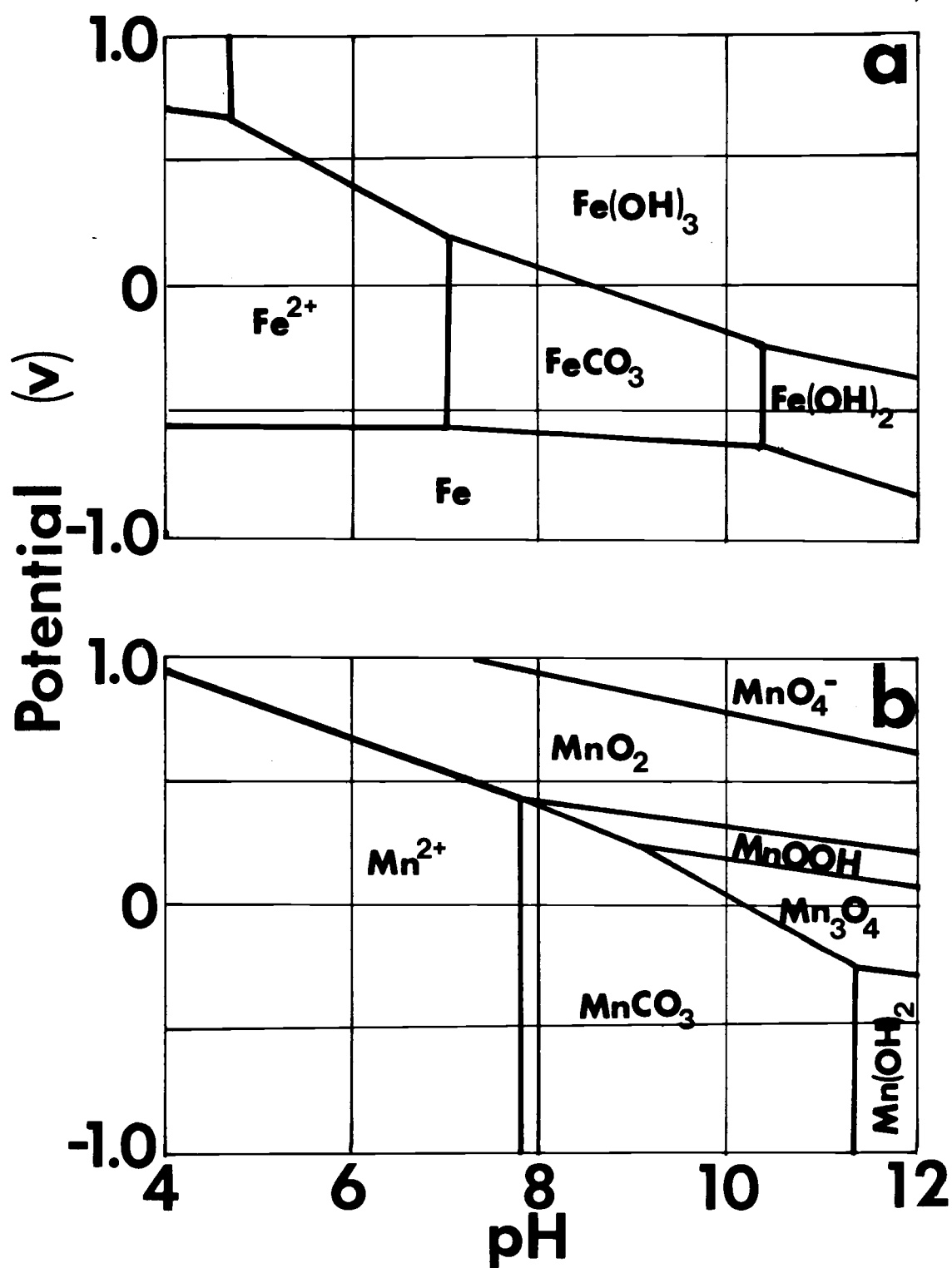


Figure 3. Oxidation potential-pH diagrams for Fe (a) and Mn (b) at 25°C and activity 10^{-5}M (redrawn from Morgan and Stumm, 1965).

C as a function of pH and the redox potential (Eh). Garrels and Christ (1965) describe the means of deriving such figures from free energy data. Other elements such as S and P could be included in deriving more complex and realistic stability field diagrams, but this diagram suffices to make two important points. (1) Low pH favors the reduction of Fe(III), usually as $\text{Fe}(\text{OH})_3$, to Fe(II) even under the redox conditions of oxygenated seawater. (Baas-Becking et al., 1960 report typical seawater Eh values of 0.4 v, although these were measured electrode potentials and may not represent the true thermodynamic Eh.) (2) Ferric iron will dominate under oxidizing conditions at higher pH, with the more soluble ferrous iron dominating under reducing conditions of low Eh.

Kester et al. (1975) recently considered the solution equilibria of Fe during the river to ocean transition. They included Cl^- , SO_4^{2-} , Br^- , F^- , $\text{B}(\text{OH})_4^-$, HPO_4^{2-} , H_2PO_4^- , and OH^- as possible complexing ligands in solution. Complexing with hydroxyl ions dominates the equilibrium with Fe^{3+} in both river water and seawater. The dominant species is $\text{Fe}(\text{OH})_2^+$ at a pH of 6 typical of river water, but it becomes $\text{Fe}(\text{OH})_3^0$ at the pH 8 of seawater. Salinity alone has little or no effect on speciation. Polymerization of $\text{Fe}(\text{OH})_3^0$ would lead to its precipitation as an insoluble compound. Through the influence of the accompanying pH increase, the river water to seawater transition should lead to the removal of Fe as

insoluble $\text{Fe}(\text{OH})_3$, which is predicted to be the stable form of Fe in seawater (Sillén, 1961; Harvey, 1937).

Under reducing conditions, as frequently occur in sediment pore waters, Fe^{2+} should be the stable form of Fe. Where S^{2-} is also present in high enough concentrations, FeS can precipitate, although its solubility is very much greater than the sulfides of Zn and Cu. FeS is frequently identified in estuarine sediments by X-ray diffraction and its typical black color imparted to the anoxic sediments (Berner, 1967). Because Fe^{2+} is fairly soluble in the presence of S^{2-} , other insoluble compounds might control its concentration in sediment pore waters. Where sulfide concentrations are not too high, FeCO_3 and $\text{Fe}_3(\text{PO}_4)_2$ have been identified as the compounds limiting Fe concentrations in anoxic pore waters in Chesapeake Bay (Bricker and Troup, 1975).

In pore waters apparently supersaturated with respect to solid FeS, high dissolved Fe concentrations may be the result of soluble complexes with organics or various sulfide species. This is also offered as an explanation of the apparent supersaturation of Cu and Zn with respect to their sulfides in some sediment pore waters (Brooks et al., 1968; Elderfield and Hepworth, 1975).

Manganese

Even more than for Fe, Mn solubility is controlled by redox

reactions. Under oxidizing conditions at the pH of seawater, Mn should theoretically exist in the Mn(IV) state as the very insoluble MnO_2 (Figure 3b). Low pH and low Eh favor reduction to the more soluble Mn^{2+} . In particular, at pH 6, typical of many rivers, Mn can exist as soluble Mn^{2+} even under oxidizing conditions. The transition to higher pH in estuaries could precipitate MnO_2 . With weaker organic and inorganic complexes than Zn, Cu, and Fe, free Mn^{2+} ion should dominate the dissolved species of Mn.

The solubility product of Mn^{2+} and S^{2-} is relatively high, and MnS is not usually precipitated under reducing, high sulfide conditions. In this case Mn solubility may be limited by the solubility of MnCO_3 . Evidence for limitation of Mn solubility by MnCO_3 has been found in anoxic pore waters of Chesapeake Bay (Holdren et al., 1975) and in the anoxic deeps of the Baltic Sea (Manheim, 1961).

Although there is great similarity in the redox behavior of Fe and Mn, oxidizing conditions favoring the precipitation of both, there are also subtle but important differences. At a fixed pH, Mn(IV) is more readily reduced and dissolved than Fe(III). Figure 3 shows that at pH 8, Mn is reduced from insoluble Mn(IV) to soluble Mn(II) at an Eh of about 0.4 v, whereas Fe reduction from Fe(III) to Fe(II) occurs at the lower pH of about 0.1 v. Thus conditions may exist where Mn is reduced and solubilized but Fe is not. Conversely, the oxidation and precipitation reactions favored by

increased Eh and pH would probably act on Fe before Mn. The kinetics of Fe oxidation are also faster than for Mn oxidation at a given pH (Morgan and Stumm, 1965). Therefore, although Mn and Fe are frequently viewed as geochemical partners, their chemical behavior is not identical. Brewer (1975) noted, for example, that the differences in kinetics and response to redox potentials resulted in different sites of precipitation for MnO_2 and $\text{Fe}(\text{OH})_3$ derived from hot Red Sea brines.

This discussion of insoluble compounds of trace metals, like that for adsorption, is simplistic, and ignores the multiplicity of chemical reactions occurring simultaneously. A beginning is being made to deal with this complexity. Morel and Morgan (1972) have developed a computer model of speciation and solubility equilibria in aqueous solution to handle the many simultaneous reactions. In a hypothetical freshwater system, the interaction of 20 metals and 31 ligands was determined, yielding calculated concentrations for more than 700 complexes and 80 possible solids. The system has been extended to include redox reactions as well. Considering the complexity of marine and freshwater environments, such sophistication can provide useful insights that might not otherwise emerge. We must await the application of such models to estuarine chemistry where the challenge is greatest.

Biogenic Components of Trace Metal Fixation

Biogenic particulate phases can exist as both living organisms and non-living detritus. Phytoplankton, major primary producers in estuaries, concentrate Mn, Fe, Cu, and Zn from seawater to high levels (Knauer and Martin, 1973). Much of the uptake is probably due to passive adsorption rather than by metabolic processes. Thus Bachman (1963) found that freshwater phytoplankton concentrated ^{65}Zn from solution as well or better when dead than alive. Davies (1967) found some marine diatoms accumulate Fe by adsorption on their surfaces as $\text{Fe}(\text{OH})_3$.

Efforts to observe changes in the dissolved trace metal concentrations associated with phytoplankton production in coastal waters have largely failed (Spencer and Brewer, 1969; Knauer and Martin, 1973), although Morris (1971) reported decreased concentrations of dissolved Mn (but not Cu or Zn) associated with dinoflagellate blooms in the Menai Straits. Arnac (1976) recently observed decreases in dissolved Cu, Cd, and Pb concentrations in the St. Lawrence estuary during the spring maximum in phytoplankton production. The high productivity of most estuaries results in the production of new particulate substrates which can serve as adsorption substrates for trace metals and cause a net removal of the metals from solution.

During decomposition, however, trace metals associated with biota and organic detritus might be released to solution. Slowey and Hood (1971) have reported vertical profiles of dissolved Cu, Zn, and Mn in the Gulf of Mexico which parallel the mid-depth maximum of phosphate thought to provide evidence of organic decomposition. Biologically mediated decomposition of organic matter can indirectly influence trace metal solubility by production of anoxic environments or of complexing organic ligands. Biota are non-equilibrium systems not readily amenable to analysis by chemical thermodynamics and usually frustrate the best efforts to quantitatively model their interactions with trace metals in natural waters.

Lowman et al. (1971) provide an extensive review and discussion of the role of marine organisms in redistributing trace metals and radioisotopes, with special consideration for estuaries.

Mineral Lattice Fixed Metals

Trace metals in the detrital mineral lattice will be inert to most exchanges with the aqueous phase. Drever (1971) reported, however, the exchange of Mg for Fe forming part of the structural matrix of clays in anoxic estuarine sediments. But in general, it seems that diffusion of metals through the solid crystalline matrix of detrital minerals would be too slow to be important on anything but geological time scales (Jenne, 1968). This would effectively

preclude them from most exchange processes in estuaries.

Recapitulation

Trace metals adsorbed to river-derived particulate matter should be partially displaced in estuaries by the abundant cations, Mg^{2+} , Ca^{2+} , and Na^+ , in seawater. The relative strength of adsorptive binding favors desorption in the order, $\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$. The increasing pH normally occurring in the river to seawater transition favors increasing adsorption of the metals as hydrated hydroxy complexes. The relative order of adsorption by this mechanism and the over all effect of competition with desorptive processes is unresolved.

Under oxygenated conditions, inorganic precipitation of Cu and Zn as insoluble compounds should not occur in estuaries because both are undersaturated with respect to their expected solubility limiting compounds in both seawater and most river waters. Higher pH in estuaries should favor the oxidation and precipitation of river-derived Mn^{2+} as MnO_2 and of Fe^{2+} as $\text{Fe}(\text{OH})_3$. Anoxic conditions (generally in sediment pore waters) would cause the reduction and solubilization of particulate MnO_2 and $\text{Fe}(\text{OH})_3$. Free sulfide production under anoxic conditions could precipitate CuS and ZnS and limit their solubility in sediment pore waters. With more soluble sulfides, Mn and Fe could maintain higher dissolved

concentrations under anoxic conditions. Pore waters might serve as a source of dissolved metals to the overlying estuarine waters.

Biological production in estuaries creates new substrates for adsorptive uptake of trace metals and might also remove them from solution by metabolic uptake processes. The decomposition of organic matter in estuaries contributes indirectly to trace metal exchange between solution and particulate matter through the formation of soluble organic complexes and the creation of anoxic conditions.

Experimental Approaches in Studying Dissolved- Particulate Exchanges in Estuaries

Theoretical considerations predict a considerable array of processes which might influence the exchange of Mn, Fe, Cu, and Zn between solution and particulate phases in estuaries. The complexity of estuarine chemistry makes it impossible to resolve this array into a coherent a priori theory as yet. In consequence, more empirical approaches have been tried. The distribution of trace metals among different components of river and estuarine particulate matter has been studied experimentally in hopes of determining what proportion might be subject to exchange with estuarine water under various conditions. Using simple laboratory analogs, clever experimenters have attempted to mimic the behavior of river-borne

material as it encounters the estuarine chemical environment or of estuarine bottom sediments in diagenetic processes.

Selective Leaching of Sediments

Many laboratory experimental approaches begin with efforts to determine the fractions of the various trace metals bound to sediments on exchangeable adsorption sites, precipitated or co-precipitated as insoluble compounds, incorporated in biogenic substrates, and bound as part of the lattice of mineral fragments. Selective leaching of sediments is used in trying to distinguish the trace metals in these fractions. Most of the methods used in sediments have evolved from standard methods used in soil science. In general, these methods are only partially selective for the fraction they seek to leach, so that ambiguous results are obtained (Cutshall, 1967).

In most techniques an exchangeable adsorbed fraction is determined by leaching with a solution of a magnesium salt or of ammonium acetate (Wiklander, 1964). Strongly adsorbed trace metals will not be removed by such leaching. Precipitated or co-precipitated metals are assumed to be insoluble carbonates, sulfides, or hydroxides and are leached with dilute acid. Alternatively, they are assumed to be acid resistant hydrous oxides of Fe and Mn, and reducing agents such as sodium dithionite or hydroxylamine

hydrochloride and a chelating agent such as citric acid are used as extractants. Organically bound metals are removed by oxidizing agents such as H_2O_2 , HNO_3 , $\text{H}_2\text{S}_2\text{O}_8$, or HClO . The residuum after this sequence of extractions is assumed to represent metals held in inert positions of the detrital mineral lattice (Gibbs, 1973).

In a study of the trace metal fractionation in the Amazon and Yukon Rivers, Gibbs (1973) used a selective leaching scheme along these lines. He found less than 1% of the Mn on suspended matter removable by MgCl_2 solution. Virtually no Fe could be so removed, and only 2% to 5% of the Cu. About 50% of the Mn was removable in the fraction susceptible to leaching with sodium dithionite and thought to be bound with hydrous Fe or Mn oxide coatings. About 5% of the Mn could be removed with NaClO and was considered organically bound. A residuum of 30% to 40% was assigned to the detrital matrix. The fractionation of Fe was very similar to that of Mn. Copper was found at less than 10% in all fractions but the detrital crystalline matrix, which contained about 80% of the total. Despite the similarity of the trace metal fractionation in the two rivers of markedly different character and climate, Gibbs (1973) was prompted to say, "The first conclusion that can be drawn from the data reported here is that no sweeping generalization can be made regarding the transport mechanism for trace metals in rivers."

The truth of this statement is emphasized in the studies of others who frequently find markedly different fractionation patterns. In studying the radioisotopes of Mn, Zn, and other trace metals in the Columbia River, Cutshall (1967) found about 10% of the ^{54}Mn and 1% to 2% of the ^{65}Zn in sediments was leachable by ammonium acetate solution as an exchangeable form. Much higher percentages of these radionuclides were found in the organic fraction of the sediments than Gibbs (1973) found for the corresponding stable elements in other rivers. A large percentage was found in the iron oxide fraction, just as Gibbs (1973) found. Huggett et al. (1975) found that about 5% to 10% of the non-crystalline Cu and Zn in the sediments of several Virginia rivers could be removed by MgCl_2 leaching. The remainder was approximately evenly divided between an organic and a precipitated-coprecipitated fraction.

Variability within a single aquatic system is frequent too. Serne and Mercer (1975) found different fractionation patterns within sediments from San Francisco Bay, presumably the result of different sources and chemical histories.

The purpose of any such attempts at trace metal fractionation is to learn how the trace metals are bound to particulate material and to subsequently predict the response of the trace metals to changes in their chemical environment. Thus the fraction extracted by sodium dithionite, thought to represent hydrous Fe and Mn oxides,

might be expected to become solubilized under reducing conditions in estuaries. Selective leaching with MgCl_2 or ammonium acetate can be used to determine the ion-exchangeable fraction of trace metals on river sediments, and thus as a measure of the trace metals that would be desorbed by the abundant cations in seawater.

Desorbable Trace Metals in River Sediments

Murata (1939) found that about 50% of the Mn on Mississippi River sediments could be leached by ammonium acetate. He predicted that when this sediment was carried into the ocean, half of its Mn would be displaced to solution. Gibbs (1973) criticized leaching with ammonium acetate as a measure of ion-exchangeable metals because this reagent tends to dissolve MnO_2 coatings on minerals. His own studies on suspended matter in the Amazon and Yukon rivers found less than 1% of the Mn removable by MgCl_2 leaching, as mentioned earlier. This suggests that little Mn would be desorbed upon mixing with seawater in estuaries.

By contrast, leaching with Mg, Ca, and Na salt solutions could remove about 20% of the sediment Mn in the Hudson River (Lentsch et al., 1973). Johnson et al. (1967) found 16% to 73% of the ^{54}Mn could be leached from Columbia River bottom sediments directly by seawater. Only a few percent of the ^{65}Zn could be leached.

Evans and Cutshall (1973) found similar results for Columbia River bottom sediments transferred to Yaquina Bay and allowed contact with seawater for 77 days. Robertson et al. (1973) repeated the experiments and results of Johnson et al., (1967), noting further that ^{59}Fe could not be leached by seawater. Evans and Cutshall (1973) found that suspended matter collected from the Columbia River could be leached of about 55% of its ^{54}Mn by seawater, but that unlike bottom sediments, up to 35% of its ^{65}Zn could also be leached. Thus with the exception of Gibb's (1973) work, it appears that a sizable percentage, at least 20%, perhaps as much as 70% of the Mn carried by river-borne sediments into estuaries should be desorbed there by the abundant cations present. A variable percentage, perhaps as high as 30% but probably less than 10% of the Zn should be desorbed. A few percent of the Cu and almost none of the Fe should be desorbed. The apparent ease of desorption is similar to the inverse of the Irving-Williams order of binding strength and seems to confirm theoretical predictions made earlier.

Laboratory Mimicry of Estuarine Chemical Processes

A second class of laboratory experiments has sought to predict the estuarine behavior of trace metals by mimicing the estuarine mixing of river water with seawater using laboratory

analogs. A particularly simple and clever group of experiments has used radioactive isotopes of metals to act as tracers. These experiments are generally naive and are distortions of actual estuarine processes.

Radiotracer Experiments

Kharkar et al. (1968) allowed several radionuclides to be adsorbed on substrates representing sediment components (hydrous metal oxides, clay minerals, peat, etc.) in distilled water suspensions. The solids were separated and allowed to contact seawater for one hour, the fractions of desorbed radionuclides being measured in the seawater filtrates. That significant but highly variable percentages of the chosen radionuclides were desorbed has been cited as evidence that trace metals, in general, will be desorbed from river-borne suspended matter upon entering estuaries. The radionuclides of Mn, Fe, Cu, and Zn were not included in the study.

Murray and Murray (1973) conducted laboratory radiotracer adsorption-desorption studies using natural sediments from the Var River in France. The influence of salinity, pH, suspended sediment concentration, and stable isotope concentration was determined, and a model predicting the adsorption-desorption behavior of ^{110}Ag , ^{60}Co , and ^{65}Zn on Var River sediments upon entering the sea was

produced. The authors predicted, as had the simpler experiments of Kharkar et al. (1968) that the stable isotopes of these radionuclides would be substantially desorbed when carried into the sea. When the model was tested by measuring Ag concentration variations in solution in the Var River plume at sea, it was felt that a good fit to the model was obtained. Unfortunately for this conclusion, variations due to possible desorption were small compared to those due to fluctuations in seawater Ag concentrations, and the goodness of fit lay with the latter rather than with any verification of the adsorption-desorption model produced from laboratory experiments.

Wolfe et al. (1975) also carried out laboratory studies using radiotracers to mimic estuarine trace metal behavior. Unfiltered Añasco River (Puerto Rico) water was mixed with seawater to cover the range of estuarine salinities, and labeled with several radionuclides. After five to ten days equilibration, the soluble and particulate fractions were separated. The samples showed an increasing percentage of all the radionuclides (including ^{65}Zn , ^{54}Mn , and ^{59}Fe) in the dissolved fraction at higher salinity which suggested that they had been desorbed from the suspended matter in significant proportions.

Such radiotracer experiments must be judged critically because they mimic real environmental conditions only remotely. The geochemical and biological processes which operate in rivers and estuaries have days, years, even millenia to distribute trace

metals among all the naturally occurring reservoirs. The one hour radiotracer equilibration by Kharkar et al. (1968), for example, is obviously inadequate to achieve real world distributions. Only the most superficial sites will be labeled. These are exactly the sites from which desorption will most readily occur. Potential metal desorption in seawater has been overestimated because slower, irreversible uptake processes which would occur over longer time periods have been ignored. Moreover, the purified kaolinite and Fe_2O_3 used by Kharkar et al. (1968) would not be expected to interact with dissolved trace metals in the same way as their counterparts in natural sediments because of surface modifications and other complex interactions (Jenne, 1968). It is unlikely, as well, to expect a solution of ^{60}Co in distilled water to adequately represent the complex speciation of Co in river waters.

Hence, in using experimental data to predict sorption processes in nature, it is necessary to consider whether the experimental conditions approximate the expected field conditions and whether the history of the water-sediment systems was similar prior to the introduction of the radionuclide. (Duursma and Gross, 1971)

In the Columbia River, natural processes have had a chance to distribute radionuclides introduced from the Hanford reactors in ways seemingly similar to that for the naturally occurring stable elements. Experiments in which unfiltered Columbia River water was mixed with filtered seawater showed an apparent desorption of 45% of the suspended particulate ^{65}Zn and about 25% of the ^{54}Mn . Filtered Columbia River water showed no evidence of precipitating

these radionuclides when mixed with seawater (Evans and Cutshall, 1973).

Other Experimental Studies

The problem of radiotracer labeling was avoided by Lowman et al. (1966) who looked at naturally occurring stable trace elements in similar mixing experiments. Filtered water from the Añasco River, Puerto Rico lost much of its dissolved Fe, Zn, Co, and Sc when mixed with filtered seawater. Lesser proportions of Mn, Ni, and Cu were also lost during the three hour mixing period. It was felt that Fe, which was found in high concentrations in the river water, precipitated as $\text{Fe}(\text{OH})_3$ in seawater, coprecipitating or adsorbing most of the other metals. The elements most readily precipitated from river water were found to be most concentrated in the sediments offshore from the river mouth.

This points up the potential role of hydrous Fe oxides (and Mn oxides) to control trace metal concentrations in natural waters, a role that has been extensively reviewed and supported by Jenne (1968), Lee (1973), and Goldberg (1954). The ability of these oxides to adsorb or "scavenge" other trace metals from solution and the observed high concentrations of trace metals in the hydrous metal oxide fractions of sediments and ferro-manganese nodules support the contention that whenever Fe and Mn are precipitated from

solution, the other trace metals can be expected to follow to various degrees depending on the particular chemical environment.

The most multifaceted experimental study of trace metal behavior in estuaries is that of Serne and Mercer (1975) as part of a project to assess the effect of dredging in San Francisco Bay (the estuary of the Sacramento River). Sediments were subjected to a large array of redox potential, salinity, and adsorption-desorption conditions. Redox changes seemed most important in determining the distribution of trace metals between sediments and solution. Metals such as Cu and Zn with very insoluble sulfides were more soluble under oxidizing conditions, presumably because the insoluble sulfides would be oxidized and release the metals. On the other hand, Fe was more soluble under reducing conditions where insoluble hydrous ferric oxides would be reduced to soluble Fe^{2+} . Under oxidizing conditions, higher salinity favored the greater solubility of Zn. However, efforts to develop a multi-parameter regression model to describe sediment:solution trace metal distributions were notably unsuccessful, accounting for only 20% to 60% of the observed variability of the data.

Recapitulation

All of these laboratory experiments suffer from the inherent faults of the approach. They seek to study complex systems by

simplifying them to a manageable level. In so doing, they neglect the multiple interactive character of real systems. For example, the studies of Kharkar et al. (1968) were only capable of detecting desorption of trace metals. Because only the particulate phase was labeled with radioisotopes, the only exchange observable upon seawater mixing was from particles to solution. Conversely, in the several studies in which filtered seawater was mixed with filtered river water, the only possible result was an increase in the trace metals in a particulate phase since none existed before. A desorptive addition to solution would not be observed since there were no particulate substrates present initially from which desorption of trace metals could occur. Yet conclusions were drawn from such studies about the net exchange of trace metals between particulates and solution.

Nevertheless, within their limitations, experimental studies do lend some support to conclusions reached from theoretical considerations. In particular, selective leaching studies indicate that desorption of particulate Mn (and lesser amounts of Zn, Cu, and Fe) should occur when they enter estuaries from rivers. Reducing conditions are also likely to increase soluble Mn and Fe concentrations by dissolving their hydrous metal oxides, and add to solution other trace metals associated with these components. But removal

processes of adsorption and precipitation can occur under other conditions.

Considering the complexity of estuarine chemistry and the seeming inability of theoretical and experimental approaches to deal with it holistically, it would seem that the best way to determine the net exchange of trace metals in estuaries would be to look directly in estuaries, hence observational approaches.

Estuarine Field Observation Studies

Field observation, because of its directness and reality, is a more satisfying approach in studying the exchange of trace metals between solution and particulate phases in estuaries than are either theoretical studies or laboratory experiments. Direct observation usually takes one of two approaches, both trying to determine the mass balance of dissolved and particulate trace metals in estuaries: (1) Input-output studies and (2) distributional studies--searching for trends or anomalous patterns of distribution of dissolved and particulate trace metal concentrations indicative of exchange processes.

Input-Output Studies

Input-output studies infer soluble-particulate exchanges from the net difference of the inflowing and outflowing fluxes of trace

metals in estuaries. Settlemyre and Gardner (1975) compared the fluxes of dissolved Cu, Zn, Pb, and Fe into and out of a South Carolina tidal creek over a period of 18 tidal cycles. The cumulative ebb flux was approximately balanced by the cumulative flood flux for Cu, Zn, and Pb. This suggested that these trace metals were neither added to nor removed from solution in this small estuary. In contrast, the flux of dissolved Fe on the ebb exceeded that on the flood, leading the authors to conclude that there was a source of dissolved Fe in the system. They felt that diffusion of dissolved Fe from bottom sediments during diagenesis was the cause.

Wolfe et al. (1973) attempted an input-output budget of Mn, Fe, and Zn in the Newport River estuary by comparing the annual average of monthly inflows from the river and outflows by tidal exchange. Because imports exceeded exports, it was concluded that these metals were being accumulated in the estuary. Unfortunately, dissolved and particulate trace metals were not distinguished, and it was not possible to say whether the apparent accumulation reflected a transfer of metals from solution to the bottom sediments or merely the sedimentation of suspended matter. Moreover, the outflow during tidal exchange was seriously underestimated by ignoring the effect of dilution by seawater on the measured export concentrations.

Windom (1975) undertook an input-output of budget of Mn, Fe, Cu, Cd, and Hg in a group of southeastern U.S. estuaries, pooling their data. Dissolved and particulate forms were measured. Assuming that all suspended particulate trace metals entering from the rivers were deposited in the estuaries, he concluded that the net flux balances indicated that most Fe and Mn were precipitated from solution in the estuaries. From similar calculations, no net soluble-particulate exchange of Cu and Cd was found, and Hg seemed to be transferred from particles to solution.

All such input-output studies are rather insensitive in detecting soluble-particulate exchanges of trace metals. They represent spatial, temporal, and even multi-estuary averages. The variability associated with these input and output estimates usually exceeds the calculated difference. There can be little confidence in the reported magnitude of the solution-particulate exchange or even in its direction under these circumstances. This does not seem to be the best way to observe trace metal exchanges in estuaries.

Distributional Studies

The exchange of trace metals between solution and particulate phases should be reflected in the distribution of the trace metals in these phases with respect to estuarine zones or chemical gradients

associated with the exchange processes (e.g. anoxic regions or pH and salinity gradients).

Sediment and Suspended Particulate Trace Metal Distributions

DeGroot et al. (1971) found that the concentrations of many trace metals in Rhine and Ems River estuary sediments decreased in the seaward direction if the concentrations were normalized to that in the less than 16 micrometer fraction. This suggested that the metals were lost to solution by some mobilization process while in the estuary. The extent of proportional mobilization increased among the metals in the same order as that of Irving and Williams (1953) for organic complex stability, with Cu and Zn being most removed from the sediments and Mn not at all. To the authors, this meant that the decomposition of organic matter in the sediments produced soluble organic compounds which complexed the trace metals and mobilized them from the sediments. Measures of organic matter decomposition such as C/N ratios in the sediments, ^{13}C concentrations in the water, and extractable fulvic acid concentrations supported this view. Tropical river estuaries low in organic matter, such as the Chao Phya in Thailand, failed to show trace metal mobilization by this criterion.

Martin et al. (1973) observed similar trace metal trends in

the seaward composition of the suspended matter of the Gironde River estuary and drew the same conclusions. Hendrix and Young (1974) found an Irving-Williams order of trace metal mobilization in the aerobic, organic rich sediments deposited in Santa Monica Bay, California from a sewage outfall (the man made analog of a polluted estuary). It would appear again that the decomposition of organic matter helps complex and mobilize soluble trace metals from sediments and suspended matter in a characteristic order.

Elderfield and Hepworth (1975) showed that some trace metals in sediment pore waters of some English estuaries existed in concentrations far above those predicted by their solubility with the free sulfides present. The degree of apparent supersaturation among the metals had the Irving-Williams order, showing that complexation by dissolved organics might have been responsible. It has been pointed out, however, that soluble sulfide, bisulfide, and polysulfide complexes could be the cause of apparent supersaturation (Gardner, 1974). These inorganic complexes also show an Irving-Williams order of stability.

This points up an interesting duality of the Irving-Williams order of binding strength. Soluble organic ligands will favor the solubilization of trace metals as soluble complexes in the order of increasing binding strength. Yet particulate organic ligands will favor retention of trace metals on solid phases in this same order.

Competition of Mg^{2+} ions in seawater will tend to displace absorbed trace metals from particulate substrates and make them soluble according to the inverse of this order. But Mg^{2+} can also displace trace metals from dissolved organic complexes in the inverse order and thereby allow them to participate in adsorption or precipitation processes which would remove them from solution.

Removal of Solubilized Trace Metals from Solution

It seems, however, that the mobilization of trace metals from estuarine sediments by organic complexation is a transient feature; they may be rapidly removed from solution. Off the mouth of the Rhine River (Eisma et al., 1966; Eisma, 1975) and off the mouth of the Gironde River (Martin et al., 1973), high concentrations of Fe, Mn, and other trace metals are found in sediments, usually forming rust colored coatings on sand grains. This suggested to the authors that the metals had been precipitated from the estuary plume waters after earlier mobilization in the estuary, perhaps coprecipitating with ferric hydroxide after the destruction or decomposition of the organic-metal complexes.

Huggett et al. (1975) observed a decreasing trend seaward of the Cu and Zn in the ion-exchangeable and organic fractions of the silt-sized sediments of the Rappahannock River estuary, Virginia.

Complementary to the decrease in these fractions, there was an increase in the concentration of Cu and Zn in the precipitated-coprecipitated fraction. This too is consistent with a model of upstream mobilization of trace metals by soluble organic complexes during organic matter decomposition and downstream precipitation of the metals. Further evidence of the rapid removal of solubilized trace metals in estuaries will be mentioned in the next section on dissolved trace metal distributions.

A difficulty in using variations in sediment and suspended matter trace metal concentrations to infer exchange processes with solution lies in the fact that non-exchange processes can cause trace metal variations as well. Trace metal concentrations in sediments are very dependent on sediment particle size; finer sizes usually having the higher concentrations. Even after normalization for variations due to particle size, variations reflecting compositional or source differences can create trends suggesting exchanges with solution. Thus the estuarine distribution of organic detritus or clay minerals of different trace metal concentration, determined by differential sorting or flocculation (Postma, 1967), can bias interpretation based on sediment trace metal distributions alone. For example, studies of the suspended particulate concentration of rare earth elements in the Gironde River estuary showed a decreasing concentration seaward (Martin et al., 1976). One might infer that

the rare earth elements had been mobilized to solution. Yet there was no corresponding increase in their concentrations in solution, but rather a decrease. Dissolved rare earths were actually being removed from solution in the estuary. The decrease in rare earth element concentrations on suspended particulate matter seaward was apparently caused by mixing of high rare earth content particulate matter from the river with low rare earth content particulate matter from offshore. Such mixing may also explain the trends of DeGroot et al. (1971), as recently proposed by Müller and Förstner (1975).

Dissolved Trace Metal Distributions

Measurement of the variations of the trace metal concentrations in solution is a more sensitive and less ambiguous means of detecting particulate-solution exchanges of the metals in estuaries. Because estuarine sediments contain much higher concentrations of trace metals than water does, a small proportional transfer of sediment trace metal to solution will result in a much larger proportional and more easily detectable change in the dissolved concentration.

Dissolved Metal Increases Associated with Tidal Intrusions of Seawater

Carpenter et al. (1975) observed that salinity intrusions into

the upper reaches of Chesapeake Bay were associated with localized increases in dissolved Zn concentrations which they attributed to ion-exchange release of bottom sediment Zn by the abundant cations of seawater. The transience of this increase suggested removal to particles again by adsorption or biological uptake shortly thereafter. Lentsch et al. (1973) reported the localized increase in dissolved Mn concentrations in the Hudson River which accompanied seawater intrusion. A complementary decrease in bottom sediment Mn concentration was observed.

Tidal intrusions in the Dutch Wadden Sea (an estuary of the Rhine River) were associated with increases in dissolved Cu and Zn concentrations (Duinker et al., 1974). The authors felt that tidal scouring had released high concentrations of the metals from the pore waters of bottom sediments into the overlying water. Nearly concurrent increases occurred in the Cu and Zn concentrations on suspended particulate matter, which suggested the rapid adsorption of at least part of the newly added Cu and Zn. The rapid removal from solution of newly solubilized trace metals is a recurrent observation in estuaries.

Trace Metal Fluxes from Sediment Pore Waters

Higher dissolved trace metal concentrations in estuarine

sediment pore waters than in the overlying waters create a concentration gradient which could drive a diffusional flux of the metals out of the bottom sediments and into overlying waters. High concentrations of dissolved Mn, Fe, and other trace metals have been found in the interstitial pore waters of anoxic sediments from the deep sea (Li et al., 1969; Bischoff and Ku, 1971), coastal sediments (Presley et al., 1967; Brooks et al., 1968), sediments of lochs and fjords (Duchart et al., 1973; Presley et al., 1972) and estuarine sediments (Elderfield and Hepworth, 1975; Troup and Bricker, 1975; Matisoff et al., 1975; Holdren et al., 1975). The elevated Mn and Fe concentrations are produced by reduction and dissolution of their insoluble hydrous oxides at the low redox potential of the anoxic pore waters. Other trace metals such as Cu and Zn appear to be maintained above the low concentrations in equilibrium with their sulfides by complexation with dissolved organic or inorganic ligands.

Chemical reactions in the oxidizing surface sediments (such as the oxidation of Mn^{2+} to insoluble MnO_2) could prevent the upward flux of dissolved metals from reaching the overlying water (Bender, 1971; Troup and Bricker, 1975). Where the surface sediment layer is also anoxic, the flux of Mn and Fe would be unimpaired. Thus, Presley et al. (1972) found elevated dissolved Mn concentrations in the bottom waters of a fjord where the surface sediments and

overlying water were reducing. In lakes subject to seasonal stratification, anoxic conditions can develop because of impeded replacement of dissolved oxygen to the bottom waters. The consequent development of reducing conditions in sediments and bottom waters has been observed to coincide with elevated concentrations of dissolved Mn and Fe in the bottom waters as a result of reduction-mobilization of the two metals from bottom sediments (Mortimer, 1971; Delfino and Lee, 1968). Fluorié (1972) observed the development of elevated dissolved Mn concentrations in several fjords and restricted coastal basins in association with the development of reducing conditions in the water column. Introduction of oxygenated waters resulted in the precipitation of most of the dissolved Mn until reducing conditions could develop again. The lake studies of Delfino and Lee (1968) had also shown the oxidative precipitation of dissolved Mn during periodic oxygenation.

In estuaries there is some evidence for the flux of dissolved trace metals from sediment pore waters. Bryan and Hummerstone (1973) observed elevated concentrations of dissolved Mn in the middle reaches of some English estuaries which they attributed to diffusion from pore waters. Elevated concentrations of Zn but not of Cu or Fe were also found. Harris et al. (1975) reported elevated dissolved Mn and Fe concentrations in bottom waters of Chesapeake Bay which were attributed to the dissolution of insoluble oxides of

Mn and Fe under the anoxic conditions present. Halcrow et al. (1973) measured positive dissolved Mn and Zn gradients in the bottom waters immediately above organic rich sediments in the Firth of Clyde. Finally, Sankaranarayanan and Reddy (1972) determined Cu concentrations in estuarine and nearshore bottom waters of the central west coast of India which were much higher than in the surface waters just above. They proposed a flux from bottom sediments as the source as well.

A final observational approach, and the one used in my own study, has sought to interpret the distribution of dissolved trace metal concentrations in estuaries, under presumed steady state conditions, in terms of a mass balance of the inputs from river water and seawater and the endogenous estuarine exchanges of trace metals between dissolved and particulate reservoirs. The distribution of dissolved trace metal concentrations as a function of salinity can be interpreted in terms of deviations from conservative mixing of river water and seawater, these deviations being attributable to the exchange processes. This approach has only recently been applied to trace metal distributions in estuaries. A later section describes this approach in detail.

Summary

The foregoing discussion of the theoretical, experimental, and

observational predictions of Mn, Fe, Cu, and Zn exchange between dissolved and particulate phases in estuaries is filled with contradictions. Perhaps this is to be expected from the complexity and diversity of estuaries and their chemistries. But a set of consistent processes does emerge: (1) Some elements are solubilized upon the initial mixing of river water and seawater, (2) organic decomposition solubilizes some metals as soluble complexes, (3) diagenesis in bottom sediments affects the overlying waters, and (4) some trace metals are lost from solution as they are carried further seaward. While not all estuaries reflect all the processes consistently, this pattern recurs time and again. On a more explicit level:

(1) Trace metals adsorbed to suspended particulate matter in river water will be partially displaced by Mg^{2+} and other seawater cations when they enter an estuary. Perhaps as much as 50% of the particulate Mn will be desorbed. Lesser percentages of Zn and Cu and little if any Fe will be desorbed.

(2) Decomposition of particulate organic matter will produce soluble organic ligands which can complex and solubilize Cu, Zn, and Fe. These processes will probably be more important in suspended matter or in oxidizing bottom sediments which favor the decomposition of particulate organic detritus.

(3) Reducing conditions in anoxic sediments will favor the release of insoluble Fe and Mn oxides as soluble Fe^{2+} and Mn^{2+} . Copper and zinc associated with these hydrous oxides might be transiently released to solution when the oxides dissolve but could quickly precipitate as insoluble sulfides if not complexed by soluble organics. Oxidation of insoluble ZnS and CuS will favor solubilization of the metals. The competition between sulfide precipitation and organic complexation will depend on the relative abundance of the competing ligands, which will depend in turn on the pathways of organic decomposition, the intensity with which reducing conditions develop, and secondary competition for the ligands. Elevated dissolved trace metal concentrations in sediment pore waters will result in a flux of the metals to the overlying waters by diffusion or sedimenturbation.

(4) Dissolved trace metals in the overlying waters are subject to increasing processes of removal as they are carried further seaward. High dissolved oxygen concentrations and increasing pH should precipitate MnO_2 and $\text{Fe}(\text{OH})_3$. Organic complexes of Cu, Zn, and Fe should tend to decompose under oxidizing conditions or dissociate in competition with the major seawater cations. The freed metal ions would then be scavenged from solution by existing particulate substrates, phytoplankton production, or precipitating MnO_2 or $\text{Fe}(\text{OH})_3$.

Mixing Models

Mass balance models seek to account for variations in the amount of a substance within a system among inputs, outputs, and internal sources and sinks. Within estuarine systems, inflowing river water and seawater are the main inputs, and outflow to the ocean the main output. Exchanges among water, sediments, and biota within the estuary provide the main sources and sinks, although certain substances such as radionuclides can be removed by irreversible degradation processes.

The variable proportions of river water and seawater within an estuary often confound efforts to estimate the internal source and sink processes by causing variations in the concentration of the substance of interest as the proportion of river water and seawater changes. It is possible, in theory, to determine the proportion of river water and seawater in an estuarine water sample and to remove the effect of simple mixing from the effect of source and sink processes in determining the composition of the estuarine water. This has led to the development of mixing models in the mass balance in estuaries.

For a conservative substance (one with no internal sources or sinks), its concentration at any point within an estuary would be given by:

$$(1) \quad C = f_r C_r + f_o C_o$$

where C is the expected concentration of the substance, C_r its concentration in river water in the sample, C_o , its concentration in ocean water in the sample, f_r , the sample fraction of river water, and f_o , the sample fraction of ocean water; ($f_r + f_o = 1$). For a non-conservative substance, equation 1 becomes:

$$(2) \quad C = f_r C_r + f_o C_o + \Delta C$$

where ΔC is the source or sink contribution (ΔC is negative in the case of a sink). ΔC can be determined from the difference between the measured concentration and that predicted under the assumption of conservative behavior.

The values of f_r and f_o can be determined if a substance known to be conservative is measured in the samples as well. Salinity provides a convenient conservative property of estuarine water in making this determination.

$$(3) \quad S = f_r S_r + f_o S_o = (1 - f_o) S_r + f_o S_o$$

$$(4) \quad f_o = (S - S_r) / (S_o - S_r)$$

S_r can generally be taken as 0, so that

$$(5) \quad f_o = S / S_o$$

and equation 2 becomes

$$(6) \quad C = f_o C_o + (1 - f_o) C_r + \Delta C$$

$$(7) \quad \Delta C = C - C_r + (S/S_o) (C_r - C_o)$$

In the case where C is conservative ($\Delta C = 0$), it is obvious that C is a linear function of S .

$$(8) \quad C = C_r - S(C_r - C_o)/S_o$$

The graph of C plotted against S should yield a straight line if C is conservative. The non-linearity of such a plot can be taken as evidence of the non-conservation of C , and the magnitude of ΔC can be easily determined.

Figure 4 from Peterson et al. (1975) shows hypothetical plots of dissolved micronutrients versus salinity showing trends indicative of conservative mixing in estuaries and of internal sources and sinks.

This approach rests on five assumptions:

- (1) The concentration of the conservative property used to determine f_o is constant in the river water entering the estuary. Zero salinity is approximated commonly in most rivers for the purpose of calculating f_o .
- (2) The concentration of the conservative property entering

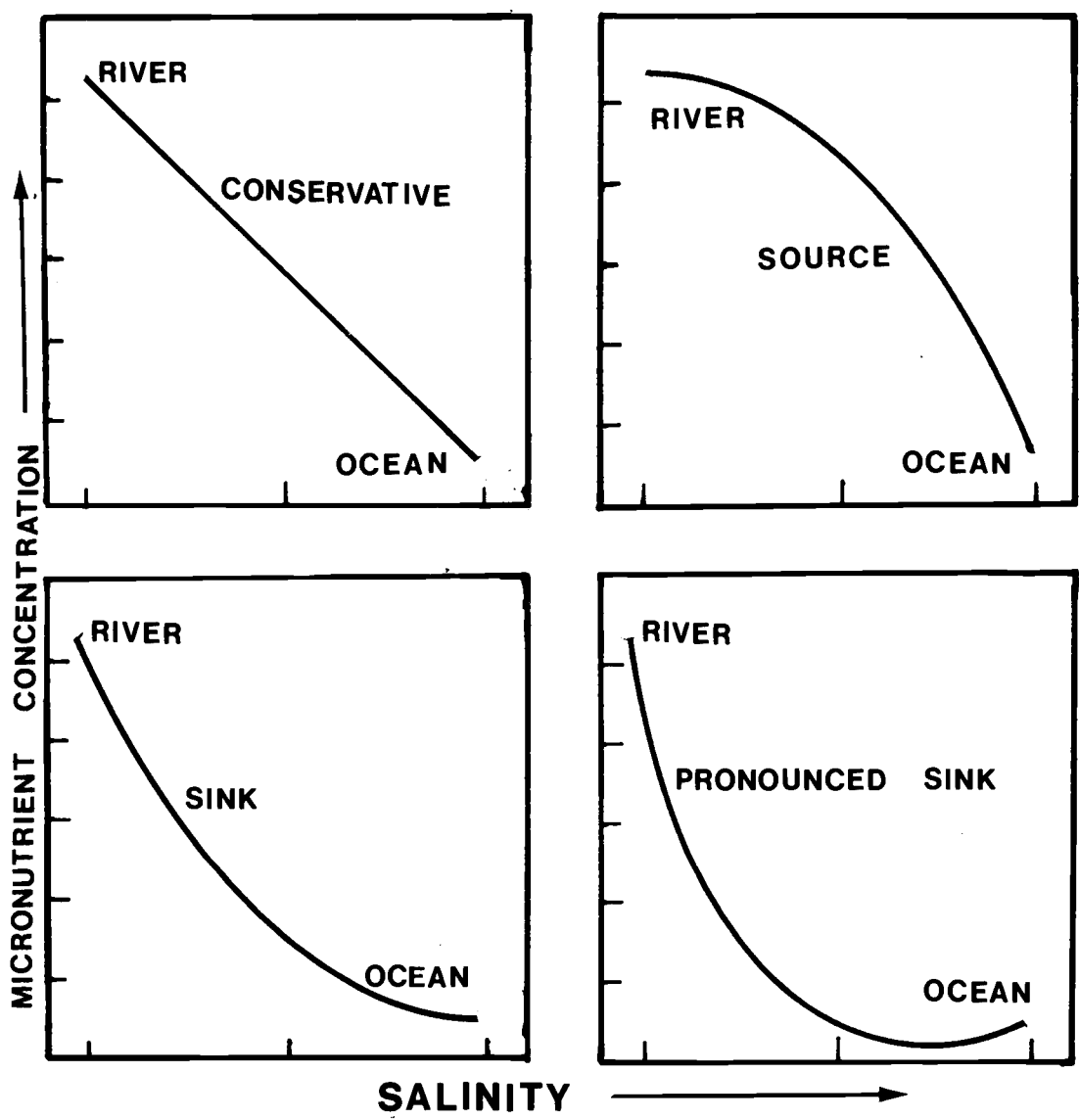


Figure 4. Hypothetical relationships between micronutrient concentrations and salinity in estuaries, showing conservative behavior and internal sources and sinks of the micronutrient (redrawn from Peterson *et al.*, 1975).

the estuary is also constant. This amounts to assuming constant S_o , the salinity of ocean water entering the estuary.

- (3) Constant concentration, C_r , of the potential non-conservative substance in the incoming river water.
- (4) Constant concentration, C_o , of the potential non-conservative substance in the incoming ocean water.
- (5) Ocean water and river water are the only two water types entering the estuary; precipitation and evaporation make negligible contributions to the composition of the estuary.

The requirement of constant input concentrations means that the model is time independent (i. e. steady-state), an assumption that is not always recognized. When applied to dissolved substances, inferred sources and sinks can usually be interpreted as exchanges with particulate reservoirs of the substance (e. g. sediments and suspended particulate matter). If applied to suspended substances, source or sink processes might represent mere physical resuspension or deposition of bottom sediments and not a chemical exchange with solution. This ambiguity rules out the application of such mixing models to suspended particulate trace metals in inferring exchanges with solution.

This mixing model approach has been applied to a number of different substances in estuaries to test whether there are sources

or sinks therein. Boyle et al. (1974) have listed some of these studies. Most were studies of dissolved silica in which the effect of inorganic precipitation, adsorption, and biological uptake in removing silica from solution was estimated. Table 3 shows an updated compilation of studies in which such mixing models were used in estuaries. Pytkowicz (1971) used an analogous method to show the non-conservation of apparent oxygen utilization in the open ocean.

The mixing model approach has met with some degree of success, but has attracted some criticism as well. Criticism has usually been prompted by inadequate consideration of the assumptions of the mixing model on the part of the original investigators.

One such misapplication of linear mixing models is that of Windom (1975). In this case, dissolved trace metal concentrations were measured in eight estuaries in samples collected bimonthly for more than a year. Jointly plotted against sample salinities, the trends were interpreted in terms of possible sources or sinks of dissolved metals using the mixing model approach. This pooling of data from many rivers and different times totally ignores possible differences in trace metal concentrations entering the different estuaries from their respective rivers. Also ignored is the likelihood that in any single river, the metal concentrations will vary over a year's time. In other studies (Windom et al., 1971), trace

Table 3. Previous studies using linear mixing models and salinity trends in estuaries to infer sources and sinks of chemical substances.

Reference	Substance	Estuary
Bien et al. (1958)	Si	Mississippi
Maeda (1952, 1953)	Si	Various Japanese
Makimoto et al. (1955)	Si	Various Japanese
Maeda and Tsukamoto (1959)	Si	Various Japanese
Maeda and Takusue (1961)	Si	Various Japanese
Fa-Si et al. (1964)	Si	Jim Long
Kobayashi (1967)	Si, N	Kiso, Nagara
Burton et al. (1970)	Si	Southampton
Burton (1970)	Si	Vellar
Liss and Spencer (1970)	Si	Conway
Wollast and de Broeu (1971)	Si	Scheldt
Liss and Pointon (1973)	Si, B	Alde
Dengler (1973)	Si	Various New England
Fanning and Pilson (1973)	Si	Orinoco, Savannah, Mississippi
Stefánsson and Richards (1963)	Si, N, P	Columbia
Hosokawa et al. (1970)	S, B, Mg, Ca, F, Si, Al	Chikugogawa
Van Bennekom et al. (1974)	Si	Dutch Wadden Sea
Abdullah et al. (1973)	Si, N, P, UV absorbance, particulate C, N, and P	Bristol Channel
Helder (1974)	NH_4^+ , NO_2^- , NO_3^-	Dutch Wadden Sea
Milliman and Boyle (1975)	Si	Amazon
Beck (1972)	Si, Na, Mg	Ogeechee
Peterson et al. (1975)	Si, $\text{N}(\text{NO}_3^- + \text{NO}_2^-)$, pH, O_2	San Francisco Bay

Table 3. Continued

Reference	Substance	Estuary
Park et al. (1972)	Si, P, N, Temperature, pH, O ₂ , Alkalinity, TCO ₂	Columbia
Simpson et al. (1975)	Si, P	Hudson
O'Connors and Duedall (1975)	Si, NO ₂ ⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Chl _a , P, Temperature, Suspended Solids	New York Bight
Yentsch (1975)	P	New England coastal waters
Zimmerman and Rommets (1974)	Natural fluorescence	Dutch Wadden Sea
Kalle (1949)	Fluorescence, Gelbstoff	Baltic
Foster and Morris (1974a, b, c)	UV absorbance	Various estuaries and coastal waters western UK
Warner (1972)	F	Chesapeake Bay
Jones (1974)	Mo	Conway
Okabe (1973)	Mo, V	Suruga Bay (Fuji and Kano Rivers)
Head and Burton (1970)	Mo	Southampton
Burton (1969)	Mo	Vellar
Berrang and Grill (1974)	Mo	Saanich Inlet
Coonley et al. (1971)	Fe	Mullica
Bewers et al. (1974)	Fe, (Ni, Cu, Zn)	St. Lawrence
Abdullah and Royle (1973)	Zn, Ni, Si, N	Mersey
Boyle et al. (1974)	Fe	Merrimac
Eisma (1975)	Fe, pH, O ₂	Rhine
Holliday and Liss (1976)	Fe, Mn, Zn	Beaulieu
Windom et al. (1971)	Fe, Zn, Cu, Ni, Mn	Various S.E. U. S.
Windom (1975)	Fe, Mn, Hg, Cu, Cd	Various S.E. U. S.

Table 3. Continued

Reference	Substance	Estuary
Abdullah and Royle (1974)	Zn, Cu, Cd, suspended solids	Bristol Channel
Harris et al. (1975)	Fe, (Mn, Cu, Zn, Pb)	Chesapeake Bay
Wolfe et al. (1975)	Fe	Añasco
Sundararaj and Krishnamurthy (1972)	Cu	Porto Novo (Vellar)
Boyle (1976)	Fe Ni, Cu, Ba	Various E. U. S. Amazon
Lindberg et al. (1975)	Hg	Mississippi
Park et al. (1965)	^{137}Cs ^{90}Sr	Columbia
Forster (1972)	^{51}Cr ^{65}Zn ^{46}Sc	Columbia
Frederick (1966)	^{51}Cr	Columbia
Evans and Cutshall (1973)	^{51}Cr , ^{65}Zn , ^{54}Mn , ^{124}Sb , ^{46}Sc	Columbia
Lentsch et al. (1973)	Mn	Hudson
Martin et al. (1976)	Nd, Ce, Yb, Pr, Lu, Eu	Gironde

metal concentrations in a particular river were compared with their concentrations in the estuary of a different river using a mixing model approach, and removal processes inferred about both systems. The need to sample estuaries individually and synoptically is obvious from the above if linear mixing models are to be properly applied.

Other potentially damaging faults recur in the use of mixing models. Frequently the range of salinities sampled within an estuary and the number of samples taken are inadequate to define a trend with dissolved metals which can be tested for non-linearity. For example, the study of Abdullah and Royle (1973) covered a salinity range of only 30⁰/oo to 34⁰/oo. Yet they extrapolated an apparent linear trend to 0⁰/oo salinity to estimate the trace metal concentration entering from the river. The study of Okabe (1973) reported the conservative behavior of Mo and V in a Japanese estuary based on a single analysis at 0⁰/oo salinity and two clusters of determinations at about 23⁰/oo and 34⁰/oo salinity.

Most studies lack replicate samples to detect spurious trends due to outlying analyses or contamination. Multiple sampling transects to determine the short term and long term repeatability of observed trends are only rarely done; approximate steady-state behavior cannot be distinguished from one-time-only phenomena.

Most studies rely on mere visual impressions of the dissolved metal:salinity trend or a high correlation coefficient to define linearity and thus test for non-conservative behavior. This is inadequate. A few studies (Boyle et al., 1974; Evans and Cutshall, 1973; Warner, 1972) have used statistical tests of linearity, the former deriving a formal test criterion of curvature.

The inflow of more than one river or ocean water type into an estuary has complicated use of the linear mixing model approach (Abdullah and Royle, 1974; Burton, 1970; Boyle et al., 1974). One must consider the possibility that other water types are the cause of apparent estuarine trace metal sources or sinks before soluble-particulate exchanges can be inferred from non-linear trends with salinity.

Perhaps the most serious potential trouble that must be considered is that observed non-linear trace metal:salinity trends can be caused by variations in trace metal concentrations of inflowing river water. Carpenter et al. (1975) have argued recently that variations of input concentrations with time may exceed the magnitude of variations due to the exchange reactions being sought, a condition which "frustrates efforts to demonstrate the other [exchange] processes in estuaries." Few studies actually measure the variations in inflowing river trace metal concentrations over time which would allow a test of this pessimistic prediction and perhaps some remedy.

These were important considerations in my study, which used the mixing model approach as the primary method of detecting exchanges of Mn, Fe, Cu, and Zn between soluble and particulate phases in the Newport River estuary.

Two final points should be made again. (1) The mixing model approach can detect and measure additions or removals from solution attributable to exchange processes with particulate phases, but can say nothing of the mechanism of exchange. This must be inferred from other information. (2) The model cannot be used to infer soluble-particulate trace metal exchanges from trends of suspended particulate metal concentrations (as $\mu\text{g metal/l}$) with salinity because of physical movement of bottom sediments into and out of the water column. Trace metal concentrations on suspended particulate matter (as $\mu\text{g metal/g}$) can provide, however, indirect evidence of exchanges with solution.

ENVIRONMENTAL SETTING OF THE NEWPORT RIVER ESTUARY

The Newport River estuary is located near Beaufort, North Carolina, 120 km southwest of Cape Hatteras (Figure 5). It is a small coastal plain estuary typical of many along the coast of the southeastern United States.

The Atlantic Estuarine Fisheries Center (AEFC) of the National Marine Fisheries Service, National Oceanic and Atmospheric Administration has conducted ecological studies of this estuary for the past 25 years. Emphasis has been placed on the relation between potential fisheries productivity and the impact of pollutants derived from various activities of energy production, especially by nuclear reactors. One part of this multidisciplinary program has sought to study the cycling of contaminants (both radioactive nuclides and stable isotope pollutants) within estuarine ecosystems. My study on the soluble-particulate exchange of Mn, Fe, Cu, and Zn was part of a program which seeks to understand the estuary as a system.

The Newport River estuary is a shallow "drowned river mouth" estuary with a mean depth of about one meter at low tide and an area of 31 km^2 (Figure 6). The Newport River supplies the major source of freshwater, with an average rate of flow of $3.6 \text{ m}^3/\text{sec}$. Its drainage basin covers 340 km^2 of low lying pine forests, cypress pocosins, marshland, and agricultural lands. These have developed

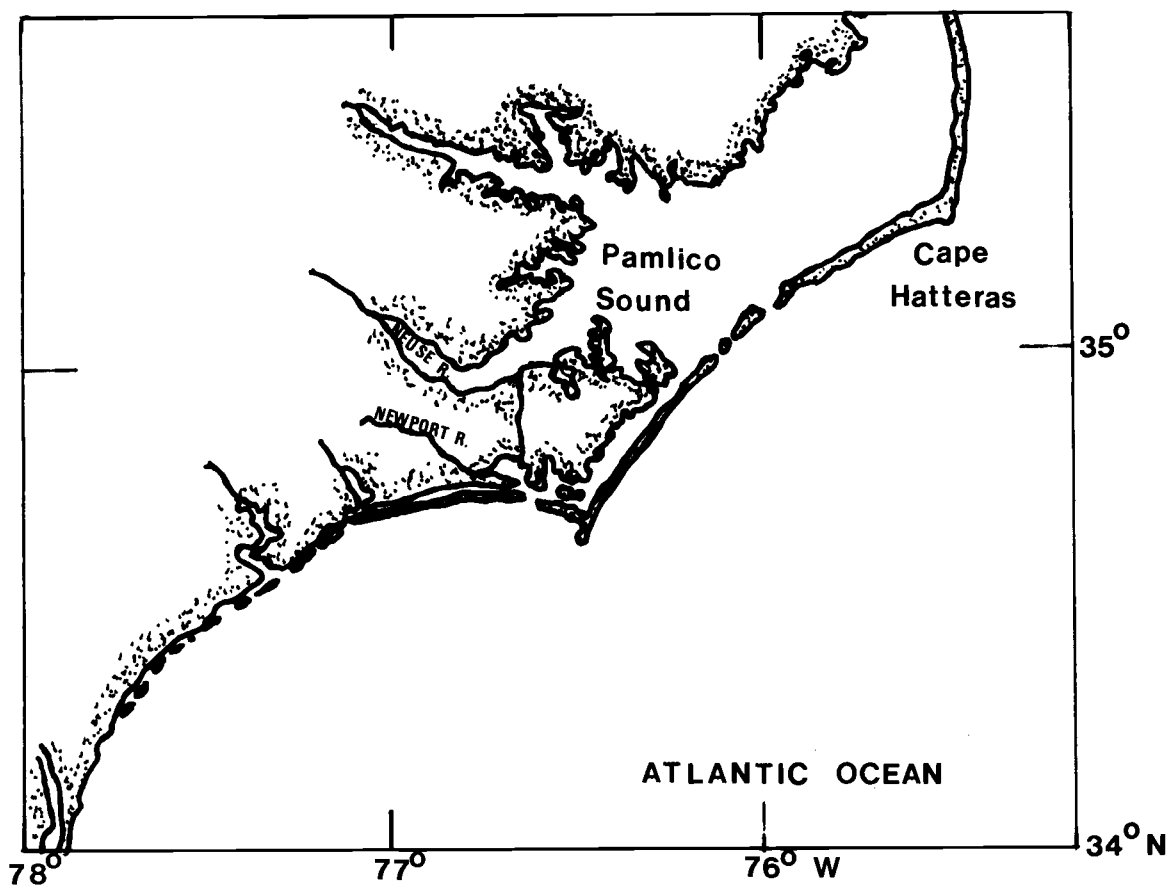


Figure 5. Coastal North Carolina.

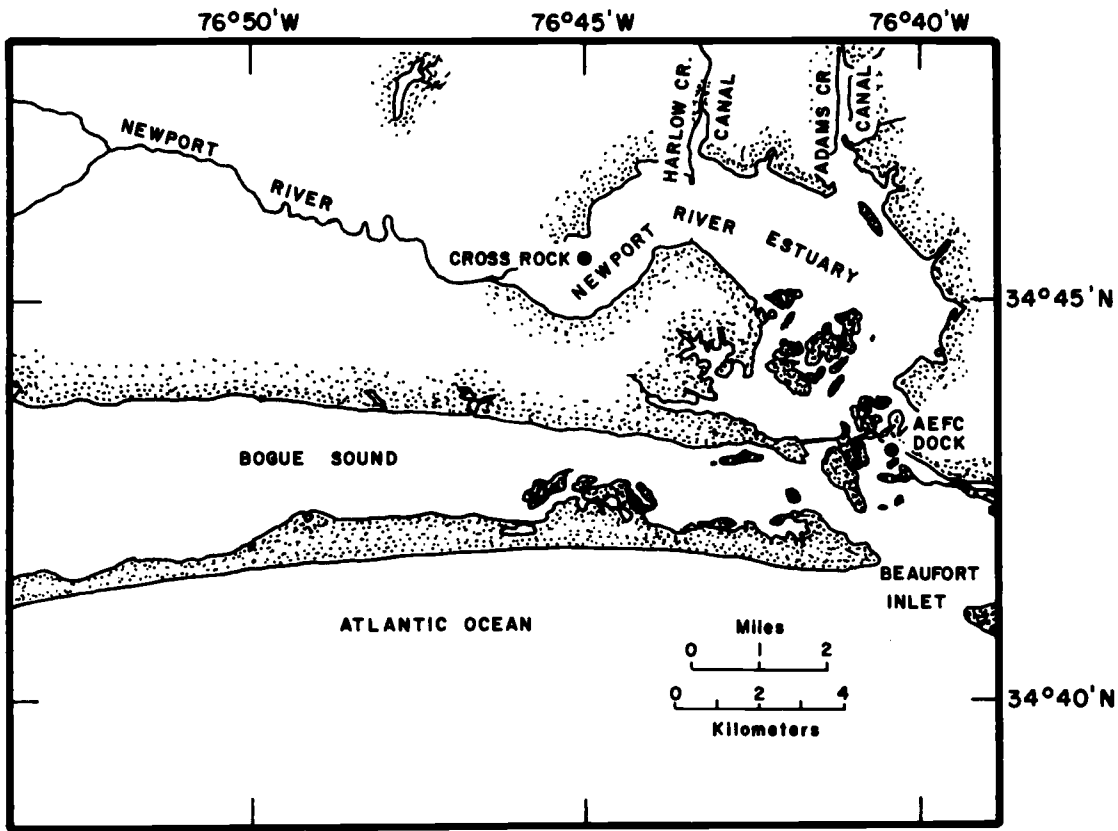


Figure 6. Newport River estuary.

on soils derived from relict beaches of recent origin. The highest point in the drainage basin is less than 20 m above sealevel. Rainfall averages about 100 cm per year, with winter and summer rainy seasons and spring and fall dry periods. Hurricanes are occasional visitors, and can drop more than 20 cm of rain in less than 24 hours, with profound effects on the estuary's hydrology, salinity regime, sediment transport, and biota. The flushing time of this estuary has been estimated to range from 4.5 to 9.6 days depending on river flow (Jennings et al., 1970). The mean tidal range is about 0.8 m. Extensive mud flats are exposed at low tide, and marshes of the cord grass, Spartina alterniflora, rim the estuary, especially at its upper end. Winds and tidal currents dominate mixing and prevent vertical salinity stratification. The estuary is well mixed, but tidal oscillations and variations in river flow cause wide variations in salinity at fixed stations within the estuary over time scales from minutes to months.

The U.S. Army Corps of Engineers maintains the Intracoastal Waterway along the east side of the estuary at a depth of 3.7 m and a width of about 70 m. The waterway runs from Beaufort Inlet to Adams Creek Canal which connects with the Neuse River estuary, 20 km distant. Some water exchange through the canal is expected, especially during northeast winds characteristic of the period

December to May. The magnitude and variability of this postulated flow are not known.

Primary productivity within the estuary is nearly equally divided between phytoplankton and Spartina. Wolfe (1975) has estimated the productivities at $110 \text{ g carbon/m}^2\text{-year}$ and $94 \text{ g/m}^2\text{-year}$, respectively. There is a marked seasonality to productivity, with a summer maximum. Spartina begins growing from perennial roots in the early spring, reaches maximum biomass in late summer (with foliage as much as three to four meters tall) and dies back to root level in early fall. The dead foliage provides large amounts of organic detritus to the estuary, less than half of which is exported from the estuary. This high productivity and the variety of protected habitats within the estuary support a system of high secondary and tertiary productivity. This system is dominated by benthic epifauna and infauna and migratory fish which use the estuary as a nursery ground for larval and juvenile forms.

Johnson (1959) has described the sediments of the Newport River estuary. He summarizes as follows:

"The sediments of the upper estuarine environment are supplied by the streams that empty into the area and to a lesser extent by erosion of wave cut banks. Their distribution is controlled predominantly by wind induced currents in the shallow water environment. The lithology generally conforms to a pattern of fine to coarse sand near the shores grading into very fine to fine sand in the shallow bay environment and then into a clayey silt or a silty clay in the central channel. Sediments near the

tidal inlet consist of fine to coarse clean sand being washed into the area from the sea by tidal currents."

In shallow estuaries, bottom sediments generally represent the major reservoir of trace metals. Reservoirs in water or biota are usually of a much smaller size (e.g. studies of Mn, Fe, Zn, and Co in Redfish Bay, Texas by Parker, 1962 and Parker et al., 1963; of radioisotopes of trace metals in an arm of the Columbia River estuary by Renfro, 1973, and of Mn in the Hudson River estuary by Lentsch et al., 1973). Table 4, taken from Wolfe et al. (1973), shows the distribution of Mn, Fe, and Zn among sediments, water and biota in the Newport River estuary. More than 90% of these metals is found in the sediments (here represented by the acid extractable fraction in the surface two cm).

Table 4. Reservoirs of Mn, Fe, and Zn in the Newport River estuary (from Wolfe et al., 1973). Values are as total kilograms of metal. Water includes both dissolved and suspended particulate forms. Sediments are from 0.1 N HCl extracts of surface two cm only.

	Mn	Fe	Zn
Water	240	1800	19
Biota	10	120	56
Sediments	17000	380000	4600

This view of the importance of sediments in the trace metal cycling in estuaries is a biased one in a certain sense, because it is based on a static perspective. The dynamics of trace metal cycling is determined by fluxes and rates of exchange among all the reservoirs. With this perspective, water and biota take on more importance because of their more rapid reaction kinetics and physical mobility. The static perspective does show, however, the potential of the sediment reservoir to influence the trace metal concentration of other reservoirs because of its size. Wolfe (1975) has estimated the annual fluxes of Mn, Fe, and Zn entering and leaving the estuary in water flows and their fluxes through the food web. The fluxes between water and sediments or other particulate substrates have not been determined.

Obviously the annual fluxes based on reservoir size, flushing rates, and rates of biological productivity should be reflected in spatial and temporal concentration variations of the metals within the reservoirs of the estuary. The main problem in studying lies in sorting out the variations among the causative factors. Of prime concern is the flux of metals between bottom sediments and suspended particulate matter on one hand, as the largest reservoir, and water on the other hand, as the reservoir mediating exchanges with most other reservoirs.

METHODS AND MATERIALS

Sampling and analytical methodology were designed to obtain river and estuarine concentrations of Mn, Fe, Cu, and Zn in solution and in suspended particulate matter. The previously discussed mixing model approach could then be applied to the dissolved metal data to detect and measure exchanges between dissolved and particulate phases in the estuary. Corollary data on salinity, temperature, pH, dissolved oxygen concentration, and ultraviolet (UV) absorbance of the water were obtained concurrently.

Estuarine sampling was carried out in five longitudinal transects: October 30 and 31, 1974, February 4 and 5, 1975, and April 14, 1975. Efforts were made to obtain samples covering the full range of salinity in the estuary, from 0⁰/oo in unmixed Newport River water to greater than 30⁰/oo frequently found at the AEFC dock, near the inlet to the estuary. Samples of February 5, 1975 were taken within two hours of low tide. All other samples were taken within two hours of high tide. A cruise aboard R/V Eastward, December 3-6, 1974, provided the opportunity to obtain offshore samples to better define the composition of ocean water mixing in the estuary. During the three weeks prior to the estuarine transects of October, 1974 and February, 1975, periodic samples were collected in the Newport River at 0⁰/oo salinity to determine the

variability of river water input concentrations which might affect the assumptions of the linear mixing model. This three week period represented several flushing times of the estuary. Periodic samples were also taken from the AEFC dock during this same period.

Sample Collection

Estuarine water samples were collected from the upstream side of a five meter long aluminum boat. Salinities were measured in the field with a Beckman RS5-3 inductive salinometer and later on water samples returned to the laboratory, using an Aminco Cotlove chloride titrator with accuracy of $\pm 0.3^{\circ}/\text{oo}$. The field salinometer also provided temperature measurements. A Beckman Model G pH meter measured pH in the field. Dissolved oxygen was measured in the field with a YSI Model 54A polarographic dissolved oxygen probe.

UV absorbance was measured on water samples filtered through Gelman Type E glass fiber filters. The sum of the absorbances at 250 nm, 300 nm, and 350 nm in a one cm cell was measured by a Cary 14 UV recording spectrophotometer. This summed UV absorbance has been used as a measure of dissolved organic matter (Foster and Morris, 1971). A sample from the Newport River on April 5, 1975, had a UV absorbance of 2.34. It contained 109 mg/l

of dissolved solids of which 48.0% was ash. On an ash free basis, the material was 45.8% C, 2.5% H, and 0.7% N as determined on an F and M Model 185 CHN analyzer. Studies on the dissolved organic matter composition of rivers of the southeastern U.S. similar to the Newport have shown the dissolved organic matter to be mostly fulvic and humic acid substances with multiple carboxylic acid functional groups (Beck et al., 1974).

Water samples for trace metal analysis were collected in a cylindrical, 400 ml plexiglass pressure vessel specially constructed for the purpose. This material had a low risk of contaminating the samples because of its low trace metal content (Robertson, 1968). The samples were immediately pressure filtered with 30 psig nitrogen gas through Nuclepore filters (47 mm diameter, 0.4 μ m pore size) held in acid washed polycarbonate Nuclepore filter holders which screwed into the pressure vessel. This provided an operational separation of dissolved and suspended particulate phases. The filters had been previously weighed on a Mettler M5 balance so that suspended particulate concentrations could be determined later. Filtration was carried out until the filters clogged. This provided samples from about 50 ml in freshwater to 400 ml in seawater. Two filters were often required to provide a minimum 50 ml sample at the low salinity stations. Blanks were run identically using 300 ml of deionized distilled water (DDW). Filtrates were collected directly in acid washed 500 ml conventional polyethylene bottles

and acidified with 0.1 ml redistilled concentrated HNO_3 .

When returned to the laboratory, the filtrates were frozen until time for analysis, and the filters were carefully washed free of sea salts with 15 ml DDW. The filters were then dried in a dessicator for 48 hours before being reweighed.

Dissolved Trace Metal Analysis

It was necessary to develop an analytical technique for trace metals which could overcome three limitations imposed by estuarine sampling. (1) Low metal concentrations in water samples. This required the use of preconcentration techniques and high sensitivity analytical methods. (2) Possible interferences by the high concentration and variable salt matrix of the estuarine water samples. This required a separation of the metals from Na, Mg, Cl, etc. in the samples. (3) Limited sample size and other logistical considerations. This required that the preconcentration and matrix separation schemes extract all four metals of interest together and in one operation.

The method finally developed utilized extraction of Mn, Fe, Cu, and Zn on Chelex-100 chelating resin as the preconcentration-matrix separation method. Extraction of trace metals from seawater using Chelex-100 resin had been done previously by Riley and Taylor (1968) and has been used increasingly since that time. The resin

contains iminodiacetic acid groups which chelate transition metal ions but have a low affinity for Na, Mg, and Ca. This allows a separation of metals such as Mn, Fe, Cu, and Zn from the bulk salts of seawater. Elution with strong acid strips the extracted metals from the resin. Analysis by atomic absorption spectrophotometry using flameless graphite furnace atomization provided the needed analytical sensitivity and specificity. Blessed with 10 liter samples, Riley and Taylor (1968) had been able to use the less sensitive but more precise flame aspiration atomization.

In preparation for extraction, the frozen filtrates were thawed and weighed. Five ml of 5% $K_2S_2O_8$ solution were added to the samples, still in their original bottles. The caps were screwed tight, and the samples were allowed to digest for 16 hours at $90^{\circ}C$ in a drying oven. This procedure oxidized dissolved organic matter which might otherwise bind the trace metals and prevent their subsequent extraction (Slowey and Hood, 1971). Appendix A shows the effect of this treatment on Mn, Fe, and Cu recovery from Newport River water with its high organic content.

The cooled digested samples were brought to pH 6-7 with five ml 8% $NaHCO_3$ solution. Samples of October, 1974 used NH_4OH as the acid neutralizer-buffer. This reagent interfered with Fe extraction, hence its subsequent replacement with $NaHCO_3$. The samples were allowed to flow through previously prepared Chelex-100

resin columns at an uncontrolled flow rate of about 2.7 ml/min.

The columns were then purged of interstitial sample with two 15 ml washes of DDW. The extracted trace metals were eluted with 15 ml of 2N HNO_3 . The eluant was evaporated to dryness in 30 ml FEP Teflon beakers on a hot plate, and redissolved in DDW which had been acidified with 50 μl concentrated redistilled HNO_3 . The samples were brought up to 10 ml volume and stored in capped, acid washed polypropylene test tubes (15.5 ml capacity).

The resin columns had been prepared from Chelex-100 resin of 100-200 mesh (BioRad Laboratories), with an actual wet mesh of 50-100. The original resin was given two washes in bulk with 2N HNO_3 and five subsequent washes with DDW. It was converted to the ammonium form with 4N NH_4OH (isothermally redistilled in polyethylene), and washed twice with DDW to remove excess NH_4OH . Three ml of the resin slurry were pipetted into each extraction column. The columns were made by friction coupling disposable polyethylene ion-exchange columns (BioRad) to the necks of 200 ml tall form polyethylene bottles whose bottoms had been cut out. The added resin just filled the 0.7 cm diameter by 4 cm lower section of the columns. Two DDW washes of the resin in the columns were followed by two washes of 2N HNO_3 to elute any remaining contaminating trace metals, and washed twice more with 15 ml DDW. Two ml of concentrated NH_4OH reconverted the resin to the

ammonium form in situ and were followed by two final DDW washes. The prepared columns were now ready for the extraction of Mn, Fe, Cu, and Zn from the samples as described above or could be used to purify the NaHCO_3 and $\text{K}_2\text{S}_2\text{O}_8$ solutions. After use the resin was discarded and the columns reused after soaking for 24 hours in 8N HNO_3 and further DDW rinsing.

The 10 ml extracts from the Chelex-100 columns were analyzed for Mn, Fe, Cu, and Zn by injecting small aliquots into a Perkin Elmer Model HGA 2000 Graphite Furnace coupled to a Model 403 atomic absorption spectrophotometer. Injection was by Eppendorf pipets with polypropylene tips. Instrument parameter settings are shown in Table 5. Output was in absorbance to a Perkin Elmer Model 56 strip chart recorder from which the peak absorbances were read. The relationship between concentration and absorbance was not linear but could be adequately fitted by a quadratic curve. For some samples, 10:1 dilutions with DDW were required to keep output absorbances below 0.6, above which uncorrectable nonlinearities in calibration curves occurred. Standards were made up in both DDW and in seawater which had been previously stripped of trace metals by passage through a column of Chelex-100 resin. The standards were 0, 1, 2, and 3 $\mu\text{g}/\text{l}$ in Mn and Zn, 0, 2, 4, and 6 $\mu\text{g}/\text{l}$ in Cu, and 0, 4, 8, and 12 $\mu\text{g}/\text{l}$ in Fe. One hundred ml of these standards were extracted by Chelex-100 resin (as for the

Table 5. Instrument settings used in trace metal analysis using the Perkin Elmer Model HGA 2000 Graphite furnace and Model 403 atomic absorption spectrophotometer.

Element	Wave length (nm)	Silt (A)	Recorder response setting	Usual volume of sample injected (μ l)	Dry temp ($^{\circ}$ C)	Dry time (sec)	Ash temp ($^{\circ}$ C)	Ash time (sec)	Atomize temp ($^{\circ}$ C)	Atomize time (sec)
Fe	298.8	20	2 (1 sec)	20	125	30	1250	10	2500	12
Mn	280.1	20	2	20	125	30	1100	10	2400	12
Zn	213.8	20	2	5	125	20	550	10	2000	12
Cu	324.7	20	2	50	125	50	1000	10	2500	12

Gas interrupt was employed and Deuterium arc background correction was used on all samples.

samples) to generate calibration curves.

The Chelex-100 extraction also extracts some Na, Mg, and Ca from the samples. When injected into the furnace, these produce smoke which interferes with the trace metal analyses. Correction for this non-atomic absorption is made using a Deuterium Arc background corrector. Suppression of the atomization of the trace metals is also caused by presence of the extracted Na, Mg, and Ca. A small correction for this is required and is discussed in Appendix A along with other aspects of the trace metal analyses.

Particulate Analysis

Dried and weighed Nuclepore filters with the collected suspended particulate matter were placed in 15.5 ml polypropylene test tubes containing 0.1 ml each of concentrated redistilled HNO_3 and 48% HF. Capped tightly, they were placed in a drying oven at 90°C for 16 hours. Upon cooling, volume was made up to 10 ml with DDW. Dilutions were made if necessary. Blanks were obtained using the same filters used for the dissolved metal blanks. The graphite furnace was used for Mn, Cu, and Zn analysis. Flame aspiration and atomization could be used for Fe.

RESULTS AND DISCUSSION

Manganese, iron, copper, and zinc should show different patterns of distribution and pathways of transfer within the Newport River estuary because of their different chemistries. To avoid the repeated comparison and contrast of their behavior under each of the sampling and experimental conditions, these trace metals will be dealt with individually, starting with Mn which shows the most consistent behavior. The other metals will be discussed in turn, the model developed for Mn serving as a basis for comparison.

Manganese

As a first approach in modeling the behavior of Mn in the Newport River estuary, one can hypothesize that dissolved Mn does not participate in any net exchanges with other reservoirs of Mn in the estuary (e.g. sediments or biota). Its concentration at any point in the estuary is therefore determined solely by the proportions of the water types mixing in the estuary and their dissolved Mn concentrations. Most simply this would be the river water and ocean water flowing into the estuary. As discussed earlier, this hypothesis predicts that a plot of dissolved Mn versus salinity is a straight line if the salinity and dissolved Mn concentrations of river water and ocean water are constant.

In Figure 7, dissolved Mn concentrations are plotted versus salinity for each of the three sampling periods, October, 1974, February, 1975, and April, 1975. Included in Figure 7 are the concentrations of dissolved Mn flowing into the estuary from the Newport River and at the Atlantic Estuarine Fisheries Center (AEFC) dock during the three weeks prior to the estuarine transects. Table 6 shows the mean and standard deviation of these inflowing dissolved Mn concentrations as well as those for Fe, Cu, and Zn. Particulate concentrations of the metals are also summarized in this table. Complete data on metal concentrations as well as corollary data on such concurrently collected properties as pH, dissolved oxygen, temperature, and UV absorbance are found in Appendix B.

The trends of dissolved Mn versus salinity are remarkably similar for transects taken on adjacent days (October 30 and 31, 1974 and February 4 and 5, 1975). This demonstrates the short term repeatability of the observations. It seems justifiable, therefore, to group the data from adjacent days' samples for statistical and interpretive purposes. This was also done for the other metals. It is convenient to discuss the data in terms of three sampling periods: October, 1974, February, 1975, and April, 1975.

Figure 7 shows that dissolved Mn concentrations do not fall on a straight line when plotted versus salinity, but rather they

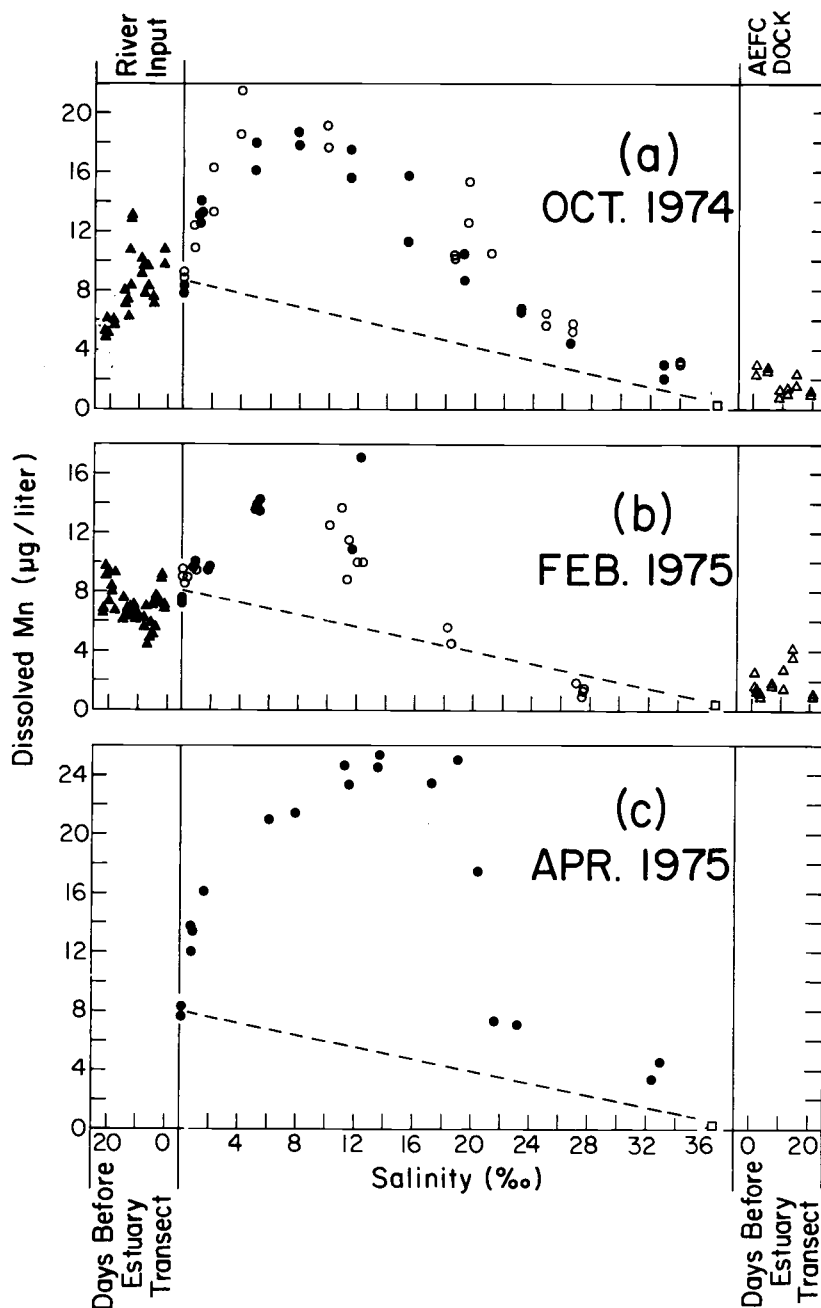


Figure 7. Dissolved Mn relationship with salinity in the Newport River estuary during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (●). A dashed line representing conservative mixing connects the mean dissolved Mn concentration in river water on the day of the transects with the dissolved Mn concentration in primary ocean water (□). Also shown are the dissolved Mn concentrations in Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuarine transects.

Table 6. Summary statistics of dissolved and suspended particulate Mn, Fe, Cu, and Zn in Newport River and at AEFC dock during three weeks prior to October, 1974 and February, 1975 estuary transects. All values are $\mu\text{g/l}$. Mean (\bar{x}) and standard deviations (sd).

		Mn		Fe		Cu		Zn		
		\bar{x}	sd	\bar{x}	sd	\bar{x}	sd	\bar{x}	sd	
Dissolved	Oct.	7.8	2.7	---	---	.5	.3	.8	.5	N.R.
	Feb.	7.1	1.3	259	50	.7	.6	1.5	.3	
	Oct.	1.6	.7	---	---	.3	.1	.1	.1	AEFC
	Feb.	1.7	.9	6.2	3.6	.4	.2	.3	.1	
Particulate	Oct.	1.1	1.1	---	---	.2	.1	.8	.6	N.R.
	Feb.	.2	.1	114	60	.2	.4	.3	.3	
	Oct.	2.6	.8	---	---	.2	.1	.8	.3	AEFC
	Feb.	1.4	.6	195	70	.1	.1	.5	.1	

consistently display a maximum. The line predicted by conservative mixing is shown by dashes and connects the mean $0^{\circ}/\text{oo}$ salinity dissolved Mn concentration for the days of the estuary transects in each sampling period to the dissolved concentration measured December 3, 1974 in water collected at station P2, 31 km seaward of the estuary mouth (See Appendix C). This latter concentration is assumed to represent primary ocean water mixing in the estuary.

Statistical Tests of Non-Linearity

It is obvious in Figure 7 that plots of dissolved Mn concentrations versus salinity are not linear. However, it would be well to establish criteria which are applicable in less obvious cases. Two approaches to testing linear hypothesis are applicable. In the first, where replicate measurements at each salinity are available, the contribution of pure error (variability associated with replicate measurements) can be calculated. This sum of squares, when subtracted from the residual sum of squares after fitting a linear least squares model to the data, yields the sum of squares due to lack of fit (Draper and Smith, 1966). The ratio of the mean square (lack of fit) to the mean square (pure error) calculated from the respective sums of squares yields an F statistic which can be tested for significance against tabulated values with the appropriate degrees of freedom. If the calculated F statistic exceeds the

tabulated value (the maximum value that might be expected merely by chance), it is reasonable to conclude that the data lack fit to the linear model. Table 7 shows an analysis of variance table derived for this purpose and applied to the dissolved Mn data of October, 1974. The F value of 15.6 exceeds the tabulated 95% F value of 2.09 and leads to rejection of the linear hypothesis. When applied to the dissolved Mn data of February and April, 1975, the linear model is also rejected, suggesting that a non-linear model would provide a better fit. The duplicate samples used in calculating pure error were not of exactly identical salinity although collected from the same position in the estuary only a few minutes apart. This causes a slight overestimation of pure error, an underestimation of the lack of fit error, a smaller calculated F statistic, and a conservative criterion for rejecting the linear hypothesis.

A second approach to testing linearity seeks a non-linear model which significantly improves the fit to the data. If a quadratic salinity term (S^2) is added to the linear model applied to the data for dissolved Mn of October, 1974, a significant improvement in fit is found. This is also shown in Table 7. In this test, an F statistic is calculated as the ratio of the mean square error due to addition of the quadratic term to the mean square residual. This F statistic is again significant at the 95% level, implying that the quadratic model is significantly better than the linear one (i. e. the linear

Table 7. Analysis of variance testing for nonlinearity in dissolved Mn-salinity trends of October, 1974.

Source	DF	Sum of Squares	Mean Square	F Ratio
Total	42	1274		
Linear regression	1	668	668	
Residual	41	606	14.8	
Lack of fit	20	569	28.4	15.1
Pure error	21	37	1.8	
Addition of quadratic (S^2) term	1	236	236	25.5
Residual	40	370	9.2	

model is inadequate). Higher order polynomial models will successively increase the fit to the data, but a point will be reached where addition of higher order terms does not result in significant improvement. Table 8 summarizes results of metal linearity tests.

Table 8. Summary of statistical tests of non-linearity of dissolved trace metal-salinity trends in Newport River estuary. Calculated F statistics for both lack of fit and addition of quadratic term to the linear model are shown with minimum F values for 95% significant difference from linearity shown in parentheses.

		F (lack of fit)	F (addition of quadratic term)
October 1975	Mn	15.6 (2.09)	25.5 (4.08)
	Cu	3.2 (2.09)	11.4 (4.08)
	Zn	1.3 (2.14)	1.2 (4.09)
February 1975	Mn	9.2 (2.39)	43.6 (4.18)
	Fe	8.8 (2.44)	51.3 (4.20)
	Cu	5.0 (2.37)	2.1 (4.18)
	Zn	12.1 (2.37)	63.8 (4.18)
April 1975	Mn	121.5 (3.39)	37.4 (4.49)
	Fe	4.9 (3.44)	7.9 (4.54)
	Cu	0.4 (3.44)	0.2 (4.54)
	Zn	6.9 (3.39)	9.5 (4.49)

Variations in River Input Concentrations as Possible Causes of the Observed Non-Linearities

Variations in the concentrations of dissolved Mn flowing into the estuary are insufficient to explain the magnitude of the observed deviations from linearity. For example, in Figure 7a, the difference between the maximum dissolved Mn concentration and that predicted by the linear mixing model is about $13 \mu\text{g/l}$, whereas the standard deviation of the concentrations entering from the river is but $2.7 \mu\text{g/l}$. Moreover, the increasing trend of inflowing dissolved Mn concentrations from the river during the three weeks prior to estuary sampling would predict that a negative deviation from the linear prediction line should occur. (Dissolved Mn concentrations within the estuary would represent a contribution from river water which mixed in the estuary earlier and hence had a lower dissolved Mn concentration than the river water value used in drawing the linear mixing line). Variations in inflowing river dissolved Mn concentrations are likewise inadequate to explain the magnitude of the February, 1975 dissolved Mn maximum in Figure 7b. Nothing can be said of possible contributions of variations in inflowing river concentrations to the observed dissolved Mn non-linearity of April, 1975, because no such input measurements were made (Figure 7c).

It is possible to treat the river and ocean water concentrations of dissolved Mn (equivalent to C_r and C_o in equation 1) as random variables rather than as constants when defining a theoretical mixing line. The mixing proportions, f_r and f_o , might also be considered random variables if the salinities, S_r and S_o , which define them also vary. However, C_r is the major source of overall variability in defining the theoretical mixing line:

$$(1) \quad C = f_r C_r + f_o C_o = (1 - S/S_o) C_r + (S/S_o) C_o$$

$$(S_r \text{ assumed} = 0)$$

If $V(C)$ and $V(C_r)$ are respectively the variances of the dissolved Mn concentrations at a particular salinity in the estuary and of inflowing river water, and the variances of C_o and S_o are assumed equal to 0, then the uncertainty in the estimate of the mixing line is given by:

$$(9) \quad V(C) = (1 - S/S_o)^2 V(C_r)$$

Standard deviations are defined as the square roots of these variances. Figure 8 shows the linear mixing line defined by the mean concentration of dissolved Mn flowing into the estuary during the prior three week period rather than the point estimate made on the day of the estuarine sampling (using the same data shown in

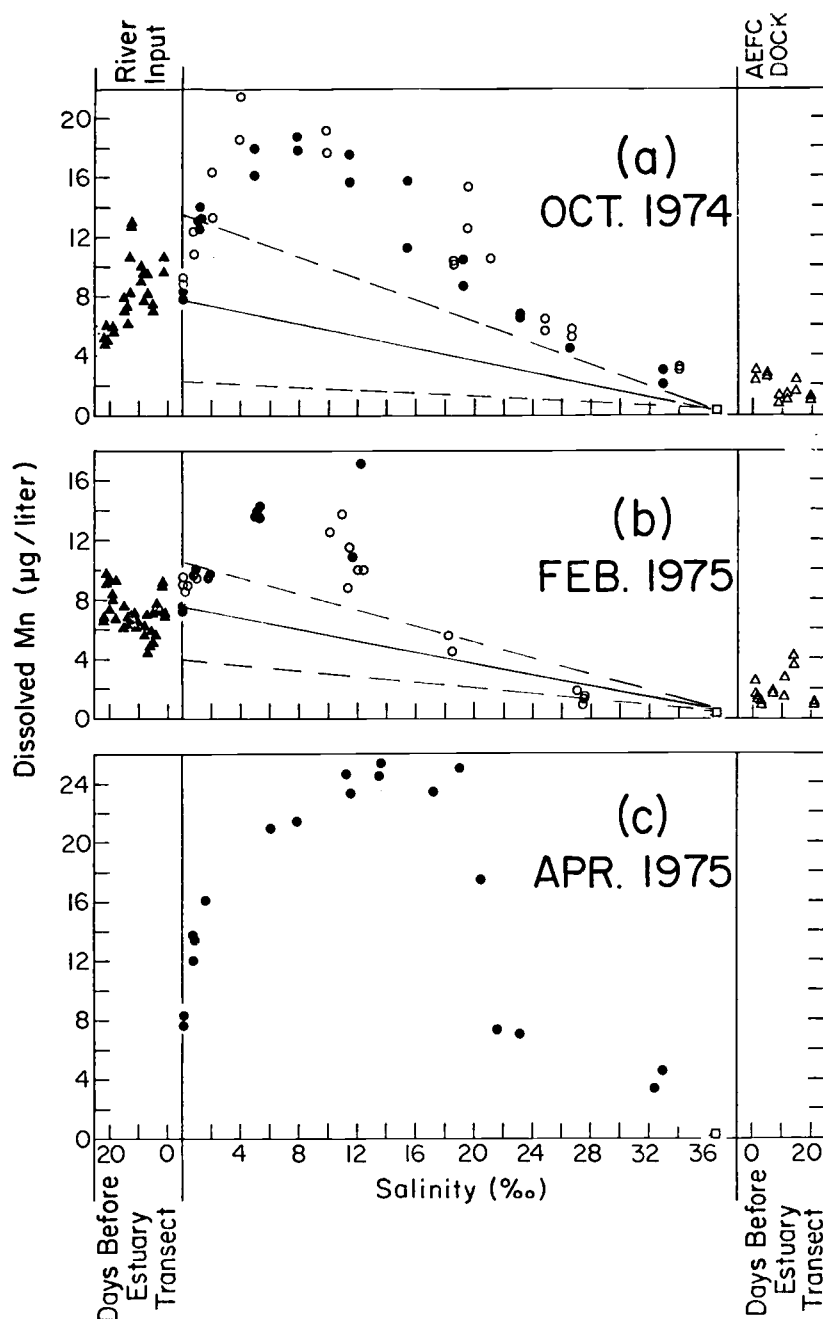


Figure 8. Dissolved Mn relationship with salinity in the Newport River estuary during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (●). Also shown are the dissolved Mn concentrations in Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuary transects. A solid line connects the mean dissolved Mn concentration in the river during these three weeks with the dissolved Mn concentration of primary ocean water (□). The dashed lines represent 95% confidence limits about this conservative mixing line, calculated from the standard deviation of the dissolved Mn concentrations in the river.

Figure 7). Two standard deviation confidence limits are drawn on either side of this line, using the means and standard deviations summarized in Table 6. This shows simply that as the salinity of an estuarine water sample increases and its proportion of river water decreases, the variability in inflowing concentrations of dissolved Mn in river water diminishes in possibly explaining observed deviations from a linear mixing prediction. This approach can be extended, if need be, to include variations in ocean input concentrations of dissolved Mn and of river and ocean salinity (with suitable assumptions about independence). The specific point to make again is that variations in the input concentrations of dissolved Mn to the estuary are insufficient to explain the magnitude of the observed deviations from the hypothetical conservative mixing model.

Several recent studies have used non-linear dissolved Mn versus salinity trends to infer sources and sinks of dissolved Mn within estuaries. Studies by Bryan and Hummerstone (1973) reported dissolved Mn trends with salinity in some English estuaries which suggested that Mn was added to solution. Cutshall et al. (1974) found positive deviations from linear mixing in the upper Columbia River estuary suggesting additions there, but detected evidence from the trends in the lower estuary suggestive of losses there. Evans and Cutshall (1973) detected trends of radioactive ^{54}Mn in the

Columbia River estuary which also indicated an endogenous source, probably ion-exchange desorption from sediments and suspended particulate matter. Trends indicating losses from solution have been reported by Harris et al. (1975). Only in the study of Cutshall et al. (1974) were variations in the inflowing concentration of dissolved Mn determined and evaluated.

Desorption of River-Derived Suspended Particulate Matter as the Source of the Dissolved Mn Maximum

Since the distribution of dissolved Mn in the Newport River estuary is not the result of simple conservative mixing of river water and ocean water, it is necessary to look for the cause of the positive deviation from linearity in some internal sources of dissolved Mn within the estuary. There are no important local inputs of dissolved Mn from industrial wastes or atmospheric fallout. The addition of dissolved Mn must result from the in situ dissolution or desorption of Mn from sediments or suspended particulate matter.

In a steady-state condition, which seems justified approximately by the repeatability of the dissolved Mn-salinity trends, the only original supply of particulate Mn is that carried into the estuary in suspension or as traction load by the river and deposited in or transported through the estuary. Upon entering the saline environment in the estuary, river-derived particulate matter can be

expected to lose some of its bound Mn to solution as a result of ion-exchange with the abundant major cations in seawater.

Such a mechanism seemed likely to explain the observed addition of dissolved Mn shown in Figure 7. But examination of other data shows that this mechanism is inadequate to explain the magnitude of the dissolved Mn additions if the observed additions are long term, quasi-steady-state phenomena. Figure 9 shows the concentrations of dissolved Mn in excess of that predicted by conservative linear mixing and after correction for dilution by seawater. They are concentrations of excess dissolved Mn per volume of river water, $\Delta C/f_r$. From Figure 10 and Table 6, it can be seen that the concentration of suspended particulate Mn flowing into the estuary from the river rarely exceeds $4 \mu\text{g/l}$. If all of this inflowing Mn on suspended particulate matter were to be added to solution, it would still be inadequate to supply the $14 \mu\text{g/l}$ to $38 \mu\text{g/l}$ (on a seawater free basis) of excess dissolved Mn at the maxima.

Another observation further argues against ion-exchange desorption from suspended particulate matter as the dissolved Mn source. If this were the operative process, one would expect the desorption to be very dependent on salinity. Because ion-exchange processes are generally quite rapid, and because the proportional change in seawater cation concentrations is greatest at low salinities, one would expect to find Mn desorbed from river-derived suspended

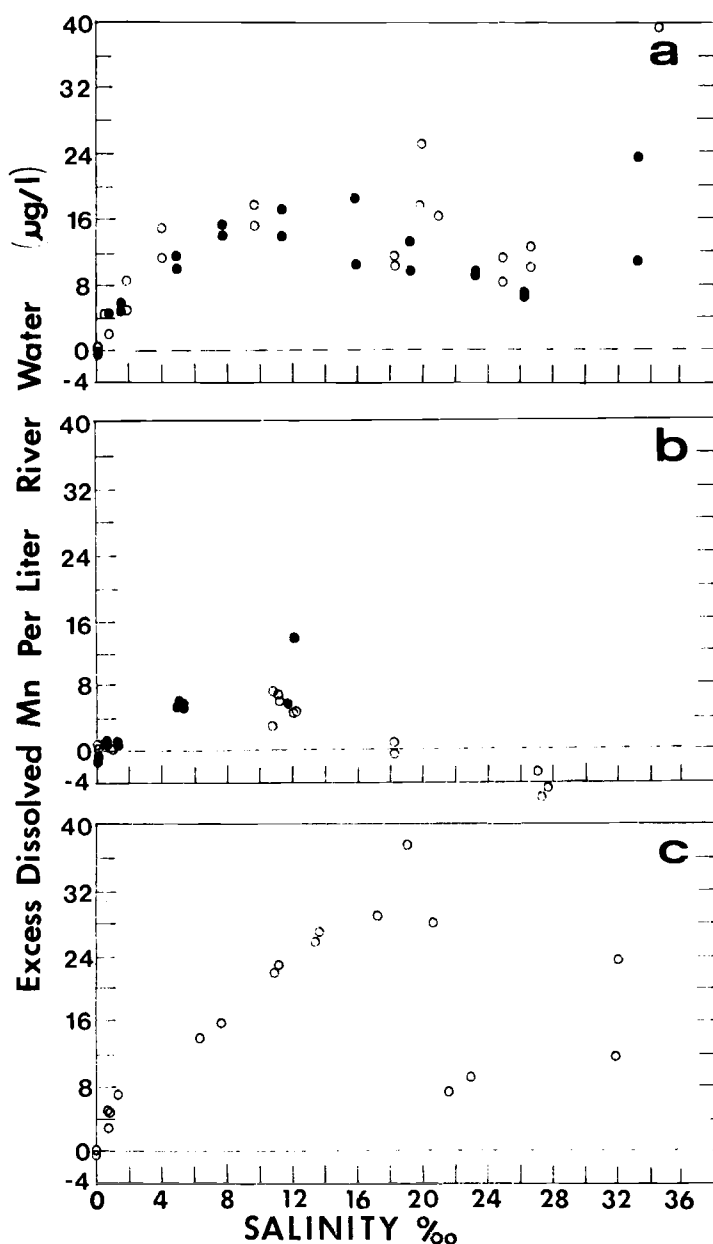


Figure 9. Excess dissolved Mn concentrations in relation to salinity during five sampling transects in the Newport River estuary: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○) 1975; and (c) April 14, 1975 (○). Dissolved Mn concentrations are those in excess of that predicted by conservative mixing and are calculated per volume of river water of 0 ‰ salinity.

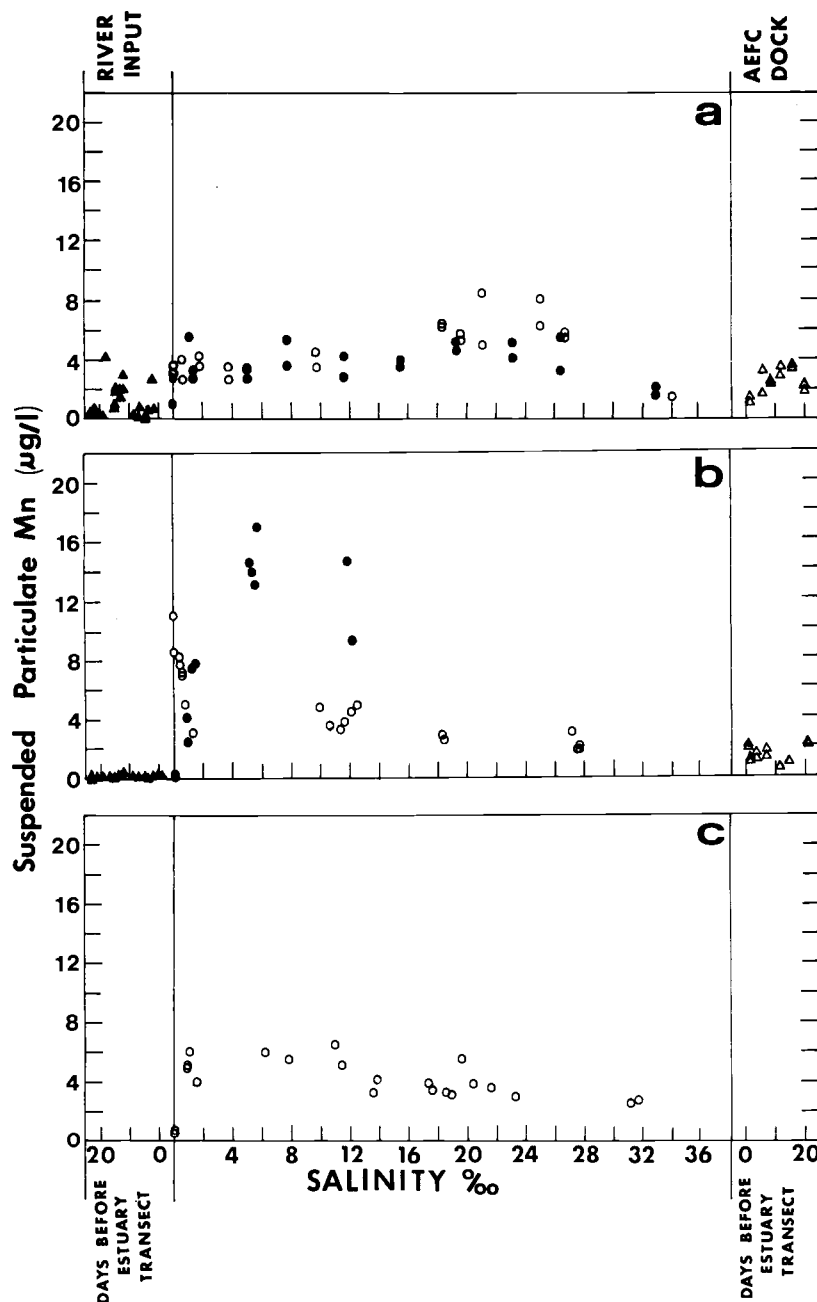


Figure 10. Concentrations of suspended particulate Mn per liter of water in relation to salinity during five sampling transects in the Newport River estuary: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the suspended particulate Mn concentrations in inflowing Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuarine transects.

particulate matter most noticeably over a narrow range of low salinities, as observed by Lentsch et al. (1973) in the Hudson River estuary. However, Figure 7 shows that the dissolved Mn maxima occur over a broad range of salinities from 4⁰/oo to as high as 19⁰/oo salinity. This does not mean that ion-exchange desorption of Mn from river-derived suspended particulate matter is not occurring, only that it is not the major cause of the observed additions of Mn to solution.

Bottom Sediments as a Source of Added Dissolved Mn

If dissolved Mn is plotted versus location in the Newport River estuary rather than against salinity, a suggestive pattern emerges (Figure 11). For both February and April, 1975 transects, the dissolved Mn maxima are located in the region between kilometers 0 and -2.2. Kilometer 0 is located at the point where the river widens into the estuary proper. Kilometer -2.2 is located at Cross Rock (Figure 6). (AEFC dock is at kilometer -14.2). Fine sediments are deposited between these two sites. The dissolved Mn maximum of October, 1974 lies upstream from this region. October, 1974 was a period of extremely little rainfall and very low river flow, however, with a resulting upstream transgression of saline estuarine waters. If it is true that the sediments in the

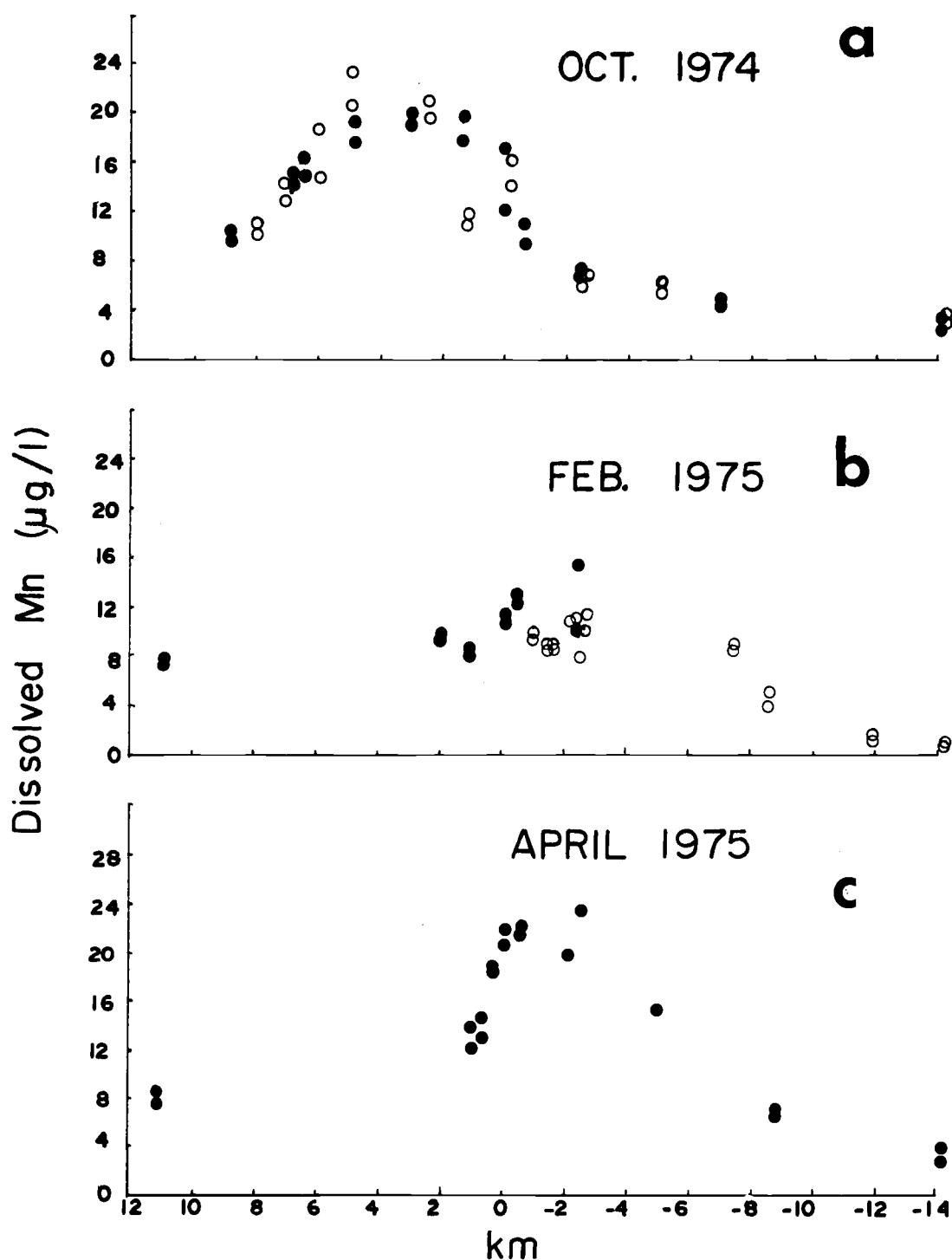


Figure 11. Dissolved Mn concentrations plotted versus longitudinal location in the Newport River estuary during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (●). The river mouth is located at km 0, Cross Rock at km -2.2, and the AEFC dock at km -14.2.

region just upstream of Cross Rock are a major source of the added dissolved Mn, as will be suggested, then the upstream intrusion of estuarine waters would carry the dissolved Mn maximum upstream of its fixed benthic source on the high tide when the October, 1974 samples were taken.

Between kilometers 0 and -2.2, the sediments accumulate rapidly as fine flocculant material rich in organic matter. Carbon content of these sediments exceeds 4% (Price et al., 1974). Under these conditions, the sediments here become reducing several centimeters below the surface. Where reducing conditions develop, sediment bound Mn in valence state (IV), as MnO_2 , would be reduced to valence state (II), where it is readily soluble as Mn^{2+} (Stumm and Morgan, 1970; Matisoff et al., 1975; Holdren et al., 1975). Interstitial pore waters under reducing conditions should have dissolved Mn concentrations much higher than those in the overlying water. Sanders (1975) recently reported dissolved Mn concentrations of about 300 $\mu\text{g}/\text{l}$ in sediment pore waters of Calico Creek, a brackish water sidearm of the Newport River estuary. Dissolved Mn concentrations in the water column are much lower than this throughout the estuary (Figure 7). The concentration gradient between interstitial water and overlying waters implies a net flux of dissolved Mn from the sediments to the overlying water, a process reported in the previously cited studies of Presley et al.

(1972), Bryan and Hummerstone (1973), and Halcrow et al. (1973).

A crude but simple test was made to determine if the sediments in the region just upstream from Cross Rock could supply dissolved Mn and other trace metals to the overlying water. Sediment cores with about 30 cm of overlying water were collected on April 17, 1975 near Cross Rock. One group of three cores was inverted to resuspend the top 5 cm of sediment, then righted, and the sediment allowed to settle for one hour. A second group of three cores was allowed to remain upright without inversion for the one hour period; only minor resuspension of surface sediments appeared to take place. Duplicate coring tubes containing only the overlying water were collected as controls and allowed to stand for one hour. Duplicate samples of overlying water were collected and filtered immediately as a control on possible adsorption-desorption interactions with the polyethylene coring tube walls. The overlying water was filtered from each of the coring tubes after the one hour period, and the filtrates and suspended particulate matter collected on the filters analyzed as described earlier. The results are shown in Table 9. In the coring tubes containing sediment, dissolved Mn concentrations are higher in the overlying water compared to the controls, with the increase in dissolved Mn concentrations greater for the samples which had been disturbed most by being inverted. For the cores which were inverted, dissolved Mn

Table 9. Dissolved and suspended trace metal concentrations in water overlying sediment cores from Cross Rock, April 17, 1975. Controls contained no sediment in coring tubes. Inverted cores had about 5 cm of sediment resuspended into 30 cm of overlying water. Uninverted cores remained upright without intentional resuspension. Contact time was one hour. Samples of overlying water provided an additional control.

Sample	Susp. Part. sample wt. (mg)	Sample volume (ml)	Dissolved				Suspended Particulate			
			Mn µg/l	Fe µg/l	Cu µg/l	Zn µg/l	Mn µg/g	Fe mg/g	Cu µg/g	Zn µg/g
Overlying Water	1.04	91	18.8	70	2.3	.5	240	43	23	160
	1.54	102	18.8	42	1.6	.5	240	38	17	225
Controls	.56	80	19.0	50	2.2	1.3	220	43	--	85
	.54	82	17.9	54	2.2	1.1	230	48	50?	115
Uninverted cores	6.44	83	28.8	36	2.4	.6	190	28	25	75
	1.37	70	21.1	45	2.3	.8	240	43	29	130
	6.86	107	28.8	45	1.6	.4	210	25	22	75
Inverted cores	2.34	76	27.4	42	2.2	.7	200	42	35	200
	5.30	90	46.9	35	1.7	.5	210	32	26	80
	1.38	111	36.7	38	1.1	.4	240	36	46	95

increased by $18 \mu\text{g/l}$, from $19 \mu\text{g/l}$ to $37 \mu\text{g/l}$ (based on the mean concentrations). Uninverted cores containing sediment showed a mean increase in dissolved Mn of $7 \mu\text{g/l}$ over the controls. It is not clear from this experiment what the mechanism is which caused the transfer of Mn from the sediment core to solution in the overlying water. Further experimentation would be required to determine this. Nevertheless, it appears that the sediments in the Cross Rock region can supply dissolved Mn to the overlying water.

In passing, it should be noted that there was no significant increase in the dissolved concentrations of Fe, Cu, and Zn in the core experiments, suggesting, that at this time, sediments and their interstitial water in this region did not act as a net source of these metals in solution to the overlying waters, at least under the conditions of this experiment. Interstitial water may have Fe, Cu, and Zn concentrations in excess of that in the overlying water as observed elsewhere (Elderfield and Hepworth, 1975). But these metals may not be readily transferred to the overlying water because processes of precipitation or adsorption rapidly remove most of them from solution. Alternatively, the difference in interstitial and overlying water concentrations of these metals may be too small to be observed within the errors of analysis.

Flux of Dissolved Mn from Cross Rock Sediments

The flux of dissolved Mn added in the estuary can be estimated from the accumulated dissolved Mn in excess of that predicted by linear mixing and the flushing time of the estuary. Figure 12 shows the product of excess dissolved Mn and estuarine cross sectional area at each sampling location plotted against the longitudinal location of the samples in the estuary. The area under the curves represents accumulated excess dissolved Mn.

Approximate flushing times have been assigned to each of the three sampling periods: nine days for October, 1974, five days for February, 1975, and seven days for April, 1975. The chosen times represent an approximate maximum, minimum, and intermediate time for the estuary from earlier work by Jennings et al. (1970) who reported a range of flushing times ranging from 4.5 to 9.6 days. These choices seem justified because October, 1974 was a period of very low river flow expected to have near the maximum flushing time; February, 1975 was a period of very high river flow; and April 1975 was a period of intermediate river flow. The rainfall during the three weeks prior to each of these estuary sampling transects was 4.52 cm, 15.91 cm, and 8.15 cm respectively.

The flux of added dissolved Mn was calculated as the quotient

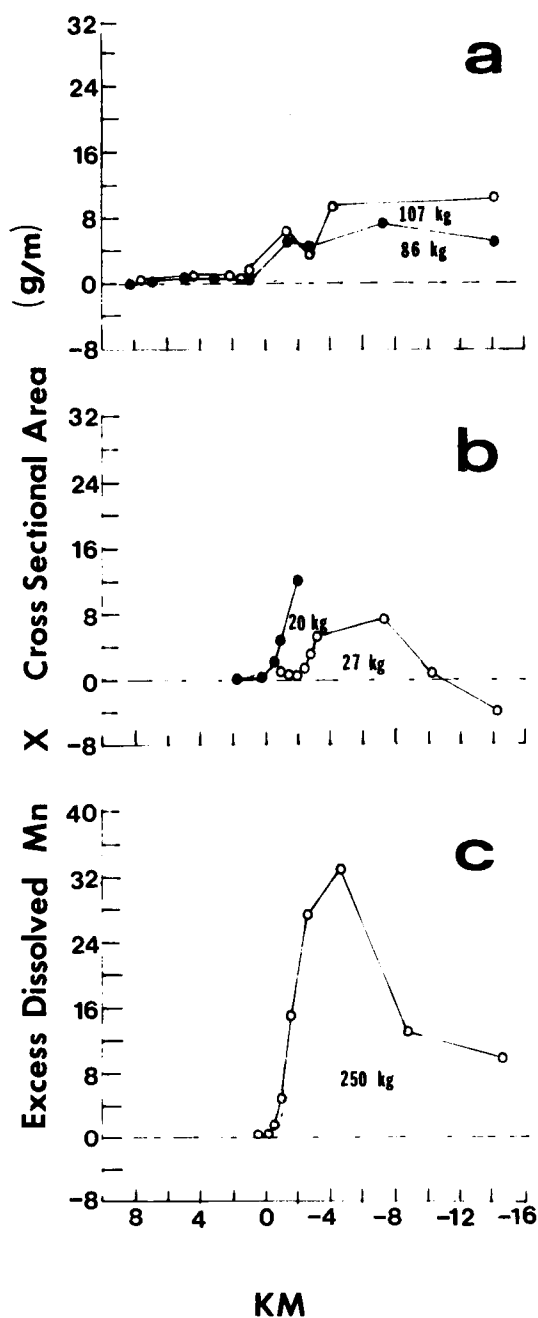


Figure 12. Excess dissolved Mn accumulated in the Newport River estuary during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). The vertical axis shows the amount of dissolved Mn above that predicted by conservative mixing in a one meter wide transverse slice across the estuary's main axis.

of accumulated excess dissolved Mn and flushing time. Because excess dissolved Mn nearer the estuary mouth will be flushed in less than the total flushing time of the estuary, these estimates are low, perhaps by a factor of two. The calculation assumes a steady-state; the rate of addition of excess dissolved Mn is just balanced by its rate of export from the estuary. Because there is evidence, presented later, that not all of the added dissolved Mn is exported from the estuary, this flux estimate is further underestimated. Data are shown in Table 10. The calculated fluxes range from 4 kg/day (1400 kg/year) in February, 1975 to 36 kg/day (13000 kg/year) in April, 1975.

Table 10. Fluxes of dissolved Mn added in the Newport River estuary calculated from the excess dissolved Mn and estimated flushing time.

Date	Excess Dissolved Mn(Kg)	Flushing Time(Days)	Flux
Oct. 30 1974	107	9	12 kg/day 4300 kg/yr
Oct. 31 1974	86	9	10 kg/day 3400 kg/yr
Feb. 4 1975	27	5	5 kg/day 2000 kg/yr
Feb. 5 1975	> 20	5	>4 kg/day >1500 kg/yr
Apr. 14 1975	250	7	36 kg/day 13000 kg/yr

If all of this flux is contributed by dissolved Mn emanating from bottom sediments in the two km² area upstream from Cross Rock, the flux from the sediments here would range from 70 to 630 $\mu\text{g}/\text{cm}^2$ -year. If sediments from a wider area supply the Mn, the flux would be proportionally reduced.

For comparison, Elderfield and Hepworth (1975) estimated diffusive fluxes of trace metals from estuarine bottom sediments with elevated pore water concentrations, using a Fickian diffusion constant of $2 \times 10^{-6} \text{ cm}^2/\text{sec}$. Dissolved Mn was measured at 2 $\mu\text{g}/\text{l}$ in the overlying water and 4700 $\mu\text{g}/\text{l}$ in subsurface sediment pore waters, with a linear gradient of five cm length assumed to lie in between. A flux of 59.2 $\mu\text{g}/\text{cm}^2$ -year was calculated.

The higher calculated flux in the Newport River estuary could result from either a sharper concentration gradient between pore waters and overlying water (implying a higher pore water concentration than Elderfield and Hepworth, 1975 found) or from higher diffusion or mixing rates. Turbation of sediments by biota or waves and currents could supply dissolved Mn faster than simple diffusion. Alternatively, pore waters could be drained from bottom sediments in exposed tidal mud flats during falling tides, as proposed by Bella (1975).

Replenishment of Exported Excess Dissolved Mn

The excess dissolved Mn thought to originate largely in the Cross Rock region could be supplied from the bottom sediments in steady-state if the Mn in the bottom sediments can be replenished at the same rate it is lost to solution. It was shown earlier that the observed supply of Mn on suspended particulate matter from the Newport River was inadequate to supply the observed excess dissolved Mn at steady-state. Bed load movements of sediments from the river or the ocean are a possible source of such sedimentary Mn, however. These inputs have not been measured. Alternatively, pulse inputs of suspended particulate Mn could occur at times not sampled in this study. Williams and Murdoch (1972) have noted that the Newport River carries large amounts of sediments during freshets. Bricker and Troup (1975) stated that tropical storm Agnes flushed into Chesapeake Bay and deposited in one week, the equivalent of 100 years' "normal" load of river-derived sediment.

Deposition of sediments in such pulse inputs could supply dissolved Mn to the overlying waters on a nearly continuous basis by slowly bleeding out the dissolved Mn in interstitial waters as reduction made it available. It is nearly impossible to assess directly the input of sedimentary Mn by such pulse inputs or as bed load inputs. An indirect estimate can be made, however, from the

rate of deposition of sediments in the Cross Rock region. Wolfe et al. (1973) estimated the sedimentation rate in the Newport River estuary at from 1 mm/year to 4 mm/year, using rates estimated for Chesapeake Bay by Biggs (1970). The higher rate of 4 mm/year was thought to apply to the Cross Rock region. Other estimates support this figure as an upper limit. Meade (1972a) estimated sedimentation rates for the east coast of the U.S. at 2 mm/year south of Cape Lookout, North Carolina and 2.6 mm/year north of there, basing these estimates on the rate of stream supply of sediments. This is close to the rate of sealevel rise of 2.5 mm/year to 3.5 mm/year along this coast during the last 30 years, suggesting a balance. Williams and Murdoch (1972) measured sedimentation rates in and around the Newport River estuary using sedimentation traps. Rates were highly variable, ranging from 0.01 to 30.40 kg dry weight/m²-year, with a median near 1 kg/m²-year. Assuming a water free density of 0.5 g/cm³, this median rate is equivalent to 2 mm/year. The rate in the region near Cross Rock was probably greater than this estimate. However, comparison of 1870 and 1968 hydrographic charts for the Cross Rock region fails to detect a change in depth profiles of more than one foot (30.48 cm). This places an upper limit on the rate of sedimentation in this area at about 3 mm/year. In light of these studies, the estimate of 4 mm/year of Wolfe et al. (1973) seems prudent. This amounts to about

0.2 g/cm^2 -year, assuming a water free density of 0.5 g/cm^3 again. Wolfe et al. (1973) measured a density of 0.493 g/cm^3 in this region.

Sediment samples subjected to total dissolution with concentrated HNO_3 and HF had concentrations of Mn in this area averaging $150 \text{ } \mu\text{g/g}$. Extraction of similar sediments with 0.1 N HCl yielded an average of $30 \text{ } \mu\text{g/g}$ in earlier studies of Wolfe et al. (1973) and Cross et al. (1970). The latter procedure is expected to remove only that fraction of the sediment bound Mn that was absorbed, precipitated (e.g. as MnO_2), or coprecipitated with insoluble compounds (Gibbs, 1973; Duinker et al., 1974). This is the fraction which would probably be solubilized under reducing conditions. If all $150 \text{ } \mu\text{g/g}$ of the Mn in the sediments deposited at a rate of 0.2 g/cm^2 -year were solubilized, then $30 \text{ } \mu\text{g/cm}^2$ -year of dissolved Mn could be supplied to the overlying water. This could raise the concentration of the average one meter water column by $300 \text{ } \mu\text{g/l}$ of dissolved Mn. Because the flushing time of the estuary averages about six days or 60 times per year, the dissolved Mn concentration of the water column could be raised by only $5 \text{ } \mu\text{g/l}$ at any particular time. If only $30 \text{ } \mu\text{g/g}$ of Mn in the sediments were available for solubilization, the concentration of dissolved Mn in the water column could be raised by only $1 \text{ } \mu\text{g/l}$. In either case, this is still far less than the $9 \text{ } \mu\text{g/l}$ to $18 \text{ } \mu\text{g/l}$ of excess dissolved Mn observed in this region.

Recycling Hypothesis

An alternative model to explain the maintenance of a quasi-steady-state dissolved Mn maximum in the region of Cross Rock, postulates the upstream recycling of Mn which had been removed from solution in the lower estuary. Under this model, dissolved Mn^{2+} is carried seaward from its source near Cross Rock by the net downstream flow of water in the estuary. In the well oxygenated environment of estuary surface waters, Mn^{2+} in solution is slowly oxidized and precipitated as insoluble MnO_2 (uptake by phytoplankton or adsorption on existing particulate substrates provides alternative means of removing Mn^{2+} from solution). The new suspended particulate Mn is then recycled upstream by a counter circulation to be deposited in the Cross Rock region and to reenter the cycle of reduction and solubilization within the sediments.

This model is analogous to that used by Spencer and Brewer (1971) to model the Mn distribution in the Black Sea. There, dissolved Mn is concentrated below the zero oxygen boundary separating oxic surface water from anoxic deep water. Reducing conditions and negative platinum electrode potential develop and hydrogen sulfide can be measured in the deep water. Soluble Mn^{2+} is carried upward through the zero oxygen boundary by diffusion and slow advection. Upon reaching oxygenated waters, soluble Mn^{2+} is oxidized to

insoluble MnO_2 which precipitates and is carried downward with sinking particles. Recrossing the oxygen zero boundary, this particulate Mn is redissolved to complete the cycle. In this system, a strong dissolved Mn maximum is observed just below the zero oxygen boundary where the sinking particulate Mn most rapidly dissolves. A corresponding strong particulate Mn maximum is observed just above the zero oxygen boundary where the rising dissolved Mn is most rapidly precipitated. Fluorié (1972) has proposed a similar vertical model to explain like distributions of dissolved and particulate Mn in several coastal basins and fjords with anoxic deeper waters. The model proposed for the Newport River estuary turns these vertical models horizontally and locates the zone of Mn reduction and solubilization within the interstitial waters of anoxic sediments rather than in the water column.

This model requires that several conditions must hold. Most significantly, a mechanism to recycle particulate Mn upstream against the net seaward flow of water must be demonstrated. Second, an increase in the particulate Mn in the lower estuary must be shown. Third, Mn must be shown to be lost from solution in the lower estuary.

Upstream Movement of Estuarine Particulate Matter

In stratified estuaries, the net landward flow of more saline

bottom waters makes possible the return flow of particulate suspended matter which has sunk from a seaward flowing surface layer. This contributes in part to the development of the turbidity maximum found in the low salinity region of the upper parts of many estuaries (Meade, 1972b) and in the relatively high deposition rates there. Even in vertically homogeneous estuaries such as the Thames, there can be a net upstream movement of sediments counter to the net downstream flow of water. Postma (1967) has explained this phenomenon in terms of the asymmetric distribution of tidal velocities on ebb and flow. Such a process would be expected in the vertically homogeneous Newport River estuary, and is supported by the observed high deposition rates of the sediments in the Cross Rock region. Meade (1972a) has further observed that along the eastern seaboard of the United States, very little, perhaps only 10%, of the suspended particulate matter carried by rivers to the Atlantic Ocean is actually transported over the continental shelf to be deposited in the deep ocean. The remainder is carried back landward to be deposited in coastal wetlands. It therefore appears that the upstream recycling and deposition of suspended particulate matter is the normal occurrence in the Newport River estuary.

Particulate Fixation of Dissolved Mn

Precipitation of insoluble Mn in the lower estuary should be

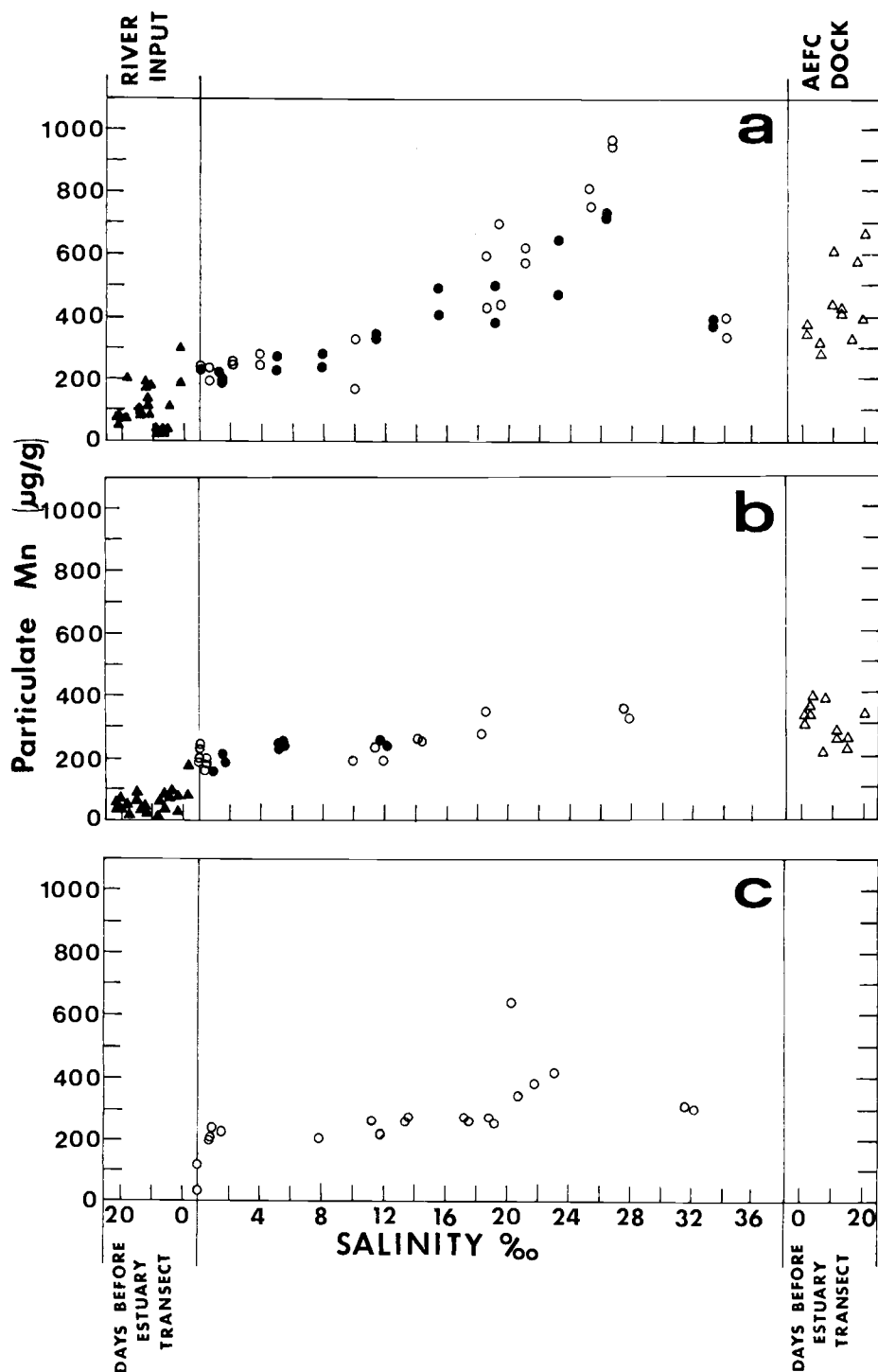


Figure 13. Concentrations of Mn on suspended particulate matter in relation to salinity during five sampling transects in the Newport River estuary: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the particulate Mn concentrations in inflowing Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuarine transects.

reflected in the increasing concentrations of Mn on suspended particulate matter as one samples at progressively higher salinities. This can be observed in Figure 13, where particulate Mn concentrations per gram of suspended particulate matter are plotted against salinity. Concentrations of Mn on suspended particulate matter increase with progressively higher salinities, dropping somewhat at the extreme seaward end. This is consistent with upstream cycling of Mn enriched suspended particulate matter.

Resuspension of bottom sediments could cause the increased concentration of Mn on suspended particulate matter in the lower estuary if the sediments have a higher Mn concentration than the inflowing suspended particulate matter in the river. Surface sediments from Cross Rock and from the Newport River were analyzed for Mn to test this hypothesis. Using the ultrasonic disaggregation technique of Genrich (1972) and the sieving and settling methods of Jackson (1956), sediments collected April 10, 1975 were separated into four size classes ($< 2 \mu\text{m}$, $2-10 \mu\text{m}$, $10-43 \mu\text{m}$, and $>43 \mu\text{m}$). Metal analyses were by the same HNO_3 -HF digestion and atomic absorption analysis used for suspended particulate matter. Results are shown in Table 11. None of the four size classes exceeds $200 \mu\text{g/g}$ in Mn concentration. The increasing metal concentration trend with decreasing particle size that is evident for Fe, Cu, and Zn, does not appear for Mn. Concentrations are more nearly

Table 11. Mn, Fe, Cu, and Zn concentrations in four size fractions of sediments from the Newport River and its estuary (Cross Rock) collected April 20, 1975. All data are mean \pm one standard deviation of triplicate samples except (*) duplicate.

	Size Fraction	Mn $\mu\text{g/g}$	Fe mg/g	Cu $\mu\text{g/g}$	Zn $\mu\text{g/g}$
Cross Rock	<2 μm	123 \pm 36	40.8 \pm 3.6	16.7 \pm 1.4	84 \pm 16
	2-10 μm	193 \pm 34	28.2 \pm 8.4	10.2 \pm 3.9	51 \pm 7
	10-43 μm	136 \pm 16	7.9 \pm 1.2	3.3 \pm 2.2	22 \pm 0*
	>43 μm	46 \pm 13	1.6 \pm 0.4	1.5 \pm 0.6	30 \pm 25*
Newport River	<2 μm	79 \pm 9	29.6 \pm 14.9	16.5 \pm 2.3	91 \pm 12
	2-10 μm	108 \pm 25	10.1 \pm 3.0	8.3 \pm 1.3	53 \pm 15
	10-43 μm	102 \pm 34	6.0 \pm 2.3	10.0 \pm 1.3	20 \pm 3
	>43 μm	60 \pm 30	1.8 \pm 0.8	0.9 \pm 0.2	9 \pm 1

constant among size classes. In particular, the smallest class, which is expected to be most easily resuspended, lacks Mn concentrations large enough to supply those observed in suspended particulate matter in the lower estuary which may exceed 900 $\mu\text{g/g}$.

Resuspension of sediments collected in coring tubes showed suspended particulate Mn concentrations clustering around 220 $\mu\text{g/g}$ (Table 9), the same as in the controls without resuspension. This also shows that resuspension would not increase the concentration of Mn on suspended particulate matter in the lower estuary.

A second possibility is that suspended particulate matter, high in Mn content, is entering the estuary from the ocean. Mixing of low Mn particulate matter from the river with high Mn particulate matter from the ocean could cause the increasing seaward trend of Mn on suspended particulate matter. However, Mn concentrations on suspended particulate matter are lower in samples at the mouth of the estuary (AEFC dock) and offshore than within the estuary (Figure 13, Tables 12 and 21). This possibility is rejected. The only alternative hypothesis is that Mn has been added from solution to the suspended particulate matter while in the estuary.

If 220 $\mu\text{g/g}$ is accepted as the average Mn concentration of resuspended particulate matter, it is possible to calculate the concentration of suspended particulate Mn due to possible additions from solution. The equation is: Excess particulate Mn ($\mu\text{g/l}$) =

Suspended matter concentration (g/l) times (particulate Mn - 220 ($\mu\text{g/g}$)). Results of this calculation are plotted in Figure 14. The excess particulate Mn at higher salinities is obvious, roughly coinciding with the region of observed Mn loss from solution discussed subsequently (Figures 7 and 9). If this suspended particulate Mn and dissolved Mn moved together in the water column (e. g. no settling or resuspension of particulate Mn), then this excess added particulate Mn would just balance the loss of dissolved Mn. However, an exact balance is not to be expected just because settling and resuspension will occur. Moreover, the recycling hypothesis requires differential movement of soluble and particulate phases to move particulate Mn back upstream. It is because of these differential movements that suspended particulate metal (as $\mu\text{g/l}$) versus salinity plots are not useful in inferring soluble-particulate exchanges from deviations from linear mixing of river water and seawater. Dissolved salts will move covariantly with the water, but particles will not.

Removal of Mn from Solution in the Lower Estuary

Complementary to the increase in particulate Mn concentrations at higher salinities in the estuary, dissolved Mn should decrease as it is lost from solution. A straight line connecting the dissolved Mn maximum at intermediate salinity with the ocean end member

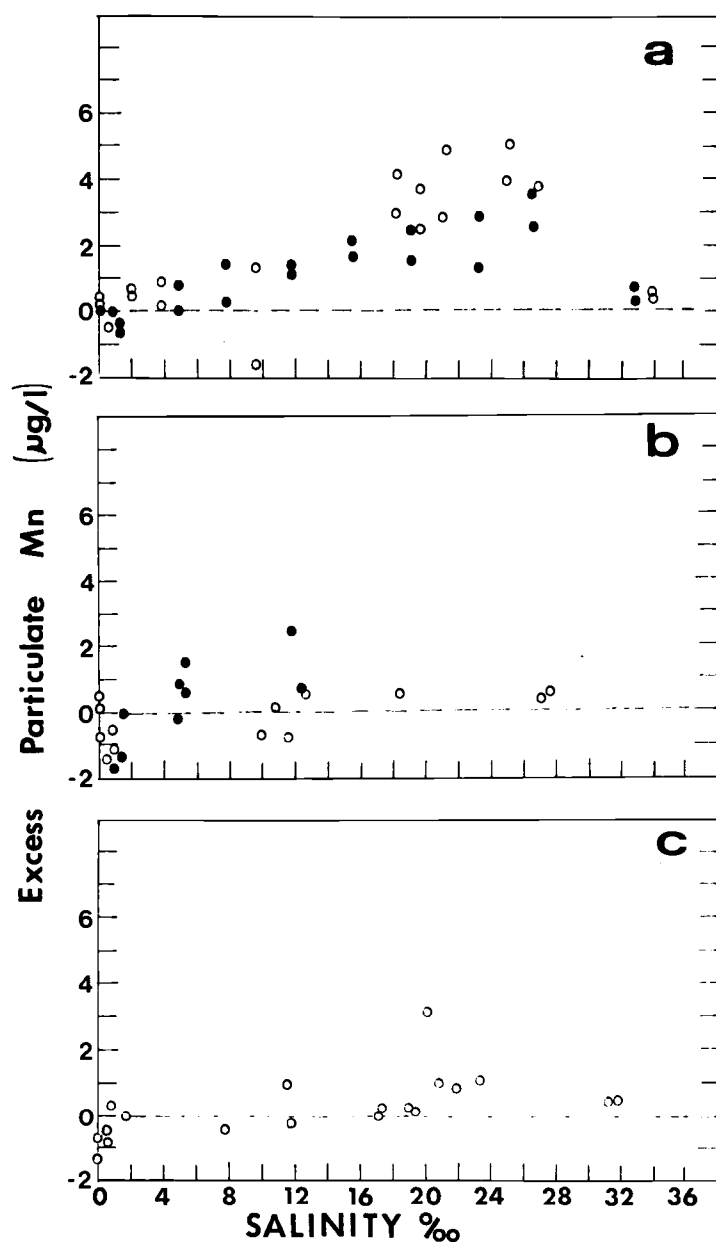


Figure 14. Excess particulate Mn in the Newport River estuary in relation to salinity during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Concentrations are those calculated to be in excess of that that can be supplied by resuspension of bottom sediments of Mn content 220 µg/g.

would be the result if no dissolved Mn is lost in the higher salinity region of the estuary. Loss of dissolved Mn implies that the observed dissolved Mn concentrations should lie below this conservative prediction line, with concavity upward. Visual inspection of Figure 7 shows that indeed the predicted upward curvature in the dissolved Mn:salinity plots exists at higher salinities, and a linear fit to the data in this region is not adequate. As in testing linearity before, curvature and lack of fit exist in the data, implying a loss of Mn from solution. This may be more obvious in Figure 9, where the dissolved Mn in excess of that predicted by linear mixing of river and ocean water per volume of river water is plotted against salinity. Here the maximum associated with a source at the Cross Rock region is evident. But a decline from that maximum is observed at higher salinities, however, thus showing that dissolved Mn is lost from solution. Thus the three criteria needed to support the recycling model have been demonstrated.

Oxidation of Mn^{2+} as the Removal Mechanism

The oxidation of Mn^{2+} to MnO_2 is a slow process, dependent on pH. This might argue against it as the removal mechanism. Morgan (1967) extrapolated from laboratory experiments to predict that 1000 years would be required to oxidize 90% of the initial Mn^{2+} at the pH of seawater. Data of Spencer and Brewer (1971) suggest

that the upper limit on the half-time of Mn^{2+} oxidation in the surface waters of the Black Sea is about 50 years. This is still too slow to remove appreciable Mn^{2+} during the six day residence time of water in the Newport River estuary. However, it must be noted that the estimate of Spencer and Brewer (1971) is an upper limit and Morgan's (1967) study excluded many naturally occurring substances from the experimental system which would accelerate the oxidation rate. The oxidation of Mn^{2+} is autocatalytic; that is, MnO_2 accelerates the oxidation of Mn^{2+} . Hydrus MnO_2 coatings on suspended particulate matter in estuaries would provide a site for increased oxidation rates. Hydrus Fe oxides and other surface active agents also promote Mn^{2+} oxidation. Lee (1974) points out as well that a microzone of higher pH on the surface of calcium carbonate particles favors Mn^{2+} oxidation. Calcium carbonate forms an increasing fraction of Newport River estuary sediments (1-10%) toward the mouth. Lee (1974) also notes the potential of microorganisms such as phytoplankton to promote Mn^{2+} oxidation. All of these considerations point to the expectation that the oxidation rate of Mn^{2+} to MnO_2 in estuaries is much faster than predicted by laboratory experiments.

In support of this, Fluorié (1972) and Delfino and Lee (1968) both found that Mn^{2+} could be rapidly oxidized in anoxic fjords, coastal basins, and lakes when oxygenated waters periodically intruded. In samples collected about a month apart, during which time the

regime switched from anoxic to oxic, dissolved Mn disappeared almost entirely from the water column, and particulate Mn with Mn oxides appeared in large quantities. This suggests an environmental Mn^{2+} oxidation half-time of less than 30 days.

Oxidation of Mn^{2+} on particulate surfaces seems to be preceded by adsorption of Mn^{2+} which may remain metastable for some time. In future work in the Newport River estuary, it would be interesting to sample specifically for particulate MnO_2 using a reagent such as leucomalachite green that distinguishes this form (Ormerod, 1966). This might help distinguish adsorption from oxidation as the mechanism of removal of dissolved Mn in the Newport River estuary. Sampling for dissolved and particulate Mn (and MnO_2) could be carried out seaward of the estuary mouth to determine if removal of Mn from solution continued at sea.

Alternatives to the Steady-State

Figure 9 shows for both October 1974 and April 1975, that the excess dissolved Mn per volume of river water does not return to zero at the most seaward station. This implies that excess dissolved Mn is being exported to the sea. If it is not precipitated further seaward and recycled into the estuary it would be difficult to supply the quasi-steady-state input of dissolved Mn in the Cross Rock region. Thus there appear to be problems, as yet unresolved,

in achieving a completely satisfactory mass balance of Mn in the Newport River estuary. Perhaps this is the result of insisting on a steady-state model when the estuary only appears to operate in quasi-steady-state, showing approximate steady-state behavior during the time period of several mixing periods but shifting gradually to other near steady-states over longer time periods of weeks or months or seasons.

The production of excess dissolved Mn exported to the ocean during October, 1974 and April 1975 might be the result of periodic or sporadic events which add dissolved Mn to the estuary over short time periods rather than continuously during the year. The supplies of river-derived particulate Mn, previously rejected as inadequate, might then be able to supply a smaller discontinuous supply of excess dissolved Mn for export to the ocean.

A better case for this balanced, discontinuous supply could be made if the source events could be identified and associated with the periods of excess dissolved Mn export. Two possibilities suggest themselves.

(1) Periodic intrusion of saline estuary water into upstream freshwater regions could desorb Mn from river-derived bottom sediments deposited there since the last such intrusion. The October, 1974 and April, 1975 periods were both characterized by moderate to low river flows when saline waters did intrude upstream

farther than normal. However, for the April, 1974 period at least, the source of dissolved Mn at high tide was located near Cross Rock rather than in the river proper (above Km 0) (Figure 11). This would argue against this possibility.

(2) Alternatively, flooding of extensive mud flats peripheral to the Cross Rock region during spring tides or other high water conditions could flush accumulated dissolved Mn from the pore waters on a discontinuous basis. The high flux of dissolved Mn calculated earlier argued that an area more extensive than the two Km² under continuous submergence at Cross Rock might be involved in supplying the added dissolved Mn. Both the October 30 and 31, 1974 and April 14 sampling transects occurred during spring tides when high high tides were expected to be several feet above normal. The February 4 and 5, 1975 transects occurred midway between spring and neap tides with lower expected water levels. The latter transects detected much smaller quantities of added dissolved Mn and no export of excess dissolved Mn from the estuary. Although supporting the hypothesis of periodic flushing of Mn from normally exposed tidal flats, the tidal association neglects other factors which influence water level, such as winds and river flow. In particular, the water level in the estuary was raised above normal during the time of the February 4 and 5, 1975 transects by much elevated river flow which inundated peripheral tidal mud flats in the Cross Rock region. This

non-steady-state hypothesis would be better tested if many more sampling transects were made to determine excess dissolved Mn in association with actual field measurements of water level and area of tidal mud flats inundated.

Iron

Dissolved Iron

Iron was not analyzed in the samples of October, 1974. Subsequent improvements in the analytical technique made possible Fe analyses in the transects of February and April, 1975. Dissolved Fe concentrations on these estuarine transects are shown in Figure 15. The pattern of dissolved Fe distribution is distinctly different from that of Mn. Rather than a maximum concentration at intermediate salinity as for Mn, dissolved Fe concentrations lie below the conservative linear mixing line. This implies that Fe is lost from solution in the estuary, with the loss being nearly complete by salinity 20⁰/oo to 25⁰/oo. Tests for lack of fit and for second order curvature confirm the obvious non-linearity (Table 8). However, the variability in river input concentrations of dissolved Fe could explain some of the apparent loss.

The loss of Fe from solution when river water mixes with seawater is almost universally reported. Laboratory mixing of filtered river water and seawater resulted in the almost complete flocculation and precipitation of Fe dissolved in the river water in experiments

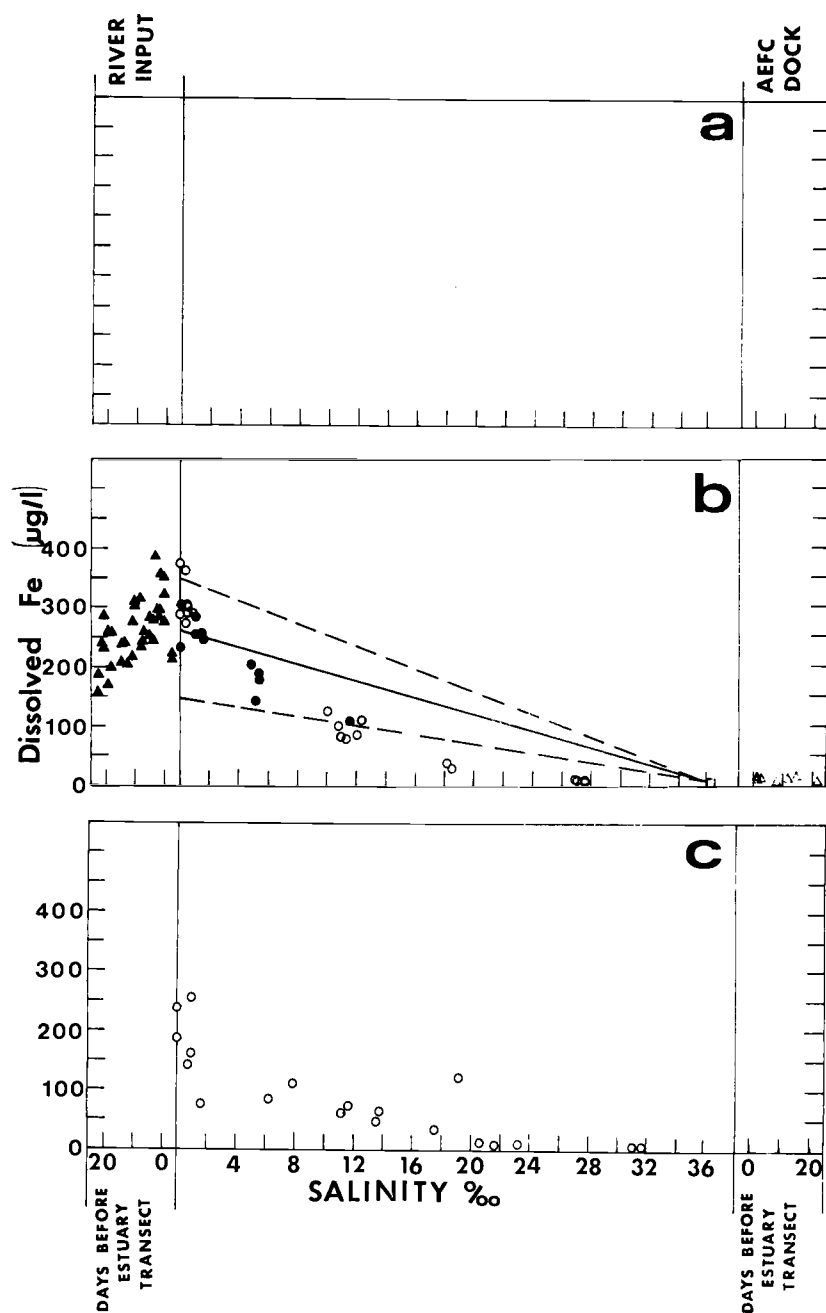


Figure 15. Dissolved Fe concentrations in relation to salinity in the Newport River estuary during three sampling transects: (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the dissolved Mn concentrations in Newport River water (▲) and at the AEFC dock (Δ) during the three weeks prior to the estuary transects. A solid line connects the mean dissolved Fe concentration in the river during these three weeks with the dissolved Fe concentration in primary ocean water (□). The dashed lines represent 95% confidence limits about this conservative mixing line, calculated from the standard deviation of the dissolved Fe concentrations in the river.

conducted by Lowman et al. (1966) with water from the Añasco River, Puerto Rico and by Sholkovitz (1976) with water from four Scottish Rivers. Application of linear mixing models to the estuarine distribution of dissolved Fe has suggested its loss from solution in the studies of Coonley et al. (1971), Beck (1972), Windom (1975), Boyle et al. (1974), Boyle (1976), Bryan and Hummerstone (1973), Bewers et al. (1974), Harris et al. (1975), and Holliday and Liss (1976). Studies by Wolfe (1975) in Puerto Rico and by Eisma (1975) in the Rhine River estuary are alone in failing to detect non-conservative behavior of dissolved Fe in estuaries.

Four mechanisms suggest themselves as possible explanations of loss of Fe from solution consequent upon estuarine mixing of river water.

(1) The increasing pH during the mixing of river water with seawater would favor the precipitation of $\text{Fe}(\text{OH})_3$. The calculations of Kester et al. (1975) predict from thermodynamic data that the predominant ferric iron species in estuaries will switch from the soluble complex, $\text{Fe}(\text{OH})_2^+$ in river water of pH 6 to the uncharged complex, $\text{Fe}(\text{OH})_3^0$, at the pH 8 of seawater. Polymerization, coagulation, and precipitation of $\text{Fe}(\text{OH})_3^0$ would remove it from solution. Alternatively, $\text{Fe}(\text{OH})_3^0$ could be adsorbed onto pre-existing particles and so removed from solution. Aston and Chester (1973) showed in laboratory radiotracer experiments that the removal

of Fe from seawater by hydrolysis is accelerated by the presence of sediment particles in suspension.

Although this is a satisfying mechanism, it is probably unimportant in most estuaries in removing much Fe from solution. The total concentration of Fe^{3+} and its hydroxy complexes in natural waters of near neutral pH is limited to about $1 \mu\text{g/l}$, (Morgan and Stumm, 1965), whereas the measured filter passing Fe concentration in the Newport River and other rivers where Fe is subsequently lost from solution is more than $100 \mu\text{g/l}$. The Fe in solution in these rivers must be in some other form, perhaps as organic complexes.

(2) Dissolved ferrous iron can exist in some rivers of low enough pH (Stumm and Morgan, 1970) or where dissolved organic compounds maintain a steady-state Fe^{2+} concentration by reducing ferric iron (Theis and Singer, 1973; Morgan and Stumm, 1965). The increasing pH and possible higher dissolved oxygen concentrations in estuaries would favor the oxidation of Fe^{2+} to Fe^{3+} and its subsequent precipitation as $\text{Fe}(\text{OH})_3$. This may explain the observed precipitation of Fe in the Mullica River (Coonley et al., 1971) which possessed both very low pH (less than 5) and very high dissolved organic and Fe concentrations.

(3) Organic complexes of Fe^{2+} and Fe^{3+} in river water could dissociate in estuarine water as Fe is displaced from the ligands by the abundant Mg^{2+} and Ca^{2+} in seawater, as suggested by Kester

et al. (1975). Again, oxidation of any freed Fe(II) to Fe(III) and subsequent precipitation of $\text{Fe}(\text{OH})_3$ would follow.

(4) Iron and high molecular weight organics (e. g. humic acids) are frequently associated in freshwater as filter-passing micro-colloids, either as peptized $\text{Fe}(\text{OH})_3$, stabilized by the organics or as Fe-organic complexes and polymers (Shapiro, 1964; Hall and Lee, 1974; Lamar, 1968). Upon entering estuaries, the increased ionic strength of seawater would coagulate and flocculate these colloids, making them filterable.

Skolkovitz (1976) recently observed in the laboratory the flocculation of dissolved organic matter, humates, Fe, Mn, Al, and P when filtered Scottish river water was mixed with seawater. These Scottish rivers drain peat bogs and are similar in many ways to the Newport River, being high in dissolved organics and Fe. Almost complete flocculation of Fe, Mn, Al, and P was accomplished by a salinity of 15-20 ppt. Dissolved organic matter was only partially flocculated (3-11%), but paralleled the trend of increasing flocculation with salinity shown by Fe and the other elements. Interestingly, increased pH did not result in flocculation of Fe, Mn, etc. This rules out direct precipitation of $\text{Fe}(\text{OH})_3$ as the operant mechanism and seems consistent with the salinity induced flocculation of organically associated Fe micro-colloids. Boyle, 1976 has recently completed studies showing that dispersed $\text{Fe}(\text{OH})_3$ is maintained in a

filter-passing colloidal state by organic matter in river waters, but flocculates along with the organic matter in seawater.

Several observations in the Newport River estuary support mechanism (4) but do not rule out (2) and (3). First, Fe in the Newport River seems to be associated with organic matter in solution. Filtered river water samples can be extracted of only about 4% of their Fe by the Chelex-100 resin extraction if not oxidized first with $K_2S_2O_8$ to destroy the organics present (See Appendix A). This resin removes ionic forms of transition metals preferentially by chelating them. Metals strongly bound to dissolved organics will not be extracted (Florence and Batley, 1975).

Second, Newport River water which is low in suspended matter rapidly clogs 0.4 μ m pore size Nuclepore filters which are not so readily clogged by estuarine water with much higher concentrations of suspended matter. This suggests that colloidal particles at or just below the pore size of the filters are abundant in river water but may have coagulated in the estuary.

Third, dissolved Fe in the Newport River was positively correlated ($R^2 = +.41$, $p < .01$), with UV absorbance, which is a measure of the organic matter content of the water. An even stronger negative correlation with pH was found ($R^2 = -.69$, $p < .01$), suggesting that the species might be colloidal $Fe(OH)_3$, stabilized by organics as a protected sol. Beck et al. (1974) have found similar

relationships between dissolved Fe, organics, and pH in other rivers of the southeastern U.S. which are similar in character to the Newport. They believe, however, that some of the Fe may be held as true soluble organic complexes as well as filter-passing colloids.

Lack of Fe Mobilization in Sediments

Since there is a strong indication that Mn is mobilized from bottom sediments in the upper estuary, probably as the result of reduction of MnO_2 to Mn^{2+} , why is there no comparable release of Fe to solution? It is also readily reduced and solubilized under anoxic conditions. Earlier experiments in which dissolved Mn was released to the overlying water from Cross Rock sediment cores failed to release significant dissolved Fe. Three possibilities suggest themselves. (1) Fe solubility is limited in the sediment pore waters at Cross Rock by some insoluble compound (e.g. FeS , FeCO_3 , and $\text{Fe}_3(\text{PO}_4)_2$). (2) The redox potential (Eh) in the sediments is low enough to reduce MnO_2 to Mn^{2+} but not low enough to reduce $\text{Fe}(\text{OH})_3$ to Fe^{2+} . (3) $\text{Fe}(\text{OH})_3$ may be reduced to soluble Fe^{2+} in the sediment pore waters, but is rapidly reoxidized either in the oxidizing surface sediment layer or in the overlying water column from which it quickly precipitates. Both (2) and (3) are mechanisms discussed in an earlier section to explain the differential mobility of Fe and Mn. If high levels of dissolved Fe could be measured in the

sediment pore waters at Cross Rock, then a kinetic mechanism similar to (3) would be strengthened. In the absence of measurably elevated Fe concentrations in pore waters, the equilibrium model explanations, (1) and (2) might be tested from theoretical considerations using measurements of the concentrations of potential precipitating anions, pH, Eh, and thermodynamic stability and solubility constants. The uncertainty in the possible explanatory mechanisms points out the need in future work to directly couple experiments designed to elucidate exchange mechanisms with distributional studies which only suggest mechanisms of trace metal exchange.

Particulate Fe

Unlike Mn, Fe does not show a complementary increase in its concentration on suspended matter along with its apparent removal from solution (Figure 16). There are several possible explanations for this. In the river and estuary, the particulate to dissolved ratio of Fe is greater than for Mn. Thus a transfer of Mn from solution to suspended particulates would have a greater effect on the Mn concentration on the particulates than a similar proportional removal of Fe from solution would have on the Fe concentration on particulates. Alternatively, if what has been called dissolved Fe is actually filter-passing micro-colloidal Fe, and its Fe content is the same as filterable particulate matter, then its flocculation in the estuary

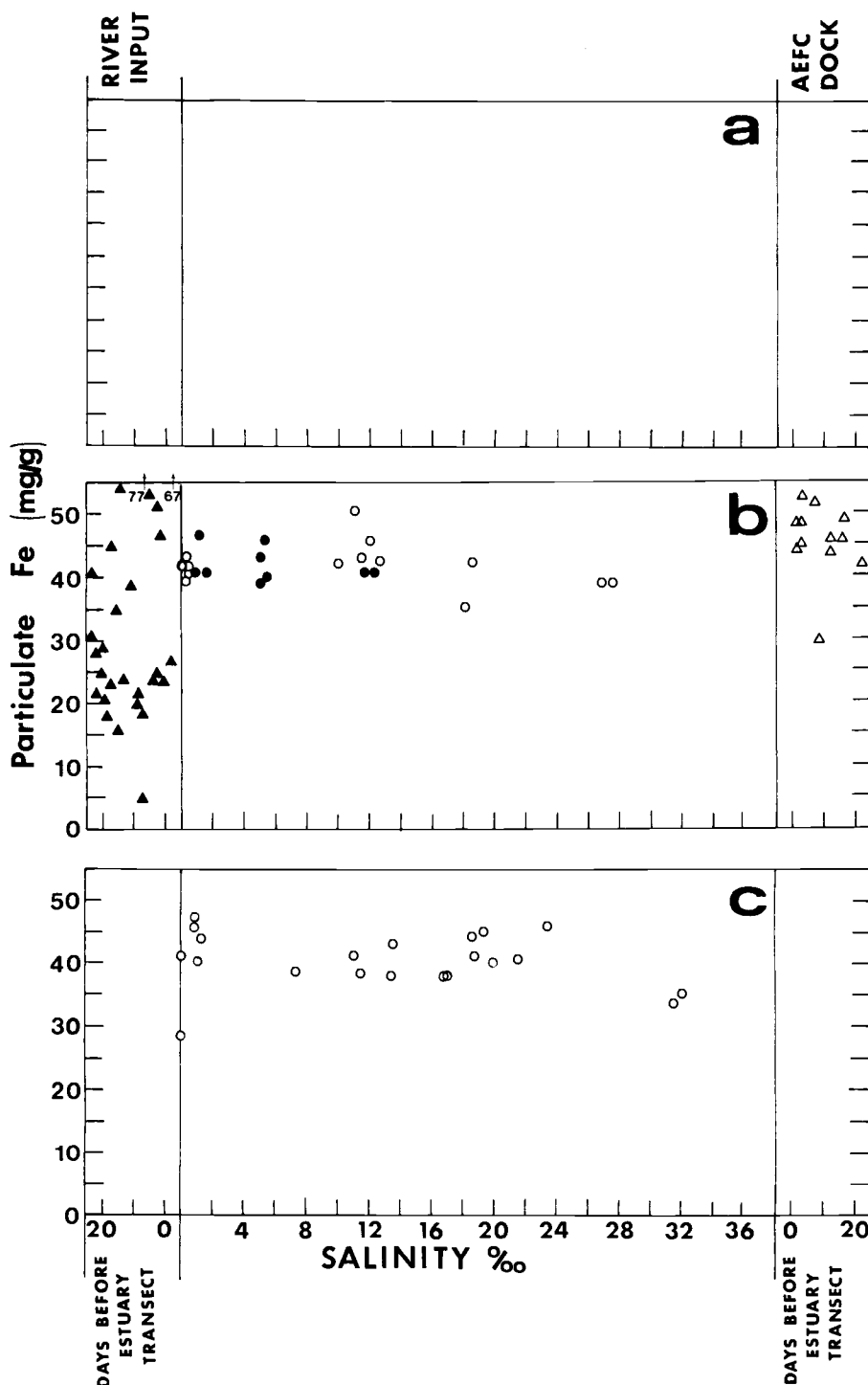


Figure 16. Concentrations of Fe on suspended particulate matter in relation to salinity during three sampling transects in the Newport River estuary: (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the Fe concentrations on suspended particulate matter in inflowing Newport River water (▲) and at the AEFC dock (Δ) during the three weeks prior to the estuary transects.

might raise the amount of suspended particulate Fe, but not the Fe concentration on the particles.

The concentration of Fe on suspended particulate matter (Figure 16) is about 40 mg/g throughout the estuary. This is the same as the concentration on the finest size fraction ($< 2 \mu\text{m}$) of bottom sediments in the estuary (Table 11). Coarser bottom sediment fractions have much lower Fe concentrations. In the core resuspension experiments, the Fe concentrations in suspended particulate matter were also about 40 mg/g in both the controls and in the resuspensions, with the exception of those samples with more than 50 mg/l of particulate matter remaining in suspension. These had 25-32 mg Fe/g (table 9). Assuming a density of 2.65, and Stokes Law settling, this experiment should have left only particles less than $12 \mu\text{m}$ in suspension (Jackson, 1956). The sediments at Cross Rock have Fe concentrations of 28 mg/g in the $2\text{-}10 \mu\text{m}$ size fraction. Those cores with high suspended matter concentrations probably reflect the greater contribution of coarser, low Fe content bottom sediment fractions rather than any exchange process with solution.

Iron in suspended particulate matter in the estuary seems to reflect the concentration of the finer fraction of resuspended bottom sediments. The small observed variations in Fe content are likely to arise from variations in the mean particle size of the suspended sediments. Variations attributable to exchange processes with Fe

in solution would not be readily observable under such circumstances because sediments have such a high Fe content compared to the water.

UV Absorbance and Possible Third Water Type in the Estuary

Sholkovitz (1976) and Sieburth and Jensen (1968) have observed that terrestrially derived humates and other color imparting organics of river water should flocculate in estuaries. In Sholkovitz's (1976) study, the flocculation of dissolved organic matter at low pH was accompanied by a decrease in absorbance by yellow organic matter. One should observe a trend of organic color versus salinity in estuaries indicative of its removal. Figure 17 shows the trend of UV absorbance with salinity in the Newport River estuary. Superficial observation shows a trend that is non-conservative, similar to that of dissolved Fe. This would be consistent with the flocculation of Fe-organic colloids. However, UV absorbance may not be caused by the same organic compounds which flocculate in seawater. In other estuaries and coastal waters, UV absorbance (in the same 250-350 nm range) is a linear function of salinity and can be successfully used as a conservative water mass tracer (Foster, 1973; Foster and Morris, 1971, 1974a, b, c; Abdullah et al., 1973).

The trend of UV absorbance with salinity is highly linear, with no significant curvature, in samples exclusive of these collected at

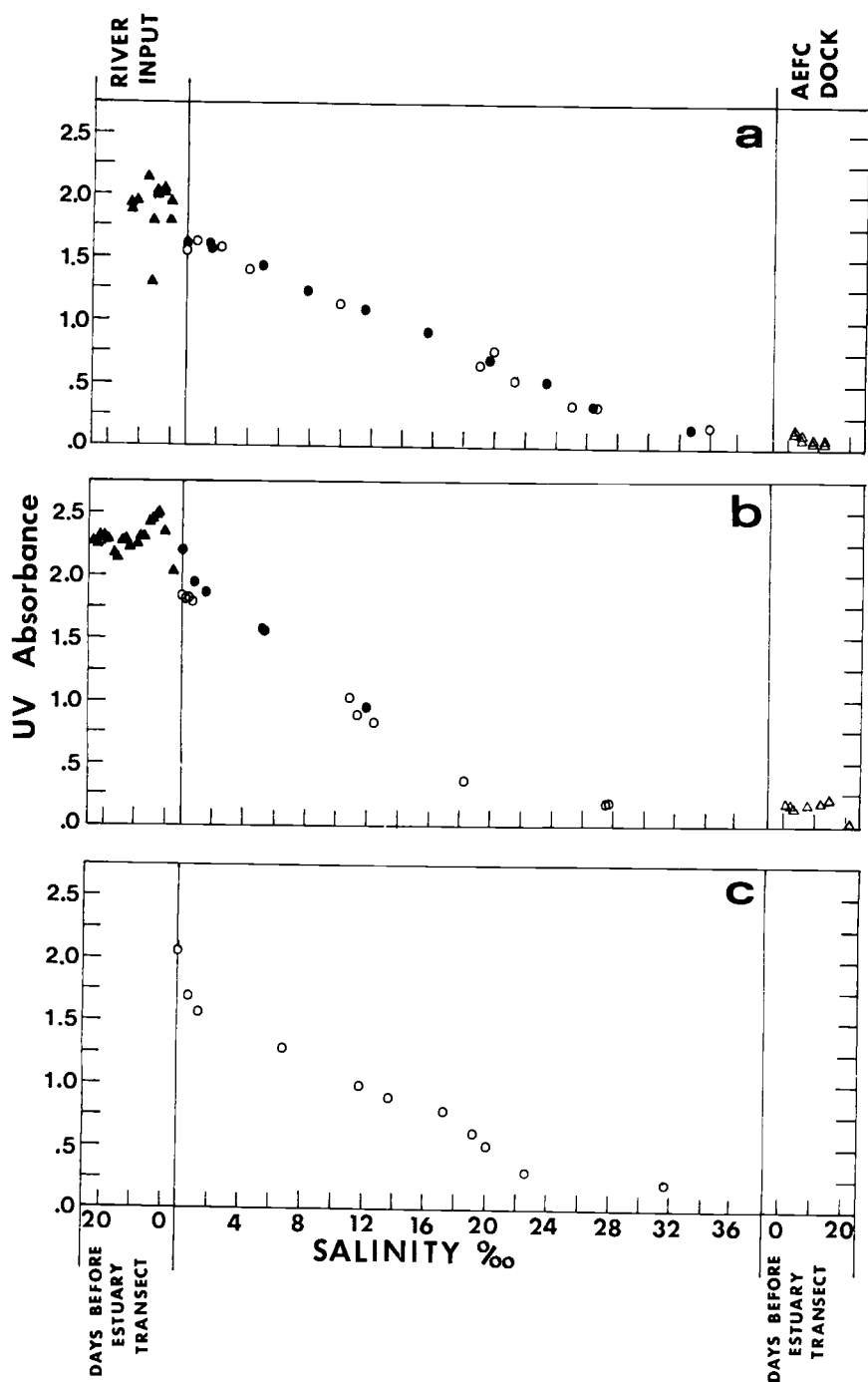


Figure 17. Ultraviolet (UV) absorbance in relation to salinity during five sampling transects in the Newport River estuary: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown is the UV absorbance in inflowing Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuary transects. UV absorbance is the summed absorbances measured in the water samples at 250 nm, 300 nm, and 350 nm in a one cm cell.

the AEFC dock at salinities greater than $27.4^{\circ}/\text{oo}$ (Figure 17). The apparent loss of UV absorbance in the estuary has disappeared and UV absorbance seems to act as a conservative water mass tracer, as was observed elsewhere. This means, if true, that a third water type, exclusive of Newport River water and open ocean water, is mixing in the middle region of the estuary. This water type would have intermediate salinity and low UV absorbance. The point of entry of this third water type appears to be located near the juncture of the Adams Creek Canal which connects with the Neuse River estuary 20 km distant. Water from that estuary may enter the Newport River estuary here. This water should have a low concentration of dissolved Fe. Measurements of water transport through Adams Creek Canal and on its salinity, UV absorbance, and trace metal concentration would be needed before this possibility could be resolved. The presence of a conservative water mass tracer, independent of salinity (perhaps UV absorbance), would enable the extension of mixing models to three point mixing problems.

If water of a third type, low in dissolved Fe, is entering at mid-estuary, it will exaggerate the apparent extent of dissolved Fe removal in the estuary. If this third water type is also low in dissolved Mn, it might also explain part of the apparent removal of Mn from solution in the lower estuary, but would certainly have little influence on the dissolved Mn maximum in the upper estuary.

Copper

Dissolved Copper

Unlike Mn and Fe, dissolved Cu concentrations in the Newport River estuary do not show a repeatable pattern among the transects of October, 1974, February, 1975, and April, 1975, although the patterns on adjacent days are similar (Figure 18).

October, 1974 concentrations of dissolved Cu are consistently low throughout the estuary. While there is some small non-linearity (Table 8), there is little indication of significant net exchanges with particulate phases. The small positive deviation from linearity might be due to varying river input concentrations (Figure 18a).

Although the two statistical tests of linearity show different conclusions about Cu linearity for February, 1975, the S^2 test is only marginally significant (Table 8). However, the February, 1975 transects show that nearly all dissolved Cu concentrations below 12⁰/₀₀ salinity lie above the conservative mixing line connecting river water and ocean water concentrations. An input of dissolved Cu apparently occurred in the upper estuary, near the Cross Rock region. Figure 20 will show that for February, 1975, dissolved Zn also showed an apparent input in this region.

As in the case of Mn, desorption of Cu from inflowing river

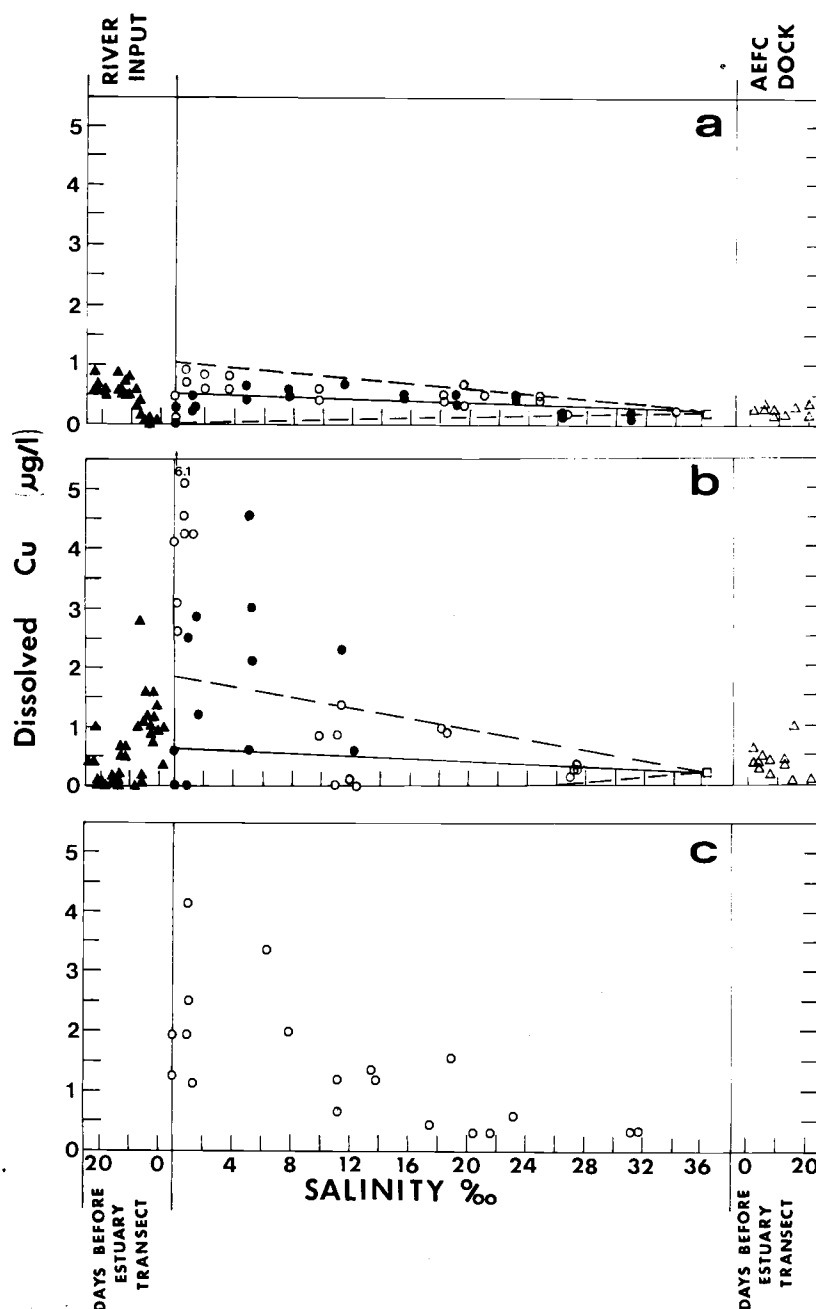


Figure 18. Dissolved Cu concentrations in relation to salinity in the Newport River estuary during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the dissolved Cu concentrations in inflowing Newport River water (▲) and at the AEFC dock (Δ) during the three weeks prior to the estuary transects. A solid line connects the mean dissolved Cu concentration in the river during these three weeks with the dissolved Cu concentration in primary ocean water (□). The dashed lines represent 95% confidence limits about this conservative mixing line, calculated from the standard deviation of the dissolved Cu concentrations in the river.

suspended particulate matter is inadequate to provide this input. About $4 \mu\text{g/l}$ of excess dissolved Cu is observed, but inflowing particulate Cu averages only $0.6 \mu\text{g/l}$, with a maximum of $2.8 \mu\text{g/l}$. Again the bottom sediments seem implicated as a source. The excess dissolved Cu is limited to low salinity and seems to be removed from solution rapidly and nearly completely above salinity, $12^{\circ}/\text{oo}$. The February, 1975 period differed from that of both October, 1974 and April, 1975 in being a time of heavy rainfall, especially in the period just preceding the sampling transects. Greatly increased river flow stirred up bottom sediments in the shallow Cross Rock region, as was indicated by increased turbidity and elevated suspended matter concentrations. Under these circumstances, if elevated concentrations of dissolved Cu were present in sediment pore waters, Cu could be released to the overlying waters. During less turbulent periods, dissolved pore water Cu might not diffuse from the sediments, but rather might react with the surface sediments to become immobilized again.

Sediment core resuspension experiments (Table 9) showed somewhat higher Cu concentrations on particulate matter than in the estuary as a whole. These experiments did not show a net release of Cu to solution when the sediments were resuspended. It is conceivable under the conditions of the experiment, however, that any dissolved Cu released from pore waters was rapidly adsorbed

to the suspended particles, thereby raising the Cu concentration in the particulate matter. Although admittedly speculative, this suggestion is consistent with the transient increase in dissolved Cu apparent in the Cross Rock region in February, 1975 when heavy rain flow increased turbation of Cross Rock sediments (Figure 18b).

Dissolved Cu versus salinity trends in other estuaries have generally failed to detect non-conservative behavior of dissolved Cu that would indicate its net exchange with particulate phases (Bryan and Hummerstone, 1973; Sundararaj and Krishnamurthy, 1972; and Bowers et al., 1974). In one of only two known exceptions, Harris et al. (1975) have noted, but not shown, positive deviations from conservative mixing indicative of inputs of dissolved Cu. Cutshall et al. (1974) have observed positive deviations from conservative mixing in the upper Columbia River estuary and negative deviations in the lower estuary. This is similar to the February, 1975 results reported here. Previous mention has been made of other studies lending support to the idea of Cu mobilization from organic rich estuarine sediments (such as those near Cross Rock) and the subsequent removal of dissolved Cu from the water column in more seaward locations.

Particulate Copper

Concentrations of Cu on suspended particulate matter in the

estuary are nearly identical to those in the $< 2 \mu\text{m}$ fraction of estuarine bottom sediments (compare Figure 19 with Table 11). Both are about $17 \mu\text{g/g}$ of Cu. This suggests that resuspension of bottom sediments largely determines the Cu concentrations on suspended matter within the estuary. Possible exchanges with soluble Cu are not evident within the scatter of the suspended particulate Cu concentrations, contrary to the case for Mn.

Table 12 summarizes metal concentrations on suspended particulate matter in river water flowing into the estuary, in estuarine waters, at the mouth of the estuary at the AEFC dock, in offshore waters of December, 1974, and in the core resuspension experiments. Also shown are concentrations in the $< 2 \mu\text{m}$ fraction of bottom sediments. Of special interest are Cu concentrations on suspended particulate matter at the mouth of the estuary and offshore. These are higher than any probable source of particulate Cu from the river or estuary. There are three likely explanations for this.

- (1) River and estuary-derived particulate Cu is sorted by size or some other criteria so that only fractions high in Cu are exported to the sea. If the increasing Cu content of sediments with decreasing particle size (see Table 11) extends to sub- μm but filterable sizes, the preferential settling of coarser suspended fractions could leave only very fine, Cu rich sediment in suspension at and beyond the estuary mouth.
- (2) The Cu content of suspended particulate matter

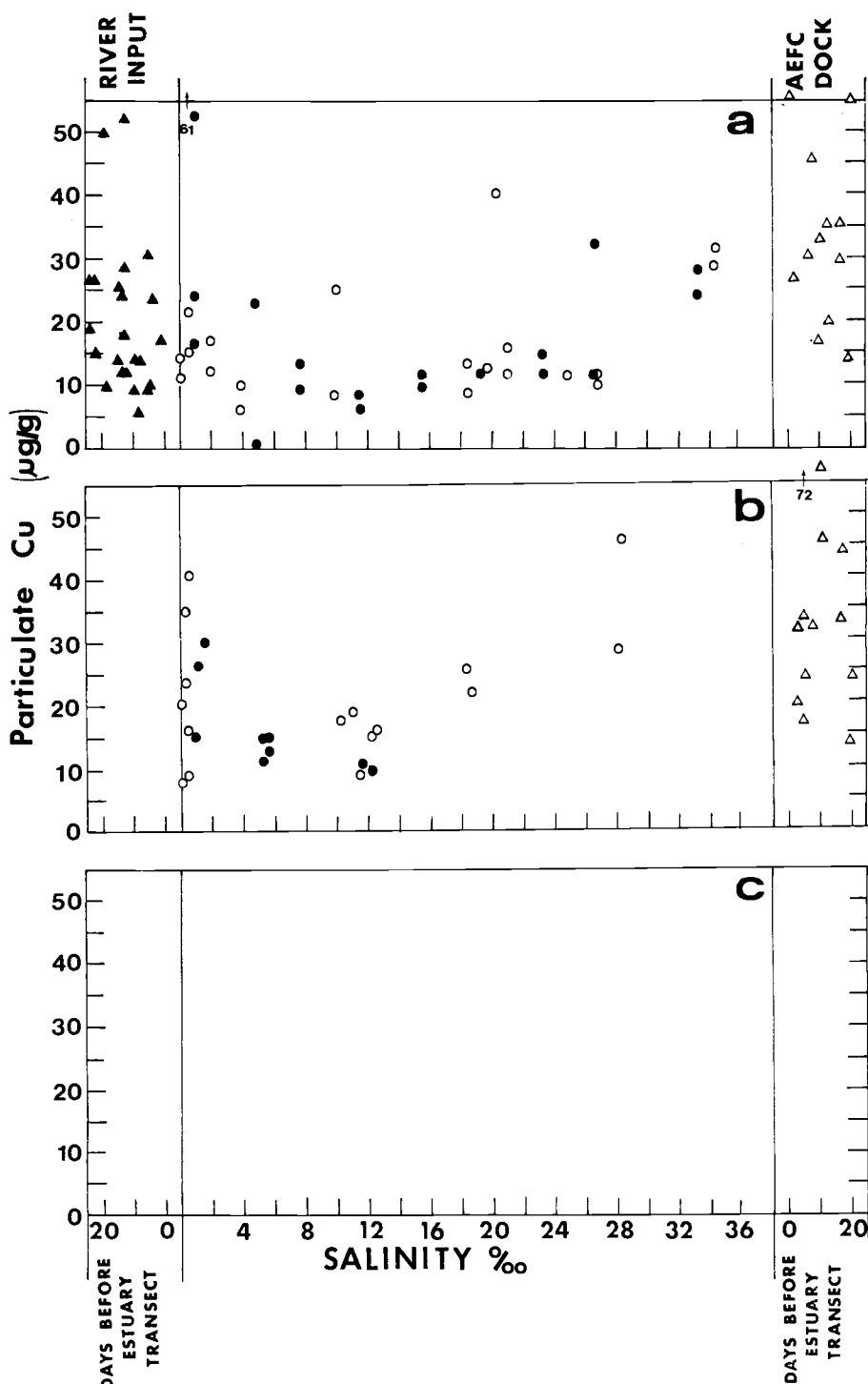


Figure 19. Concentration of Cu on suspended particulate matter in relation to salinity during five sampling transects in the Newport River estuary: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the Cu concentrations on suspended particulate matter in inflowing Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuary transects.

Table 12. Summary of trace metal concentrations in suspended particulate matter and $<2\mu\text{m}$ fraction of bottom sediments in the Newport River, estuary, and adjacent ocean. Suspended particulate matter concentrations are medians; bottom sediment concentrations are means.

		Mn (μg/g)	Fe (mg/g)	Cu (μg/g)	Zn (μg/g)	
Source						
Suspended particulate matter	October 1975	River input	80	---	18	70
		Estuary	355	---	12	105
		AEFC dock	420	---	33	130
	February 1975	River input	40	27	--	60
		Estuary	230	42	16	90
		AEFC dock	330	45	32	110
	April 1975	Estuary	250	40	--	145
	Dec. 1975	Offshore ocean	280	24	165	240
		Resuspended cores	220	34	29	95
<2 μm fraction bottom sediment	Newport River	79	30	17	91	
	Cross Rock	123	41	17	84	

could be increased by adsorption of dissolved Cu in the lower estuary and at sea. (3) Phytoplankton or other particulates high in Cu which are derived from the sea could mix in the estuary. Phytoplankton growing in the estuary might also concentrate Cu to high levels in situ. This latter hypothesis is not incompatible with the potential of phytoplankton in the estuary to cycle Cu and remove it from solution, as discussed in the conclusions. If Cu concentrations in phytoplankton in the estuary and offshore are high compared to abiogenic particulate matter in the estuary, this latter hypothesis would have increased support. Unfortunately, no directly measured metal concentrations in phytoplankton in the Newport River estuary or vicinity exist. Published values from other areas (Pequegnat, 1975) cover too wide a range to make useful comparison, although the observed offshore concentrations of suspended particulate Cu near the Newport River estuary seem to be near the upper end of the range of phytoplankton Cu values.

By comparison, Mn and Fe concentrations in offshore suspended particulate matter are lower than those in the estuary (Table 12). Although reflecting their river and estuary source to a large extent, dilution by particles poor in Mn and Fe is a consistent explanation. Most reported Mn and Fe concentrations in phytoplankton are much lower than the Mn and Fe concentrations on suspended particulate matter in the Newport River and estuary (Pequegnat, 1975).

Abdullah and Royle (1973) also found lower Mn and Fe concentrations offshore than inshore in the Bristol Channel. But Cu and Zn concentrations were higher offshore than inshore during the summer period of maximum offshore phytoplankton production, whereas no such relationship existed earlier in the year when phytoplankton production was low. A strong positive correlation between particulate Cu and Zn and particulate N also supported the association of Cu and Zn with phytoplankton. This relationship suggests that phytoplankton will be more important in the removal of Cu and Zn from solution than of Mn and Fe.

Zinc

Dissolved Zinc

Dissolved Zn has a distribution pattern in the Newport River estuary very similar to that of Cu (Figure 20). October, 1974 transects are low in concentration throughout the estuary, with no statistically significant non-linearity. February, 1975 transects show a significant maximum at intermediate salinity, with dissolved Zn concentrations above the linear mixing line. This apparent input of dissolved Zn is in the Cross Rock region, like that of dissolved Cu during the same time period. Suspended particulate Zn flowing in from the river during this time period is of inadequate concentration to supply the observed addition of dissolved Zn, even by complete desorption. Losses from solution seem to occur at higher salinities,

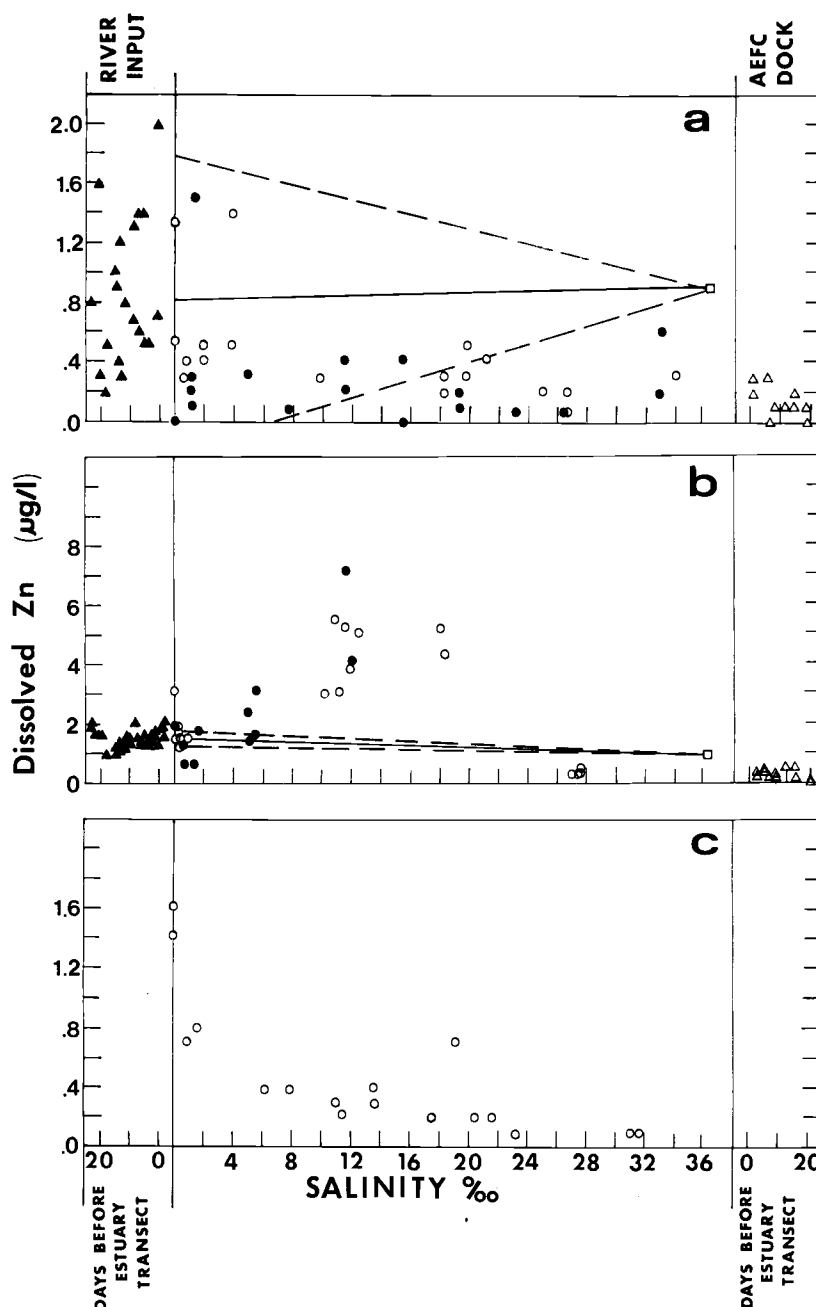


Figure 20. Dissolved Zn concentrations in relation to salinity in the Newport River estuary during five sampling transects: (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the dissolved Zn concentrations in inflowing Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuary transects. A solid line connects the mean dissolved Zn concentration in the river during these three weeks with the dissolved Zn concentration in primary ocean water (□). The dashed lines represent 95% confidence limits about this conservative mixing line, calculated from the standard deviation of the dissolved Zn concentrations in the river.

as was the case for Cu. Again the increased river flow of this period and the resulting turbation of Cross Rock bottom sediments could release pore water dissolved Zn to the overlying water.

The previously reported experiments which showed dissolved Mn released from Cross Rock sediment cores did not show release of either Cu or Zn. This seems in contradiction to the above hypothesis. Perhaps the contradiction could be explained by the rapid removal of solubilized Zn and Cu, by the difference in the sampling dates (February, 1975 for the hypothesized release and April, 1975 for the core experiments), or if the sampling location for the cores was not representative of the entire Cross Rock region. These are but speculations and point out the need in the future to sample sediment pore waters in the Cross Rock region and elsewhere in the estuary. The dissolved Zn transect for April, 1975 showed a statistically significant non-linearity in the dissolved Zn trend with salinity which indicated a removal from solution. No apparent input in the Cross Rock region was evident then (Figure 20).

In other estuarine studies using linear mixing models to infer exchanges of Zn, estuarine losses from solution have been found by Holliday and Liss (1976). Estuarine additions were reported by Bryan and Hummerstone (1973) and by Harris et al. (1975). Additions to solution of ^{65}Zn were found by Evans and Cutshall (1973) and Forster (1972). Failure to find either additions or losses of dissolved

Zn were reported by Bowers et al. (1974) and Abdullah and Royle (1972). Cutshall et al. (1974) observed, as for Mn and Cu, that Zn showed positive deviations from linear mixing in the upper Columbia River estuary and negative deviations in the lower estuary. This latter study is consistent with observations of February, 1975 and with previously mentioned studies which found that Zn solubilized in estuaries was rapidly removed from solution.

Particulate Zinc

The pattern of Zn concentrations on suspended particulate matter is similar to that of Cu: low in the river, intermediate in the estuary, higher at the estuary mouth, and highest offshore (Table 12 and Figure 21). Estuary concentrations are nearly identical with those of the $< 2 \mu\text{m}$ fraction of bottom sediments in the estuary. The seaward increase in suspended particulate Zn content is consistent with (1) possible removal of Zn poor particles from suspension, (2) uptake of Zn from solution onto suspended particles (either inorganic or phytoplankton) or (3) dilution of estuarine particles with relatively Zn rich particles from offshore.

The uptake hypothesis (2) is consistent with the observed loss of Zn from solution in February and April, 1975 (Figure 20). The possibility of Zn cycling and removal from solution by phytoplankton is discussed in the conclusions. Phytoplankton concentrations are

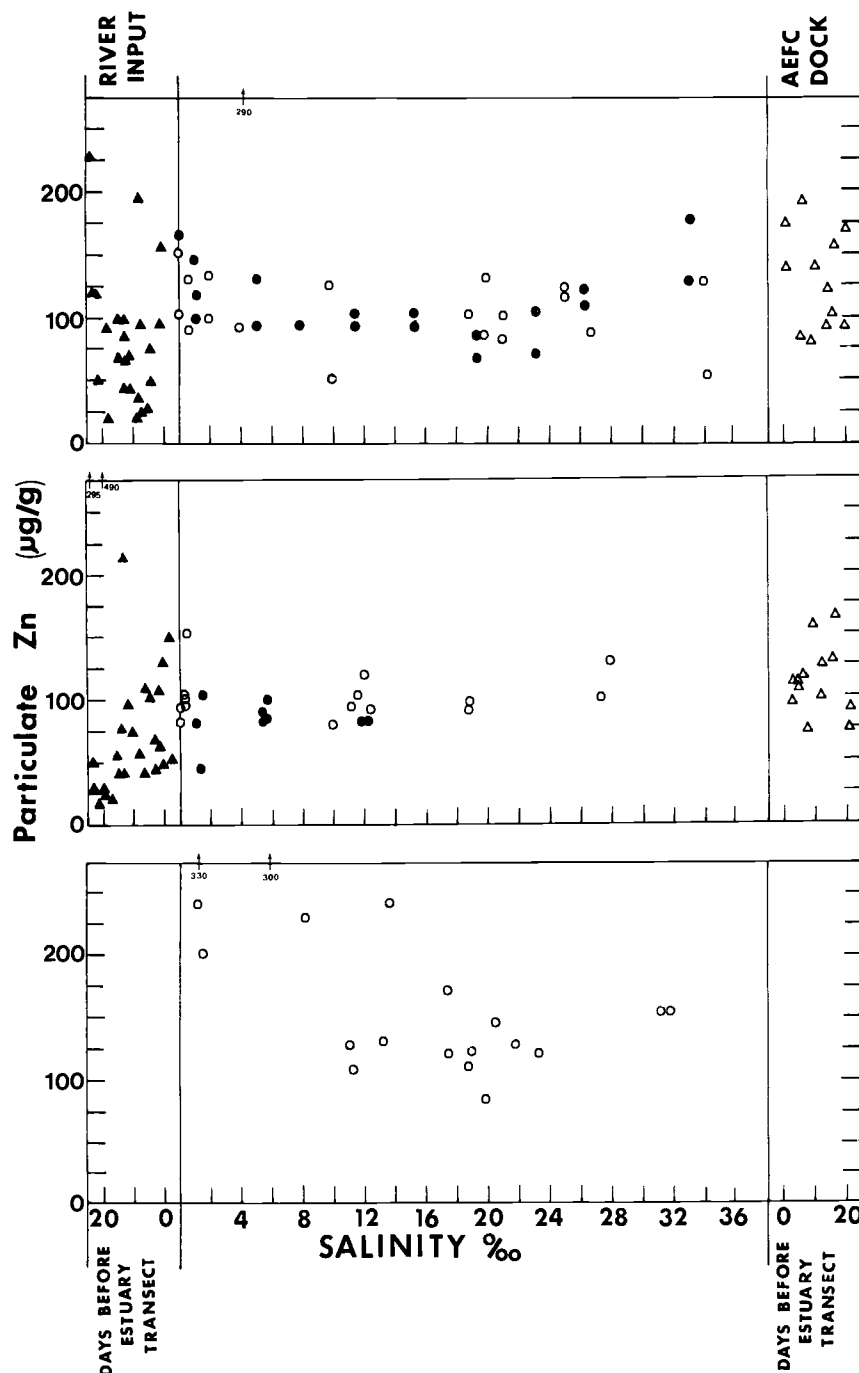


Figure 21. Concentration of Zn on suspended particulate matter in relation to salinity during five sampling transects in the Newport River estuary; (a) October 30 (●) and 31 (○), 1974; (b) February 4 (●) and 5 (○), 1975; and (c) April 14, 1975 (○). Also shown are the Zn concentrations on suspended particulate matter in inflowing Newport River water (▲) and at the AEFC dock (△) during the three weeks prior to the estuary transects.

lacking for the Newport River estuary and vicinity, precluding a possible test of this hypothesis.

Summary

Dissolved Mn concentrations in the Newport River estuary showed concentrations at intermediate salinities which were above those predicted by conservative mixing of river water and ocean water. Maximum concentrations occurred at salinities in the range of 4‰ to 19‰ and centered on the region of the upper estuary where organic rich sediments are being deposited and where the anoxic layer lies just below the sediment surface.

Desorption of Mn from inflowing suspended particulate matter in the river was inadequate to explain the magnitude of the excess dissolved Mn observed. Reduction and solubilization of Mn in bottom sediments probably supplied this dissolved Mn to the overlying water. Fixation of dissolved Mn on particles (probably as oxidation of Mn^{2+} to insoluble MnO_2) in the lower estuary and upstream recycling and deposition in the upper estuary seemed to occur, if the supply of excess dissolved Mn from the sediments was to be maintained in quasi-steady-state. Fixation of the excess dissolved Mn was only partial within the estuary but fixation was likely to continue seaward of the estuary mouth, with landward recycling required as well to maintain the observed excess Mn in solution in

the upper estuary at steady-state. Alternatively a non-steady-state may have existed. The few sampling transects may have occurred during short term events such as extreme high tides which mobilized Mn and thereby exaggerated estimates of excess dissolved Mn exported to the ocean annually.

Dissolved Fe entering the estuary from the river was removed almost entirely by flocculation. Dissolved Fe in the river probably existed as a filter-passing, organic stabilized, $\text{Fe}(\text{OH})_3$ colloid which coagulated in the high ionic strength estuarine water.

Sediment Fe in the upper estuary was not measurably transferred in solution to the overlying water, although like Mn, it might be expected to be reduced and solubilized in the anoxic sediment pore waters. Either sufficiently low Eh's failed to develop to reduce $\text{Fe}(\text{OH})_3$ to soluble Fe^{2+} or the more rapid reoxidation of Fe^{2+} than of Mn^{2+} removed the former from solution in the oxic surface sediments or overlying water and allowed the latter to remain.

Copper in solution showed a behavior that varied with the time of the sampling transects. Its trend with salinity was barely distinguishable from conservative mixing in October, 1974 and not at all in April, 1975. In transects of February, 1975, dissolved Cu was temporarily released from organic rich bottom sediments in the upper estuary by turbation by currents associated with high river flow. The introduced dissolved Cu seemed to be quickly removed

from the water column in the immediate downstream section of the estuary.

Dissolved Zn followed a pattern similar to Cu. In October, 1974, no deviation from conservative mixing was detectable. February, 1975 showed a dissolved Zn maximum in the upper estuary in association with the dissolved Cu maximum. Release from organic rich bottom sediments seems to have occurred but the addition was removed farther downstream in the estuary. In April, 1975, dissolved Zn trends with salinity showed a loss of Zn from solution in the estuary.

The possible existence of intermediate salinity, low dissolved trace metal water mixing in the lower estuary may have exaggerated the apparent removal of the trace metals from solution.

Thus there appeared to be a source of Mn, Cu, and Zn to solution during diagenesis and organic decomposition in the high organic sediments of the upper estuary. Superimposed upon this was a loss of Mn, Cu, Zn and Fe from solution throughout the estuary. Much of the dissolved Fe, Cu, and Zn supplied by the river or by sediment diagenetic processes was lost from the water column by precipitation, flocculation, adsorption, or biological uptake within the estuary. Only dissolved Mn was exported to the ocean in excess of its supply by the river. This excess may have been precipitated

at sea and recycled into the estuary to maintain the mass balance of Mn there.

The Newport River estuary is therefore a sink for most dissolved Mn, Fe, Cu and Zn entering from the river. Metals mobilized from particulate phases within the estuary are retained in the estuary by transfers back to particulate phases which accumulate within the estuary by sedimentation.

CONCLUSIONS

Cycling of Metals in Newport River Estuary

Wolfe et al. (1973) and Wolfe (1975) have discussed the flux of Mn, Fe, and Zn through the Newport River estuary and its biota. Emphasis was placed on the total imports from the watershed, exports to the ocean, and biological transfers in the food web. No adequate distinction was made between dissolved and suspended particulate forms, and the authors suggested that the exchange between solution and bottom sediments or suspended particulate matter would have important consequences to biological availability.

Table 13 shows the annual budget of Mn, Fe, and Zn as modified from Wolfe et al. (1973). Tidal exchange dominates the flux of metals, moving them into and out of the estuary in vast quantities. The net tidal exchange is very much less and is not known well.

The table shows the potential importance of biota in the cycling of Mn, Fe, and Zn within the Newport River estuary. Copper was not a part of these studies. Spartina alterniflora appears to accumulate annually an amount of these metals on the same order as that entering from the watershed. For the three transects of the present study, mobilizations of Mn from sediments to the water

Table 13. Annual budget of Mn, Fe, and Zn (kg/yr) in the Newport River estuary (From Wolfe et al., 1973).

Source	Mn	Fe	Zn
River input	3480	53200	112
<u>Spartina</u> turnover	1500	38000	170
Phytoplankton turnover	50	11000	1700
Sedimentation	920	24000	220
Emigration of biota	5	60	10
Gross tidal exchange	28000	520000	28000

column in the upper estuary were (on an annual rate basis) 4400 kg/year for October, 1974, 1800 kg/year for February, 1975, and 13,000 kg/year for April, 1975. This is comparable to or greater than the Spartina mobilization flux. Uptake from sediment pore waters is thought to supply the metals to the plants through their root systems. The seasonal dieoff produces massive amounts of metal containing detritus. This detritus is thought to serve as the trophic base for much of the productivity of higher trophic levels and the source of much of their trace metals. The proportion of this biologically accumulated metal transferred to solution by metabolic or decompositional processes is not known. The observed increases in dissolved Cu and Zn concentrations of February, 1975 were probably not due to mobilization by Spartina. The increases were local, but Spartina is distributed throughout the estuary. In particular, there are extensive Spartina marshes in the upstream, freshwater segment of the Newport River which should supply dissolved Cu and Zn if Spartina were the actual source. No extraordinary dissolved Cu and Zn concentrations were observed in the freshwater input to the estuary in February, 1975 (Figure 18). In addition, February was the dormant period in the Spartina life cycle. The detritus produced by the autumn dieoff had been largely dispersed into the estuary or decomposed in place, and the spring growth of above ground foliage had not yet begun, so there could be little metabolic pumping of sediment

trace metals to the overlying water column. There may be an indirect effect on the mobilization of trace metals from sediments due to Spartina. The detritus deposited in sediments may be the main source of organic matter there and thus contribute during its decomposition to the production of reducing conditions or of metal chelating dissolved organics.

Wolfe's (1975) estimate of the role of phytoplankton in the trace metal budget in the Newport River estuary was calculated from the product of measured annual phytoplankton productivity there and the concentrations of the metals in plankton off Panama (the only concentrations available then). On this basis, phytoplankton are important cyclers only of Zn. They turned over a quantity of Zn equal to 1500% of the annual import from the river. By comparison the Mn and Fe turnovers were only 1.6% and 21% respectively of the river inflows. To Wolfe (1975), this suggested the importance of biological recycling in maintaining an active pool of available Zn within the estuary, although the oceanic input of Zn seems more than adequate to supply phytoplankton uptake.

The large turnover of Zn by phytoplankton in comparison to river inflow suggests that uptake by phytoplankton could be a potential cause of removal of Zn from solution observed in February, 1975 and April, 1975. It would not be important in the removal of Mn

from solution and would have but a small potential effect on Fe removal.

Copper has a concentration factor from solution to phytoplankton that is about the same for Zn (Lowman et al., 1971). The arguments for phytoplankton removal of Zn from solution could apply as well to Cu. More direct efforts need to be made on the role of phytoplankton in controlling dissolved trace metal concentrations in the Newport River estuary. As discussed earlier, this was not observed directly in ocean waters, but it might be important in more productive estuarine waters. Certainly measurements of the actual trace metal concentrations in Newport River estuary phytoplankton and their variability need to be made rather than relying on averages of measurements made in entirely different ecosystems. Direct trace metal uptake studies in situ should be attempted.

Just as the role of biota in the exchange of trace metals between solution and particulates is unclear, so is the effect of that exchange on the availability of metals to biota. Many phytoplankton are thought to obtain trace metals directly from solution (Lowman, et al., 1971); Sanders (1975) observed recently the association of phytoplankton blooms with increases in the dissolved Mn concentration in a small arm of the Newport River estuary. But particulate, metals may be preferred by other phytoplankton; precipitated $\text{Fe}(\text{OH})_3$ is the preferred form for some (Goldberg, 1952; Davies, 1967).

Benthic and filter feeding organisms expected to reflect the concentrations of trace metals in the sediments they inhabit often do not (Southern California Coastal Water Research Project, 1973; Huggett et al., 1975). In some estuaries metal availability to benthic organisms is more closely related to sediment pore water concentrations than to bulk sediment concentrations (Bryan and Hummerstone, 1971). It is therefore doubtful that generalizations on the relative biological availability of particulate bound and dissolved trace metals can be made. Reference will have to be made to a specific organism, a specific chemical form of each trace metal in both particulates and solution, and a specific array of experimental or environmental conditions. Merely distinguishing between dissolved and particulate forms will be inadequate. It will be necessary to distinguish the actual chemical species present (e. g. Fe^{3+} , $\text{Fe}(\text{OH})_3$, or Fe-organic complex). As an example, Chipman et al. (1968) found that particulate $^{54}\text{MnO}_2$ was not taken up significantly by the annelid worm, Hermione hystrix, but that particulate organic ^{54}Mn was.

The importance of the dissolved-particulate distribution of trace metals on their biological availability may appear indirectly in the different physical mobilities of the two forms. Particulate metals will tend to accumulate by sedimentation, localizing their availability to biota. By reason of easier dispersion, dissolved forms will be

made available to biota over a larger area, but in diluted concentrations.

Despite transient mobilization to solution in the Newport River estuary, removal of Cu and Zn as well as Fe from solution will probably limit the river supply of these metals to biota within the estuary or in the immediate coastal zone. Only for Mn does the dissolved flux exported to the ocean from the estuary exceed that supplied in solution from the river. This might permit the wide scale dispersal of this estuarine Mn to the sea. However, the removal of Mn from solution in the lower estuary is likely to continue seaward of the estuary mouth. Mass balance considerations suggest that landward recycling of this precipitated Mn would limit the extent of Mn dispersal to near coastal areas and retain much of it within the estuary. Because the Newport River estuary seems to be a sink for Fe, Cu, Zn, and perhaps Mn, it would be an unwise location for introduction of wastes containing them or their radioisotopes.

Flux of River Derived Mn, Fe, Cu, and Zn
to the Open Ocean

Estuarine transformations of the river flux of dissolved trace metals would lead to altered estimates of the residence times of these elements in the open ocean. Many investigators have been tempted to extrapolate their own studies on a single system to the

world wide supply of dissolved trace metals to the open ocean. Thus Kharkar et al. (1968) predicted augmented supplies of dissolved Co to the ocean on the basis of their own laboratory desorption experiments. Martin et al. (1973) felt, on the contrary, that estuaries are a sink for river-derived trace metals, and that residence times of these metals in the open ocean had been underestimated as a result. This was based on studies on several European rivers, some of them grossly polluted, which may have biased this conclusion. But on the basis of the study of the Newport River estuary and on other estuaries to which it has been compared, this latter conclusion seems to be the more likely; estuaries are probably trace metal sinks.

Certainly the behavior of Mn, Fe, Cu, and Zn, in the Newport River should not be generalized too far. Although there is a repeatability in the behavior of Mn and Fe among the three time periods sampled, there is also enough variability, especially for Cu and Zn, to indicate a dynamic and changeable system. Moreover, the Newport is not a world wide representative estuary. It is very shallow, with a low river input. As a consequence, processes in bottom sediments and in resuspended sediments have a larger influence on trace metal fluxes than in estuaries with large river flows. Since these rivers, such as the Amazon, Congo, and Mississippi, are the main suppliers of freshwater to the ocean, they are more appropriate study sites in determining the influence of estuarine processes on the

trace metal flux to the oceans. The measurable influence of these large rivers would extend farther to sea and would require more typically oceanographic logistical support than the small estuaries that have dominated study to date.

Removal processes of trace metals evident in estuarine zones would likely continue over adjacent coastal waters. Brewer and Spencer (1975) considered some approaches to modeling these processes in coastal zones and encouraged more extensive systematic sampling for minor elements in coastal areas. Linear mixing models, used with some success in estuaries, could be extended to coastal studies of minor element removal where the removal rates are rapid. Yentsch (1975) has now used this approach in the study of phosphorus, considering New England coastal waters as an infinite estuary.

BIBLIOGRAPHY

- Abdullah, M. I. and L. G. Royle. 1973. Chemical evidence for the dispersal of River Mersey run-off in Liverpool Bay. *Estuarine and Coastal Marine Science* 1:401-409.
- Abdullah, M. I. and L. G. Royle. 1974. A study of the dissolved and particulate trace elements in the Bristol Channel. *J. Mar. Biol. Assoc. U.K.* 54:581-597.
- Abdullah, M. I., H. M. Dunlop, and D. Gardner. 1973. Chemical and hydrographic observations in the Bristol Channel during April and June 1971. *J. Mar. Biol. Assoc. U.K.* 53:299-319.
- Arnac, M. 1976. Variations des teneurs en Cd, Pb, et Cu dans les eaux de l'estuaire maritime du St.-Laurent durant l'été 1972. *Marine Chemistry* 4:175-188.
- Aston, S. R. and R. Chester. 1973. The influence of suspended particles on the precipitation of iron in natural waters. *Estuarine and Coastal Marine Science* 1:225-231.
- Baas-Becking, L. G. M., I. R. Kaplan, and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. *Journal of Geology* 68:243-268.
- Bachman, R. W. 1963. Zinc-65 in studies of the freshwater zinc cycle. In: *Proceedings of the First National Symposium on Radioecology*, Colorado State University, 1961, ed. by V. Schultz and A. W. Klement. New York, Reinhold. p. 485-496.
- Beck, K. C. 1972. Sediment water interactions in some Georgia rivers and estuaries. Report by the School of Geophysical Science, Georgia Institute of Technology, Atlanta, Georgia. OWWR Project No. B-033-GA. 97 pp.
- Beck, K. C., J. H. Reuter, and E. M. Perdue. 1974. Organic and inorganic geochemistry of some coastal plain rivers of the southeastern United States. *Geochimica et Cosmochimica Acta* 38:341-364.

- Bella, D. A. 1975. Tidal flats in estuarine water quality analysis. Ecological Research Series. National Environmental Research Center, Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, Oregon. 186 pp. (EPA-660/3-75-025).
- Bender, M. 1971. Does upward diffusion supply the excess manganese in pelagic sediments? *Journal of Geophysical Research* 76:4212-4215.
- Berner, R. A. 1967. Diagenesis of iron sulfide in recent marine sediments. In: *Estuaries*, ed. by G. H. Lauff. Washington, D.C., American Association for the Advancement of Science. p. 268-272. (AAAS Publication 83).
- Berrang, P. G. and E. V. Grill. 1974. The effect of manganese oxide scavenging on molybdenum in Saanich Inlet, British Columbia. *Marine Chemistry* 2:125-148.
- Bewers, J. M., I. D. MacCauley, and B. Sundby. 1974. Trace metals in the waters of the Gulf of St. Lawrence. *Canadian Journal of Earth Science* 11:939-950.
- Bien, G. S., D. E. Contois, and W. H. Thomas. 1958. The removal of soluble silica from freshwater entering the sea. *Geochimica et Cosmochimica Acta* 14:35-54.
- Biggs, R. B. 1970. Sources and distribution of suspended sediments in Northern Chesapeake Bay. *Marine Geology* 9:187-201.
- Bischoff, J. L., and T. L. Ku. 1971. Pore fluids of recent marine sediments of 35° to 45° N Gibraltar to Mid-Atlantic Ridge. *Journal of Sedimentary Petrology* 41:1008-1017.
- Boyle, E. 1976. The marine geochemistry of trace metals. Ph.D. Thesis, Woods Hole, Woods Hole Oceanographic Institution/Massachusetts Institute of Technology. 156 numb. leaves.
- Boyle, E., R. Collier, A. T. Dengler, J. M. Edmond, A. C. Ng, and R. F. Stallard. 1974. On the chemical mass-balance in estuaries. *Geochimica et Cosmochimica Acta* 38:1719-1728.
- Brewer, P. G. 1975. Minor elements in seawater. In: *Chemical oceanography* (2nd edition) ed. by J. P. Riley and G. Skirrow. London, Academic Press. Vol. I. p. 415-497.

- Brewer, P. G. and D. W. Spencer. 1970. Trace element inter-calibration study. Woods Hole Oceanographic Institution. Reference No. 70-62. Unpublished manuscript.
- Brewer, P. G. and D. W. Spencer. 1975. Minor elements in coastal waters. In: Marine chemistry in the coastal environment, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 80-96. (ACS Symposium Series 18).
- Bricker, O. P., III and B. N. Troup. 1975. Sediment-water exchange in Chesapeake Bay. In: Estuarine research, ed. by L. E. Cronin. New York, Academic Press. Vol. I. p. 3-27.
- Brooks, R. R., B. J. Presley, and I. R. Kaplan. 1968. Trace elements in the interstitial waters of marine sediments. *Geochimica et Cosmochimica Acta* 32:397-414.
- Bryan, G. W., and L. G. Hummerstone. 1971. Adaptation of the polychaete, Nereis diversicolor to estuarine sediments containing high concentrations of heavy metals. I. General observations and adaptations to copper. *J. Mar. Biol. Assoc. U.K.* 51:845-863.
- Bryan, G. W. and L. G. Hummerstone. 1973. Brown seaweed as an indicator of heavy metals in estuaries in south-west England. *J. Mar. Biol. Assoc. U.K.* 53:705-720.
- Burton, J. D. 1970. The behaviour of dissolved silicon during estuarine mixing. II. Preliminary investigations in the Vellar Estuary, southern India. *J. Conseil Perm. Int. Explor. Mer.* 33:141-148.
- Burton, J. D., P. S. Liss, and V. K. Venugoplan. 1970. The behaviour of dissolved silicon during estuarine mixing. I. Investigations in Southampton water. *J. Conseil Perm. Int. Explor. Mer* 33:134-140.
- Carpenter, J. H., W. L. Bradford, and V. Grant. 1975. Processes affecting the composition of estuarine waters (HCO_3 , Fe, Mn, Zn, Cu, Ni, Cr, Co, and Cd). In: Estuarine research, ed. by L. E. Cronin. New York, Academic Press. Vol. I. p. 188-214.

- Chester, R. and J. H. Stoner. 1974. The distribution of zinc, nickel, manganese, cadmium, copper, and iron in some surface waters from the world ocean. *Marine Chemistry* 2:17-32.
- Chipman, W., E. Schommers, and M. Boyer. 1968. Uptake, accumulation and retention of radioactive manganese by the annelid worm Hermione hystrix. *International Atomic Energy Agency, Radioactivity in the Sea Series*, 25:1-16.
- Clark, D., R. M. Dagnal, and T. S. West. 1975. The atomic absorption determination of zinc with a graphite furnace. *Analytica Chimica Acta* 63:11-18.
- Coonley, L. S., Jr., E. B. Baker, and H. D. Holland. 1971. Iron in the Mullica River and in Great Bay, New Jersey. *Chemical Geology* 7:51-63.
- Cross, F. A., T. W. Duke, and J. N. Willis. 1970. Biogeochemistry of trace elements in a coastal plain estuary: distribution of manganese, iron, and zinc in sediments, water, and polychaetous worms. *Chesapeake Science* 11:221-234.
- Cruz, R. B. and J. C. Van Loon. 1974. A critical study of the application of graphite-furnace non-flame atomic absorption spectrometry to the determination of base metals in complex heavy-matrix sample solutions. *Analytica Chimica Acta* 72: 231-243.
- Cutshall, N. H. 1967. Chromium-51 in the Columbia River and adjacent Pacific Ocean. Ph.D. Thesis. Corvallis, Oregon State University. 64 numb. leaves.
- Cutshall, N. H., R. L. Holton, and L. F. Small. 1974. Non-conservation of heavy metals in the Columbia River estuary. Unpublished manuscript.
- Davies, A. G. 1967. Studies of the accumulation of radio-iron by a marine diatom. In: *Radioecological concentration processes*, ed. by B. Åborg and F. P. Hungate. Oxford, Pergamon Press, p. 983-992.

- DeGroot, A. J., J. J. M. DeGoeij, and C. Zegers. 1971. Content and behavior of mercury and other heavy metals in sediments from the rivers Rhine and Ems. *Geologie en Mijnbouw* 50: 393-398.
- Delfino, J. J. and G. F. Lee. 1968. Chemistry of manganese in Lake Mendota, Wisconsin. *Environmental Science and Technology*. 2:1094-1100.
- Dengler, A. T. 1973. Silicates and diatoms in New England estuaries M.S. Thesis. Cambridge, Massachusetts Institute of Technology. 89 numb. leaves.
- Draper, N. and H. Smith. 1966. Applied regression analysis. New York, Wiley. 407 pp.
- Drever, J. I. 1971. Magnesium-iron replacement in clay minerals in anoxic marine sediments. *Science* 172:1334-1336.
- Duchart, P., S. E. Calvert, and N. B. Price. 1973. Distribution of trace metals in the pore waters of shallow marine sediments. *Limnology and Oceanography* 18:605-610.
- Duinker, J. C., G. T. M. Van Eck, and R. F. Nolting. 1974. On the behavior of copper, zinc, iron, and manganese, and evidence for mobilization processes in the Dutch Wadden Sea. *Netherlands Journal of Sea Research* 8:214-239.
- Duursma, E. K. 1970. Organic chelation of ^{60}Co and ^{65}Zn by leucine in relation to sorption by sediments. In: *Symposium on Organic Matter in Natural Waters*, ed. by D. W. Hood. College, Alaska, University of Alaska, Institute of Marine Science. Occasional Publication 1.
- Duursma, E. K. and M. G. Gross. 1971. Marine sediments and radioactivity. In: *Radioactivity in the marine environment*. Washington, D. C., National Academy of Sciences. p. 147-160.
- Dyrssen, D. and M. Wedborg. 1974. Equilibrium calculations of the speciation of elements in seawater. In: *The Sea*, ed. by E. D. Goldberg. New York, Wiley-Interscience. Vol. 5. p. 181-196.
- Eisma, D. 1975. Dissolved iron in the Rhine estuary and adjacent North Sea. *Netherlands Journal of Sea Research* 9:222-230.

- Eisma, D., H. A. Das, D. Hoede, J. G. Van Raaphorst, and J. Zonderhuis. 1966. Iron and trace elements in Dutch coastal sands. *Netherlands Journal of Sea Research* 3:68-94.
- Elderfield, H. and A. Hepworth. 1975. Diagenesis, metals, and pollution in estuaries. *Marine Pollution Bulletin* 6:85-87.
- Evans, D. W. and N. H. Cutshall. 1973. Effects of ocean water on the soluble-suspended distribution of Columbia River radio-nuclides. In: *Radioactive contamination of the marine environment*. Vienna, International Atomic Energy Agency. p. 125-140. (STI/PUB/313).
- Fanning, K. A. and M. E. Q. Pilson. 1973. The lack of inorganic removal of dissolved silica during river-ocean mixing. *Geochimica et Cosmochimica Acta* 37:2405-2415.
- Fa-Si, L., W. Yu-Duan, W. Long-Fa, and C. Ze-Hsia. 1964. Physiochemical processes of silicates in the estuarial region. I. A preliminary investigation of the distribution and variation of reactive silica content and the factors affecting them. *Oceanologia and Limnologia Sinica* 6:311-322.
- Florence, T. M. and G. E. Batley. 1975. Removal of trace metals from seawater by a chelating resin. *Talanta* 22:201-204.
- Fluorié, E. J. D. 1972. Particulate manganese in sea water stressing regimes in marine anoxic basins. Ph.D. Thesis. Seattle, University of Washington. 150 numb. leaves.
- Forster, W. O. 1972. Radioactive and stable nuclides in the Columbia River and adjacent northeast Pacific Ocean. In: *The Columbia River Estuary and adjacent ocean waters--bioenvironmental studies*, ed. by A. T. Pruter and D. L. Alverson. Seattle, University of Washington Press. p. 663-701.
- Foster, P. 1973. Ultraviolet absorption/salinity correlation as an index of pollution in inshore sea waters. *New Zealand Journal of Marine and Freshwater Research* 7:369-379.
- Foster, P. and A. W. Morris. 1971. The use of ultra-violet absorption measurements for the estimation of organic pollution in inshore sea waters. *Water Research* 5:19-27.

- Foster, P. and A. W. Morris. 1974a. Ultra-violet absorption characteristics of natural waters. *Water Research* 8:137-142.
- Foster, P. and A. W. Morris. 1974b. The winter distribution of ultraviolet absorption in the surface waters off the west coast of the British Isles. *Environmental Pollution* 7:121-132.
- Foster, P. and A. W. Morris. 1974c. The seasonal distribution of ultra-violet absorption in the surface waters of Liverpool Bay. *Estuarine and Coastal Marine Science* 2:283-290.
- Frederick, L. C. 1967. Dispersion of the Columbia River plume based on radioactivity measurements. Ph.D. Thesis. Corvallis, Oregon State University. 134 numb. leaves.
- Gadde, R. R. and H. A. Laitinen. 1974. Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Analytical Chemistry* 46:2022-2026.
- Gardner, L. R. 1974. Organic versus inorganic trace metal complexes in sulfide marine waters--some speculative calculations based on available stability constants. *Geochimica et Cosmochimica Acta* 38:1297-1302.
- Garrels, R. M. and C. L. Christ. 1965. Solutions, minerals, and equilibria. New York, Harper and Row. 450 pp.
- Genrich, D. A. 1972. Isolation and characterization of sand-, silt-, and clay-size fractions of soils. Ph.D. Thesis. Ames, Iowa State University. 255 numb. leaves.
- Gibbs, R. J. 1973. Mechanisms of trace-metal transport in rivers. *Science* 180:71-73.
- Goldberg, E. D. 1952. Iron assimilation by marine diatoms. *Biological Bulletin* (Woods Hole, Massachusetts) 102:243-248.
- Goldberg, E. D. 1954. Chemical scavengers of the sea. *Journal of Geology* 62:249-265.
- Goldberg, E. D., W. S. Broecker, M. G. Gross, and K. K. Turekian. 1971. Marine chemistry. In: *Radioactivity in the marine environment*. Washington, D.C., National Academy of Sciences. p. 137-146.

- Halcrow, W., D. W. MacKay, and I. Thornton. 1973. The distribution of trace metals and fauna in the Firth of Clyde in relation to the dispersal of sewage sludge. *J. Mar. Biol. Assoc. U.K.* 53:721-739.
- Hall, K. and G. F. Lee. 1974. Molecular size and spectral characterization of organic matter in meromictic lakes. *Water Research* 8:239-251.
- Harris, R. L., G. R. Helz, and R. L. Cory. 1975. Processes affecting the vertical distribution of trace components in the Chesapeake Bay. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 176-185. (ACS Symposium Series 18).
- Harvey, H. W. 1937. The supply of iron to diatoms. *J. Mar. Biol. Assoc. U.K.* 22:203-209.
- Head, P. C. and J. D. Burton. 1970. Molybdenum in some ocean and estuarine waters. *J. Mar. Biol. Assoc. U.K.* 50:439-448.
- Helder, W. 1974. Cycle of dissolved inorganic nitrogen compounds in the Dutch Wadden Sea. *Netherlands Journal of Sea Research* 8:154-173.
- Hem, J. D. 1972. Chemistry and occurrence of cadmium and zinc in surface water and ground water. *Water Resources Research* 8:661-679.
- Hendrix, T. J. and D. R. Young. 1974. Modeling the fates of metals in ocean-discharged waste waters. Southern California Coastal Water Research Project. Publication TM208. 32 pp.
- Hodgson, J. F. 1960. Cobalt reactions with montmorillonite. *Proceedings of the Soil Science Society of America* 24:165-168.
- Holdren, G. R., Jr., O. P. Bricker, III, and G. Matisoff. 1975. A model for the control of dissolved manganese in the interstitial waters of Chesapeake Bay. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 364-381. (ACS Symposium Series 18).

- Holliday, L. M. and P. S. Liss. 1976. The behaviour of dissolved iron, manganese, and zinc in the Beaulieu estuary, S. England, *Estuarine and Coastal Marine Science* 4:349-353.
- Hosokawa, I., F. Ohshima, and N. Kondo. 1970. On the concentration of dissolved chemical elements in the estuary water of the Chikugogawa river. *Journal of the Oceanographical Society of Japan* 26:1-5.
- Huggett, R. J., F. A. Cross, and M. E. Bender. 1975. Distribution of copper and zinc in oysters and sediments from three coastal-plain estuaries. In: *Proceedings of a Symposium on Mineral Cycling in Southeastern Ecosystems*. Augusta, Georgia, 1974. U.S. Energy Research and Development Administration, ERDA Symposium Series, CONF-740513.
- Irving, H. and R. J. P. Williams. 1953. The stability of transition metal complexes. *Journal of the Chemical Society (London)* October 1953:3192-3210.
- Jackson, M. L. 1956. Soil chemical analysis-advanced course. Madison, Department of Soil Science, University of Wisconsin.
- Jenne, E. A. 1968. Controls of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: *Trace inorganics in water*, ed. by R. F. Gould. Washington, D.C., American Chemical Society. p. 337-387.
- Jennings, C. D., J. N. Willis, III, and J. M. Lewis. 1970. Hydrography of the Newport River estuary: A preliminary report. In: *Atlantic Estuarine Fisheries Center, Annual report to the Atomic Energy Commission, 1970*. p. 66-70.
- Johnson, F. K. 1959. The sediments of the Newport River estuary, Morehead City, North Carolina. M.S. Thesis. Chapel Hill, University of North Carolina. 36 numb. leaves.
- Johnson, V. G., N. H., Cutshall and C. L. Osterberg. 1967. Retention of zinc-65 by Columbia River sediments. *Water Resources Research* 3:99-102.
- Jones, G. B. 1974. Molybdenum in a nearshore and estuarine environment, North Wales. *Estuarine and Coastal Marine Science* 2:185-189.

- Kalle, K. 1949. Fluoreszenz und gelbstoff im Bottnischen und Finnischen meerbusen. *Deutsche Hydrographische Zeitschrift* 2:117-124.
- Kester, D. R., R. H. Byrne, Jr., and Y. Liang. 1975. Redox reactions and solution complexes of iron in marine systems. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 56-79. (ACS Symposium Series 18).
- Kharkar, D. P., K. K. Turekian, and K. K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium, and cesium to the oceans. *Geochimica et Cosmochimica Acta* 32:285-298.
- Knauer, G. A. and J. H. Martin. 1973. Seasonal variations of cadmium, copper, manganese, lead, and zinc in water and phytoplankton in Monterey Bay, California. *Limnology and Oceanography* 18:597-604.
- Kobayashi, J. 1967. Silica in freshwater and estuaries. In: *Chemical environment in the aquatic habitat*, ed. by H. L. Golterman and R. S. Clymo. Maatschappig, N. V. Noord-Hollandesche Vitgeveps. p. 41-55.
- Krauskopf, K. B. 1956. Factors controlling the concentrations of thirteen rare metals in seawater. *Geochimica et Cosmochimica Acta* 9:1-32.
- Lamar, W. L. 1968. Evaluation of organic color and iron in natural surface waters. U.S. Geological Survey Professional Paper 600-D, D24-D-29.
- Lee, G. F. 1973. Role of hydrous metal oxides in the transport of heavy metals in the environment. Paper presented at the International Conference on Heavy Metals in the Aquatic Environment, Vanderbilt University, Nashville, Tennessee, December 4-7, 1973.
- Lentsch, J. W., T. J. Kneip, M. E. Wrenn, G. P. Howells, and M. Eisenbud. 1973. Stable manganese and manganese-54 distributions in the physical and biological components of the Hudson River estuary. In: *Proceedings of the Third National Symposium on Radioecology*, Oak Ridge, Tennessee, 1971, ed. by D. J. Nelson. Vol. 2. p. 752-768.

- Li, Y. H., J. Bischoff, and G. Mathieu. 1969. The migration of manganese in the Arctic basin sediments. *Earth and Planetary Science Letters* 7:265-270.
- Lindberg, S. E., A. W. Andren, and R. C. Harriss. 1975. Geochemistry of mercury in the estuarine environment. In *Estuarine research*, ed. by L. E. Cronin. New York, Academic Press. p. 64-107.
- Liss, P.S. and M. J. Pointon. 1973. Removal of dissolved boron and silicon during estuarine mixing of sea and river waters. *Geochimica et Cosmochimica Acta* 37:1493-1498.
- Liss, P. S. and C. P. Spencer. 1970. Abiological processes in the removal of silicate from sea water. *Geochimica et Cosmochimica Acta* 34:1073-1088.
- Lowman, F. G., K. K. Phelps, R. McClin, V. Romàn de Vega, I. Oliver de Padovani, and R. J. Garcia. 1966. Interactions of the environmental and biological factors on the distribution of trace elements in the marine environment. In: *Symposium on the Disposal of Radioactive Wastes into Seas, Oceans, and Surface Waters*. Vienna, International Atomic Energy Agency. p. 249-266. (STI/PUB/126).
- Lowman, F. G., T. R. Rice, and F. A. Richards. 1971. Accumulation and redistribution of radionuclides by marine organisms. In: *Radioactivity in the marine environment*. Washington, D.C., National Academy of Sciences. p. 161-199.
- Maeda, H. 1952. The relation between chlorinity and silicate concentration of water observed in some estuaries. *Publications of Seto Marine Biological Laboratory*. 2:249-255.
- Maeda, H. 1953. The relation between chlorinity and silicate concentration of water observed in some esuaries. II. *Journal of the Shimonoseki College of Fisheries* 3:167-180.
- Maeda, H. and M. Tsukamoto. 1959. The relation between chlorinity and silicate concentration of water observed in some estuaries. IV. *Journal of the Shimonoseki College of Fisheries* 8:121-134.

- Maeda, H. and K. Takesue. 1961. The relation between chlorinity and silicate concentration of water observed in some estuaries. V. Records of Oceanographic Works in Japan 6:112-119.
- Makimoto, H., H. Maeda, and S. Era. 1955. The relation between chlorinity and silicate concentration of water observed in some estuaries. III. Records of Oceanographic Works in Japan 2:106-112.
- Manheim, G. T. 1961. A geochemical profile in the Baltic Sea. *Geochimica et Cosmochimica Acta* 25:52-70.
- Martin, J. M., G. Kulbicki, and A. J. DeGroot. 1973. Terrigenous supply of radioactive and stable elements to the ocean. In: *Proceedings of a Symposium on Hydrogeochemistry and Biogeochemistry*, Tokyo, 1971. Washington, D. C., Clarke and Co. Vol. I. p. 463-483.
- Martin, J. M., O. Høgdahl, and J. C. Philippot. 1976. Rare earth element supply to the ocean. *Journal of Geophysical Research* 81:3119-3124.
- Matisoff, G., O. P. Bricker, III, G. R. Holdren, Jr., and P. Kaerk. 1975. Spatial and temporal variations in the interstitial water chemistry of Chesapeake Bay sediments. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D. C., American Chemical Society. p. 343-363. (ACS Symposium Series 18).
- Meade, R. H. 1972a. Sources and sinks of suspended matter on continental shelves. In *Shelf sediment transport*, ed. by D. J. P. Swift, D. B. Duane, and O. H. Pilkey. Stroudsburg, Dowden, Hutchinson and Ross. p. 249-262.
- Meade, R. H. 1972b. Transport and deposition of sediments in estuaries. In: *Environmental framework of coastal plain estuaries*, ed. by B. W. Nelson. Boulder, The Geological Society of America. p. 91-120. (Memoir 133).
- Millero, F. J. 1975. The physical chemistry of estuaries. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D. C., American Chemical Society. p. 25-55. (ACS Symposium Series 18).

- Milliman, J. D. and E. Boyle. 1975. Biological uptake of dissolved silica in the Amazon River estuary. *Science* 189:995-997.
- Mitchell, R. L. 1964. Trace elements in soils. In: *Chemistry of the soil* (2nd edition), ed. by F. E. Bear. New York, Reinhold, p. 320-368.
- Morel, F. and J. J. Morgan. 1972. A numerical model for computing equilibria in aqueous chemical systems. *Environmental Science and Technology* 6:58-67.
- Morel, F., R. E. McDuff, and J. J. Morgan. 1973. Interactions and chemostasis in aquatic chemical systems, role of pH, pE, solubility, and complexation. In: *Trace metals and metal-organic interactions in natural waters*, ed. by P. C. Singer. Ann Arbor, Ann Arbor Science Publishers. p. 157-200.
- Morgan, J. J. 1967. Chemical equilibria and kinetic properties of manganese in natural waters. In: *Principles and applications of water chemistry*, ed. by S. D. Faust and J. V. Hunter. New York, Wiley. p. 561-624.
- Morgan, J. J. and W. Stumm. 1965. Role of multivalent hydrous metal oxides on limnological transformations, as exemplified by iron and manganese. In: *Advances in water pollution research*, ed. by O. Joag. New York, Pergamon Press. Vol. I. p. 103-132.
- Morris, A. W. 1971. Trace metal variations in sea water of the Menai Straits caused by a bloom of Phaeocystis. *Nature* 233: 427-428.
- Mortimer, C. H. 1971. Chemical exchanges between sediments and water in the Great Lakes--speculations on probable regulatory mechanisms. *Limnology and Oceanography* 16:387-404.
- Müller, G. and U. Förstner. 1975. Heavy metals in sediments of the Rhine and Elbe estuaries: mobilization or mixing effects? *Environmental Geology* 1:33-39.
- Murata, K. J. 1939. Manganese in river and ocean muds. *American Journal of Science* 237:725-735.

- Murray, C. N. and L. Murray. 1973. Adsorption-desorption equilibria of some radionuclides in sediment-freshwater and sediment-seawater systems. In *Radioactive contamination of the marine environment*. Vienna, International Atomic Energy Agency. p. 105-124. (STI/PUB/313).
- Neihof, R. A. and G. I. Loeb. 1972. The surface charge of particulate matter in seawater. *Limnology and Oceanography* 17:7-16.
- O'Connors, H. B. and I. W. Duedall. 1975. Seasonal variations in sources, concentrations, and impacts of ammonium in the New York Bight apex. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 636-663. (ACS Symposium Series 18).
- Okabe, S. 1973. Molybdenum, vanadium, and manganese dioxide particles in Suruga Bay. *Journal of the Faculty of Marine Science and Technology, Tokai University* 7:119-129.
- Ormerod, J. G. 1966. A simple method for detection of oxidized manganese in particles on membrane filters. *Limnology and Oceanography* 11:635-636.
- Park, P. K., M. J. George, Y. Miyake, K. Saruhashi, Y. Katsauri, and T. Kanzawa. 1965. Strontium-90 and cesium-137 in the Columbia River plume, July 1964. *Nature* 208:1084-1085.
- Park, P. K., C. L. Osterberg, and W. O. Forster. 1972. Chemical budget of the Columbia River. In: *The Columbia River estuary and adjacent ocean waters--bioenvironmental studies*, ed. by A. T. Pruter and D. L. Alverson. Seattle, University of Washington Press. p. 123-134.
- Parker, P. L. 1962. Zinc in a Texas bay. *Publications of the Institute of Marine Science, University of Texas* 8:75-79.
- Parker, P. L., A. Gibbs, and R. Lawler. 1963. Cobalt, iron, and manganese in a Texas bay. *Publications of the Institute of Marine Science, University of Texas* 9:28-32.
- Parks, G. A. 1975. Adsorption in the marine environment. In: *Chemical oceanography* (2nd edition), ed. by J. P. Riley and G. Skirrow. London, Academic Press. Vol. I. p. 241-308.

- Pequegnat, J. E. 1975. Trace metals in phytoplankton in an area of coastal upwelling. Ph.D. Thesis. Corvallis, Oregon State University. 100 numb. leaves.
- Peterson, D. H., T. J. Conomos, W. W. Broenkow, and E. P. Scrivani. 1975. Processes controlling the dissolved silica distribution in San Francisco Bay. In: Estuarine research, ed. by L. E. Cronin. New York, Academic Press. Vol. I. p. 153-187.
- Postma, H. 1967. Sediment transport and sedimentation in the estuarine environment. In: Estuaries, ed. by G. H. Lauff. Washington, D.C., American Association for the Advancement of Science. p. 158-179. (AAAS Publication 83).
- Presley, B. J., Y. Kolodny, A. Nissenbaum, and I. R. Kaplan. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia--II. Trace element distribution in interstitial water and sediment. *Geochimica et Cosmochimica Acta* 36:1073-1089.
- Presley, B. J., R. R. Brooks, and I. R. Kaplan. 1967. Manganese and related elements in the interstitial water of marine sediments. *Science* 158:906-910.
- Price, T. J., G. W. Thayer, and G. B. Montgomery. 1974. Analysis of the invertebrates and sediments along shore-to-shore transects in the Newport River estuary. In: Atlantic Estuarine Fisheries Center, Annual report to the Atomic Energy Commission, 1974. p. 183-198.
- Pytkowicz, R. M. 1971. On the apparent oxygen utilization and preformed phosphate in the oceans. *Limnology and Oceanography* 16:39-42.
- Rashid, M. A. 1974. Adsorption of metals on sedimentary and peat humic acids. *Chemical Geology* 13:115-123.
- Renfro, W. C. 1973. Seasonal radionuclide inventories in Alder Slough, an ecosystem in the Columbia River estuary. In: Proceedings of the Third National Symposium on Radioecology, Oak Ridge, Tennessee, 1971, ed. by D. J. Nelson. Vol. 2. p. 738-746.

- Riley, J. P. and D. Taylor. 1968. Chelating resins for the concentration of trace elements from sea water and their analytical use in conjunction with atomic absorption spectrophotometry. *Analytica Chimica Acta* 40:479-485.
- Robertson, D. E. 1968. Role of contamination in trace element analysis of sea water. *Analytical Chemistry* 40:1067-1072.
- Robertson, D. E., W. B. Silker, J. C. Langford, M. R. Peterson, and R. W. Perkins. 1973. Transport and depletion of radio-nuclides in the Columbia River. In: *Radioactive contamination of the marine environment*. Vienna, International Atomic Energy Agency. p. 141-158. (STI/PUB/313).
- Sanders, J. G. 1975. Variation and concentrations of manganese and phytoplankton in Calico Creek, North Carolina. M.S. Thesis. Chapel Hill, University of North Carolina. 55 numb. leaves.
- Sankaranarayanan, V. N. and C. V. G. Reddy. 1973. Copper content in the inshore and estuarine waters along the west coast of India. *Current Science* 42:223-224.
- Serne, R. J. and B. W. Mercer. 1975. Characterization of San Francisco Bay dredge sediments--crystalline matrix study. Final report to the U.S. Army Engineer District, San Francisco, California. Contract Number DACWO7-73-0080. 215 pp. Dredge Disposal Study San Francisco Bay and Estuary. Appendix F. Crystalline Matrix Study.
- Settlemyre, J. L. and L. R. Gardner. 1975. A field study of chemical budgets for a small tidal creek--Charleston Harbor, S.C. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. New York, American Chemical Society. p. 152-175. (ACS Symposium Series 18).
- Shapiro, J. 1964. Effect of yellow organic acids on iron and other metals in water. *Journal of the American Water Works Association* 56:1062-1082.
- Sholkovitz, E. R. 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. *Geochimica et Cosmochimica Acta* 40:831-845.

- Sieburth, J. M. and A. Jensen. 1968. Studies on algal substances in the sea. I. Gelbstoff (humic material) in terrestrial and marine waters. *Journal of Experimental Marine Biology and Ecology* 2:174-189.
- Sillén, L. G. 1961. The physical chemistry of sea water. In: *Oceanography*, ed. by M. Sears. Washington, D.C., American Association for the Advancement of Science. p. 549-582.
- Simpson, H. J., D. E. Hammond, B. L. Deck, and S. C. Williams. 1975. Nutrient budget in the Hudson River estuary. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 618-635. (ACS Symposium Series 18).
- Slowey, J. F. and D. W. Hood. 1971. Copper, manganese, and zinc concentrations in Gulf of Mexico waters. *Geochimica et Cosmochimica Acta* 35:121-138.
- Southern California Coastal Water Research Project. 1973. The ecology of the Southern California Bight: Implications for water quality management. Southern California Coastal Water Research Project, 1500 East Imperial Highway, El Segundo California. (SCCWRP TR104).
- Spencer, C. P. 1958. The chemistry of ethylenediamine tetraacetic acid in seawater. *J. Mar. Biol. Assoc. U.K.* 37:127-144.
- Spencer, D. W. and P. G. Brewer. 1969. The distribution of copper, zinc, and nickel in seawater of the Gulf of Maine and the Sargasso Sea. *Geochimica et Cosmochimica Acta* 33: 325-339.
- Spencer, D. W. and P. G. Brewer. 1971. Vertical advection diffusion and redox potential as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. *Journal of Geophysical Research* 76:5877-5892.
- Stefánsson, U. and F. A. Richards. 1963. Processes contributing to the nutrient distribution off the Columbia River and Strait of Juan de Fuca. *Limnology and Oceanography* 8:394-410.
- Stumm, W. and P. A. Brauner. 1975. Chemical speciation. In: *Chemical oceanography* (2nd edition), ed. by J. P. Riley and G. Skirrow. London, Academic Press. Vol. I. p. 173-240.

- Stumm, W. and J. J. Morgan. 1970. Aquatic chemistry. New York, Wiley-Interscience. 582 pp.
- Sunda, W. G. 1976. Atlantic Estuarine Fisheries Center, Beaufort, North Carolina. Personal communication.
- Sundararaj, V. and K. Krishnamurthy. 1972. The distribution of copper in Porto Novo waters. *Current Science* 41:315-317.
- Theis, T. L. and P. C. Singer. 1973. The stabilization of ferrous iron by organic compounds in natural waters. In: Trace metals and metal-organic interactions in natural waters, ed. by P. C. Singer. Ann Arbor, Ann Arbor Science Publishers. p. 303-320.
- Troup, B. N. and O. P. Bricker, III. 1975. Processes affecting the transport of materials from continents to oceans. In: Marine chemistry in the coastal environment, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 133-151. (ACS Symposium Series 18).
- Van Bennekom, A. J., E. Krijgsman-Van Hertingsveld, G. C. M. Van Der Veer, and H. F. J. Van Voorst. 1974. The seasonal cycle of reactive silicate and suspended diatoms in the Dutch Wadden Sea. *Netherlands Journal of Sea Research* 8:174-207.
- Warner, T. B. 1972. Mixing model predictions of fluoride distributions in Chesapeake Bay. *Journal of Geophysical Research* 77:2728-2732.
- Wedepohl, K. H. (ed.). 1969-. Handbook of geochemistry. Berlin, Springer-Verlag. Vol. II-3, p. 30-H-2. Vol. II-4, p. 29-H-2.
- Wiklander, L. 1964. Cation and anion exchange phenomena. In: Chemistry of the soil (2nd edition), ed. by F. E. Bear. New York, Reinhold. p. 163-205.
- Williams, R. B. and M. B. Murdoch. 1972. The rate of sedimentation in salt marshes near Beaufort, N.C. In: Atlantic Estuarine Fisheries Center, Annual report to the Atomic Energy Commission, 1972. p. 278-292.
- Windom, H. L., K. C. Beck, and R. Smith. 1971. Transport of trace metals to the Atlantic Ocean by three southeastern rivers. *Southeastern Geology* 12:169-181.

- Windom, H. L. 1975. Heavy metal fluxes through salt marsh estuaries. In: *Estuarine research*, ed. by L. E. Cronin. New York, Academic Press. Vol. I. p. 137-152.
- Wolfe, D. A. 1975. The estuarine ecosystem(s) at Beaufort, North Carolina. In: *Estuarine research*, ed. by L. E. Cronin. New York, Academic Press. p. 645-671.
- Wolfe, D. A., F. A. Cross, and C. D. Jennings. 1973. The flux of Mn, Fe, and Zn in an estuarine ecosystem. In: *Radioactive contamination of the marine environment*. Vienna, International Atomic Energy Agency. p. 159-176. (STI/PUB/313).
- Wolfe, D. A., W. O. Forster, R. McClintock, and F. G. Lowman. 1975. Trace element interactions in the estuarine zone of the Añasco River, Puerto Rico. In: *Combined effects of radioactive, chemical, and thermal releases to the environment*. Vienna, International Atomic Energy Agency. p. 155-178.
- Wollast, R. and F. DeBroew. 1971. Study of the behavior of dissolved silica in the estuary of the Scheldt. *Geochimica et Cosmochimica Acta* 35:613-620.
- Yentsch, C. S. 1975. New England coastal waters--an infinite estuary. In: *Marine chemistry in the coastal environment*, ed. by T. M. Church. Washington, D.C., American Chemical Society. p. 608-617. (ACS Symposium Series 18).
- Zimmerman, J. T. F. and J. W. Rommets. 1974. Natural fluorescence as a tracer in the Dutch Wadden Sea and adjacent North Sea. *Netherlands Journal of Sea Research* 8:117-125.
- Zirino, A. and S. Yamamoto. 1972. A pH-dependent model for the chemical speciation of copper, zinc, cadmium, and lead in seawater. *Limnology and Oceanography* 17:661-671.

APPENDICES

APPENDIX A

Chelex-100 Extraction and Graphite Furnace Analysis

Apparent Efficiencies of Extraction and Analysis

Chelex-100 resin extracts of seawater and deionized distilled water (DDW), containing Mn, Fe, Cu, and Zn standards, produce apparent recoveries of less than 100% when analyzed by the graphite furnace-atomic absorption technique. This apparent lack of complete recovery is an analytical artifact of atomization rather than a result of incomplete extraction and elution of the metals from the resin.

Figure 22 shows Mn in DDW standards analyzed by the graphite furnace plotted against the same standards extracted by Chelex-100 resin. The slope is 0.84, which might be taken to indicate that only 84% of the Mn in the standards was recovered. However, when radioactive tracers of ^{54}Mn and ^{65}Zn in seawater and DDW were carried through the same extraction and analyzed by gamma-ray spectrometry, greater than 95% recovery was achieved. This suggests that the graphite furnace atomization analysis step rather than the Chelex-100 extraction is the cause of the apparent incomplete recovery.

Graphite furnace analyses of trace metals are sensitive to the sample matrix. Dissolved salts in the sample usually suppress the

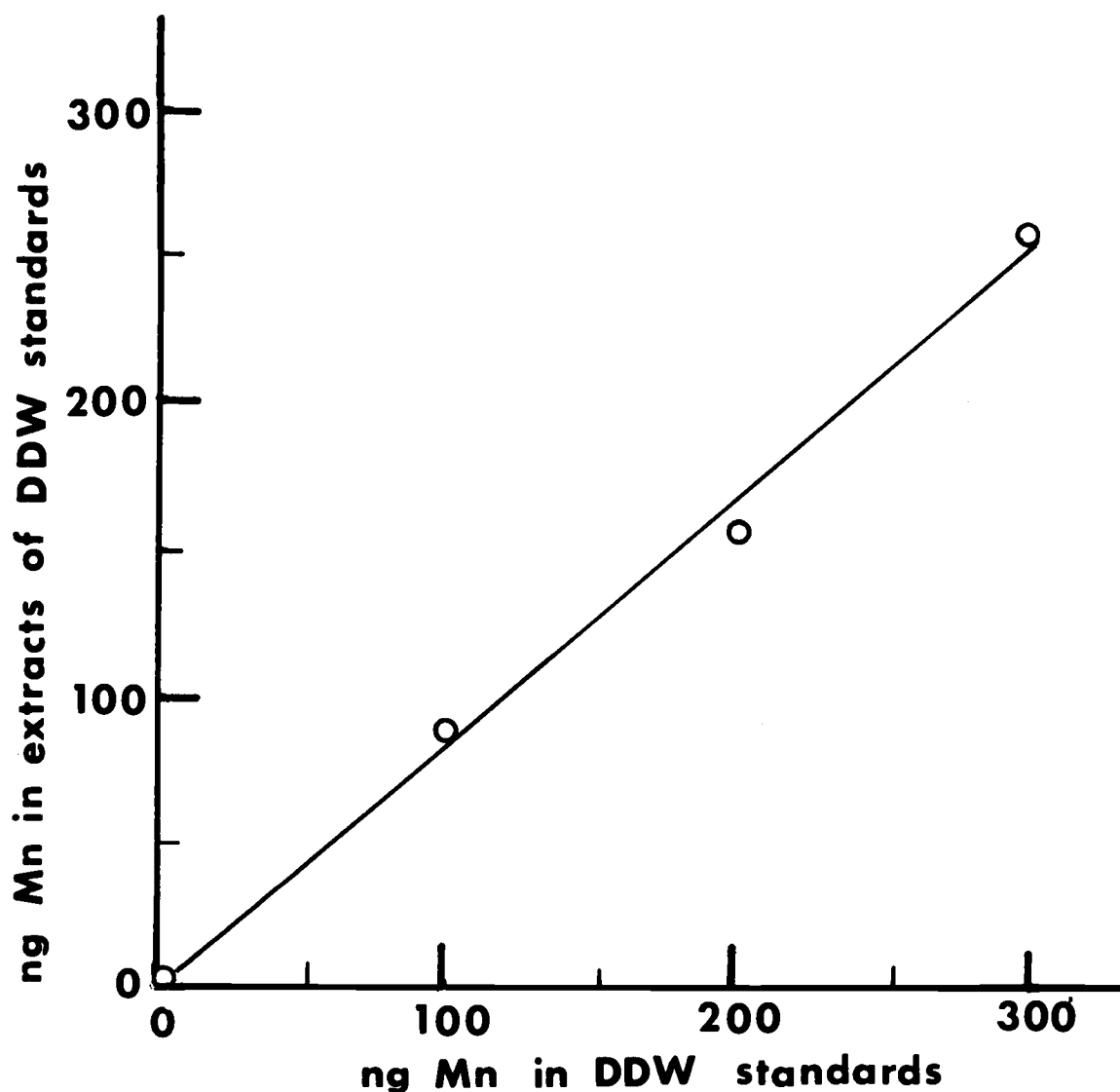


Figure 22. Analysis of Chelex-100 extracts of Mn standards by flameless graphite furnace-atomic absorption spectrophotometry compared to the direct analysis of the same standards in deionized distilled water by the same method. The slope of 0.84 shows the "apparent" recovery of only 84% which is due to interferences by coextracted elements.

atomization signal of the metal and result in apparent lower concentrations (Cruz and Van Loon, 1974; Clark et al., 1973). Chelex-100 resin preferentially extracts trace metal ions over alkali and alkaline earth ions, but does extract the latter. These latter ions are the probable cause of the suppressed atomization and low apparent analytical efficiency.

The apparent recovery of metals differs in extracts of seawater standards and of DDW standards. The two types of Chelex-100 extracts probably have different matrices. Figure 23 shows the apparent recovery of Mn in Chelex-100 extracts of standards in different salinities as measured by the graphite furnace analysis. Freshwater and low salinity standards have lower apparent recoveries than the more saline standards. The figure also shows the Na, Ca, and Mg concentrations in the extracts. Sodium was introduced into the standards as NaHCO_3 in buffering the solutions prior to extraction. This explains its presence in the zero salinity standards. The increase in apparent recovery between 0 ‰ and 2.8 ‰ salinity coincides with a decrease in Na in the extracts and an increase in Ca and Mg. The Chelex-100 resin preferentially extracts divalent Ca and Mg over monovalent Na. Sodium seems to suppress the Mn atomization signal in the graphite furnace more than Ca and Mg. As Ca and Mg replace Na in the extracts,

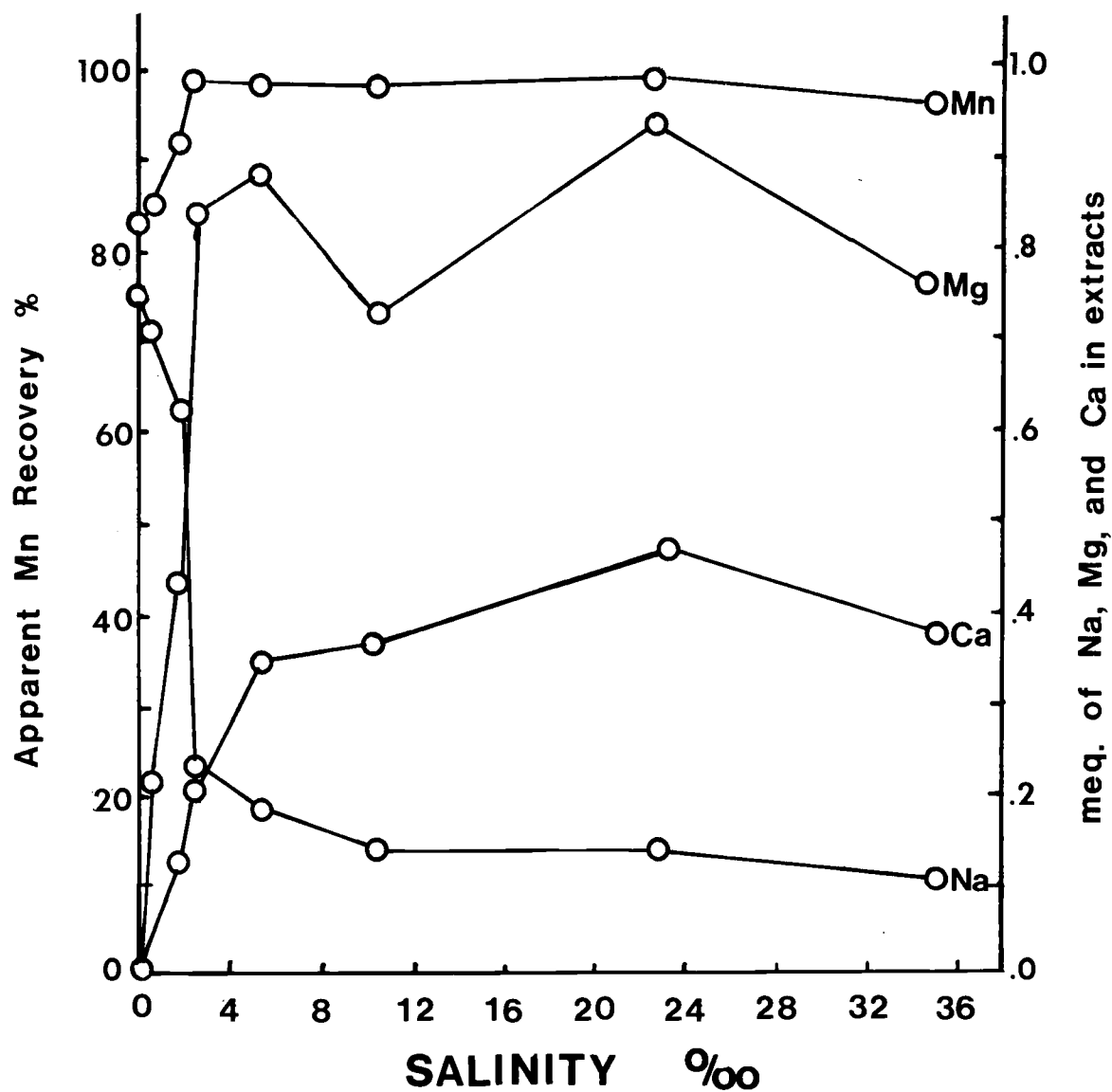


Figure 23. Relationship of "apparent" Mn recovery to the concentration of coextracted Na, Ca, and Mg in the Chelex-100 extracts at various salinities.

suppression is reduced but not eliminated. Both Ca and Mg are nearly constant in the extracts above 2.8 ‰ salinity as is the apparent Mn recovery. The resin is effectively saturated with Ca and Mg on most of its exchange sites above 2.8 ‰ salinity, when using 100 ml samples. Apparent recovery of Mn is 84% at zero salinity, 95% at greater than 2.8 ‰ salinity, with a linear transition in between. This makes possible an easily calculated correction for apparent recovery based on the salinity of the sample.

Copper and zinc show similar behavior, with 77% and 81% apparent recoveries respectively from DDW and 87% and 95% apparent recoveries from seawater of greater than 2.8 ‰ salinity, with a linear transition between 0 ‰ and 2.8 ‰ salinity. Iron has an apparent recovery of 84% at all salinities.

Distinction of Chemical Form by Chelex-100 Resin Extraction

Chelex-100 resin extracts metals by chelation of their ions. Metals bound strongly to organics or other non-ionic forms are not readily extracted. Florence and Batley (1975) found that Zn, Cd, and Pb bound to organic chelates or colloids were not extracted by Chelex-100 resin. About 20-40% of bound Cu was extracted. This points out the need for the $K_2S_2O_8$ oxidation discussed under Methods and Materials in order to change the organically bound metals to an extractable form.

Table 14 shows the concentrations of Mn, Fe, and Cu in extracts of Newport River water (collected April 23, 1975). Aliquots of a pooled filtered sample were extracted by Chelex-100 resin and analyzed by graphite furnace atomic absorption spectrophotometry after $K_2S_2O_8$ oxidation (the normal procedure) and without prior oxidation. Zinc was not analyzed because of a contamination problem. Manganese, iron, and copper all showed higher concentrations in the oxidized samples than in the unoxidized ones. One can infer that about 52% of the dissolved Mn, 94% of the dissolved Fe, and 76% of the dissolved Cu in the river at this time was bound to organic chelates or colloids not extractable by Chelex-100 resin.

Table 14. Analysis of Newport River water for dissolved Mn, Fe, and Cu by Chelex-100 extraction with and without $K_2S_2O_8$ oxidation of organic matter. All values as $\mu\text{g/l}$.

Sample treatment	Mn	Fe	Cu
Oxidized	2.5	64	9.7
	2.5	71	10.4
	2.6	66	10.2
	2.5	67	10.6
Unoxidized	1.2	4.2	2.2
	1.2	4.5	2.5

Analytical Accuracy and Precision of the Methods

Dissolved Analyses

Shown in Table 15 are results of Chelex-100 extraction and analyses of aliquots of a filtered seawater sample collected from the AEFC dock, April 23, 1975. These, together with the analyses in Table 14 give an idea of the precision of the analytical method. Further imprecision is introduced by filtering samples in the field. The analytical precision incorporating the effects of filtration can be seen in the samples from the R/V Eastward cruise in which duplicate samples were taken from the same Niskin bottle before filtration and analysis (Table 21). Duplicate samples from the estuary transects and river and ocean input sampling are not true duplicates because slightly different parcels of water were sampled as the boat drifted. Analytical precisions estimated from variability of these "duplicates" (Table 20) are therefore exaggerated.

Accuracy of the method was more difficult to obtain because no certified standards were available. Water samples from a previous trace elements in seawater intercalibration were on hand and provided an approximate substitute. The results of analyses on these samples are shown in Table 16. In parentheses are analyses of Zn on the same samples as part of the intercalibration carried out earlier by Jim Willis of the Atlantic Estuarine Fisheries Center.

Table 15. Reproducibility of dissolved and suspended particulate analyses of seawater from AEFC dock for Mn, Fe, Cu, and Zn. Dissolved analyses are in $\mu\text{g/l}$. Particulate analyses are in $\mu\text{g/g}$ except Fe in mg/g .

Sample type	Mn	Fe	Cu	Zn
Dissolved	5.5	2.0	0.8	0.24
	5.7	1.3	1.0	0.27
	6.0	1.2	0.8	0.26
Particulate	222	31	30	185?
	155	32	26	24
	209	30	23	41
	105	31	31	22
	125	26	19	20

Table 16. Concentrations of Mn, Fe, Cu, and Zn in water samples from a trace metal intercalibration analyzed by Chelex-100 extraction and graphite furnace-atomic absorption spectrophotometry. Numbers in parentheses are analyses by dithizone/chloroform extraction-spectrometry. Numbers in brackets are median values reported among many laboratories using various methods of analysis as part of the intercalibration. All values as $\mu\text{g/l}$.

Sample	Mn	Fe	Cu	Zn
3-30	0.16	13.5	1.1	5.5(5.2)
3-49	0.19	14.9	1.5	6.4(6.1)
3-55	0.18	15.9	1.3	5.4(6.6)
	[0.2]	[14.7]	[1.4]	[5.5]
1-69	0.09	6.3	1.0	3.3
1-50	0.09	6.2	1.0	3.2
1-33	0.09	5.4	1.0	3.2
	[0.85?]	[7.7]	[1.5]	[4.4]

The technique used in that case was dithizone extraction into chloroform with spectrometric analysis. A close correspondence is found. The results of the intercalibration reported in Brewer and Spencer (1970) cover an appallingly wide range among the various laboratories, often more than an order of magnitude. The numbers in brackets in Table 16 are the median values reported among all the laboratories. This is thought to be the best estimate of the true value under the circumstances. Comparison with my analyses are gratifyingly close.

Detection limits of my technique are limited by the variability of the blanks which results from reagent and filtration contamination. Table 17 shows the total process blank and its variability for each of the metals analyzed. Detection limits assuming 100 ml samples are calculated using \pm three standard deviations.

Table 17. Analytical blanks of dissolved and suspended particulate Mn, Fe, Cu, and Zn: means \pm one standard deviation in units of ng/sample. Shown in parentheses is the detection limit as three standard deviations, assuming a 100 ml sample for dissolved analyses and a one mg sample for particulate analyses.

Sample Type	Mn	Fe	Cu	Zn
Dissolved	2 ± 1 (0.03 $\mu\text{g/l}$)	162 ± 15 (0.45 $\mu\text{g/l}$)	48 ± 13 (0.39 $\mu\text{g/l}$)	33 ± 8 (0.24 $\mu\text{g/l}$)
Particulate	3 ± 1 (3 $\mu\text{g/g}$)	233 ± 122 (0.4 mg/g)	30 ± 12 (36 $\mu\text{g/g}$)	30 ± 4 (12 $\mu\text{g/g}$)

Particulate Analyses

Table 18 shows the results of analyses of NBS reference bovine liver standards (SRM 1577) by the HNO_3 -HF digestion method discussed in the Methods and Materials section. Samples were about 20 mg. In parentheses are the certified values. Analyses of Mn, Fe, and Cu seem about 10% to 20% low; Zn analyses are close to the certified value.

Table 18. Analyses of NBS bovine liver standards after HNO_3 -HF digestion. Certified values are shown in parentheses. All values are $\mu\text{g/g}$.

	Mn	Fe	Cu	Zn
Samples	9.2	246	176	130
	8.5	244	191	140
	7.7	169	142	107
	8.8	225	183	136
Mean \pm one std. dev.	8.6 \pm 0.6	221 \pm 36	173 \pm 22	128 \pm 15
NBS certified values	(10.3 \pm 1.0)	(270 \pm 20)	(193 \pm 10)	(130 \pm 10)

Suspensions of kaolinite were collected on Nuclepore filters as described for actual estuarine samples and analyzed in the same way. About 3 mg of kaolinite were collected on each filter for analysis. Table 19 shows the measured results and provides an indication of analytical precision under near normal sampling

conditions. Sample inhomogeneities probably exaggerate the observed variability. Other impressions of the variability of particulate analyses can be gained from replicates of the R/V Eastward cruise and the estuary transects and ocean and river input samplings (Tables 20, 21). The same caveats about the precision estimates that applied to dissolved trace metal analysis are applicable here.

Table 19. Reproducibility of analyses of kaolinite suspensions collected on Nuclepore filters and analyzed for Mn, Fe, Cu, and Zn after HNO_3 -HF digestion. All values are $\mu\text{g/g}$.

Mn	Fe	Cu	Zn
69	3050	6	61
70	3080	5	56
71	3890	5	81

As for dissolved trace metals, blank variability determines the method's detection limit. Table 17 shows these.

Finally, Zn and Cu seem to have high blanks in the filters. There is evidence that some of this filter-derived contamination can be leached by DDW washing, contributing to filtrate contamination. Prewashing of filters with DDW is advisable.

APPENDIX B

Table 20 shows the numerical data from the estuary transects, river input, and at the AEFC dock for October, 1974, February, 1975, and April, 1975. Column abbreviations and units are described below.

Date:	Day, month, year.
Time:	Hour, minutes.
Km:	Location in the estuary, in kilometers upstream from the mouth of the Newport River, where it widens into the estuary. Cross Rock is at km -2.2, AEFC dock at km -14.2.
S ^{°/∞} :	Salinity in ^{°/∞} .
T:	Temperature in [°] C.
DO:	Dissolved oxygen in ml/l.
pH:	
UVOrg:	UV absorbance as sum of absorbances at 250 nm, 300 nm, and 350 nm in a 1 cm cell.
Susp:	Weight of suspended matter collected for trace metal analysis as mg.
Volume:	Volume of sample collected for dissolved trace metal analysis as ml.

MnDiss:	Concentration of dissolved Mn in $\mu\text{g/l}$.
FeDiss:	Concentration of dissolved Fe in $\mu\text{g/l}$.
CuDiss:	Concentration of dissolved Cu in $\mu\text{g/l}$.
ZnDiss:	Concentration of dissolved Zn in $\mu\text{g/l}$.
MnSusp:	Concentration of suspended particulate Mn in $\mu\text{g/l}$.
FeSusp:	Concentration of suspended particulate Fe in $\mu\text{g/l}$.
CuSusp:	Concentration of suspended particulate Cu in $\mu\text{g/l}$.
ZnSusp:	Concentration of suspended particulate Zn in $\mu\text{g/l}$.
MnPart:	Concentration of Mn on suspended particulate matter in $\mu\text{g/g}$.
FePart:	Concentration of Fe on suspended particulate matter in mg/g .
CuPart:	Concentration of Cu on suspended particulate matter in $\mu\text{g/g}$.
ZnPart:	Concentration of Zn on suspended particulate matter in $\mu\text{g/g}$.
ND:	No data.
BDL:	Below detection limit.
*:	Outlying sample value suspected of contamination and therefore deleted from graphs and statistical analyses.

Table 20a. River input, October, 1974.

Date	Time	Km	S ^o /oo	T ^o C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part mg/g	Cu Part µg/g	Zn Part µg/g
081074	1330	12.0	0.0	ND	6.0	6.5	ND	0.57	96	4.4	ND	0.6	0.8	0.4	ND	0.1	1.4	80	ND	19	230
081074	1330	12.0	0.0	ND	6.0	6.5	ND	0.59	88	3.9	ND	0.9	0.8	0.5	ND	0.2	0.8	80	ND	27	120
091074	1400	12.0	0.0	17.0	6.0	6.6	ND	0.88	210	5.4	ND	0.7	1.6	0.4	ND	0.1	0.2	90	ND	27	50
091074	1400	12.0	0.0	17.0	6.0	6.6	ND	1.10	95	4.1	ND	0.6	0.3	0.7	ND	0.2	1.4	60	ND	15	120
111074	1330	12.0	0.0	16.2	8.4	6.2	ND	0.28	97	4.8	ND	0.5	0.2	0.2	ND	0.1	0.1	70	ND	50	20
111074	1330	12.0	0.0	16.2	8.4	6.2	ND	2.00	96	5.3	ND	0.6	0.5	4.4	ND	0.2	1.9	210	ND	10	90
151074	1330	12.0	0.0	18.3	6.1	6.5	ND	0.88	81	6.5	ND	0.6	0.9	0.9	ND	0.1	0.8	80	ND	14	70
151074	1330	12.0	0.0	18.3	6.1	6.5	ND	0.80	109	7.6	ND	0.8	1.0	0.7	ND	0.2	0.7	90	ND	26	100
161074	1030	12.0	0.0	19.0	6.0	6.6	ND	1.14	93	6.8	ND	0.5	0.4	2.1	ND	0.2	1.1	170	ND	18	85
161074	1030	12.0	0.0	19.0	6.0	6.6	ND	1.07	103	5.5	ND	0.6	1.2	2.0	ND	0.3	1.0	190	ND	24	100
171074	1030	12.0	0.0	19.6	3.8	6.5	1.88	1.84	97	10.9	ND	0.7	5.6*	2.0	ND	0.2	1.2	110	ND	12	65
171074	1030	12.0	0.0	19.6	3.8	6.5	1.93	1.11	96	8.0	ND	0.5	0.3	1.5	ND	0.3	0.5	130	ND	29	40
181074	1030	12.0	0.0	18.3	5.9	6.6	1.94	2.87	82	13.4	ND	0.8	0.8	2.7	ND	1.8*	2.5	80	ND	52	70
181074	1030	12.0	0.0	18.3	5.9	6.6	1.94	1.10	92	13.6	ND	0.5	13.2*	2.0	ND	0.1	0.6	170	ND	12	45
211074	1030	12.0	0.0	10.8	7.0	6.5	2.13	1.18	130	10.2	ND	0.6	1.3	0.3	ND	0.1	0.3	40	ND	14	35
211074	1030	12.0	0.0	10.8	7.0	6.5	2.12	1.32	131	8.9	ND	0.3	0.7	0.3	ND	0.1	0.2	30	ND	9	20
221074	1330	12.0	0.0	11.3	ND	6.3	1.78	2.06	115	9.5	ND	0.4	1.4	0.8	ND	0.1	0.5	40	ND	6	25
221074	1330	12.0	0.0	11.3	ND	6.3	1.39	0.74	115	7.3	ND	0.2	0.6	0.2	ND	0.1	1.3	40	ND	14	195
231074	1345	12.0	0.0	ND	7.6	6.2	2.02	0.42	349	8.0	ND	ND	0.5	0.0	ND	0.0	0.1	40	ND	31	95
231074	1345	12.0	0.0	ND	7.6	6.2	1.99	0.57	144	9.6	ND	0.1	1.4	0.1	ND	0.0	0.1	30	ND	9	30
251074	1345	12.0	0.0	12.3	5.6	6.2	2.00	0.50	143	6.5	ND	0.1	0.5	0.1	ND	0.0	0.2	40	ND	10	50
251074	1345	12.0	0.0	12.3	5.6	6.2	2.06	0.78	150	7.1	ND	0.0	0.5	0.6	ND	0.1	0.4	120	ND	24	75
291074	1345	12.0	0.0	16.2	6.0	6.6	1.90	0.45	116	10.9	ND	0.2	0.7	0.7	ND	0.4	0.6	190	ND	111	165
291074	1345	12.0	0.0	16.2	6.0	6.6	1.76	1.02	107	9.6	ND	0.1	2.0	2.9	ND	0.2	0.9	300	ND	18	90

Table 20b. AEFC dock, October, 1974.

Date	Time	Km	S ^o /∞	T ^o °C	ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part. mg/g	Cu Part. µg/g	Zn Part. µg/g
101074	1500	-14.2	32.6	19.0	7.4	8.0	ND	1.91	323	1.3	ND	0.4	0.1	2.4	ND	0.1	0.5	400	ND	14	90
101074	1500	-14.2	32.6	19.0	7.4	8.0	ND	0.94	320	1.3	ND	0.2	0.0	1.9	ND	0.2	0.5	660	ND	56	170
151074	1500	-14.2	32.1	21.8	8.3	8.0	ND	1.68	274	2.6	ND	0.3	0.2	3.6	ND	0.2	1.0	580	ND	36	160
151074	1500	-14.2	32.1	21.8	8.3	8.0	ND	3.18	286	1.7	ND	0.3	0.1	3.7	ND	0.3	1.1	330	ND	30	105
181074	1330	-14.2	33.1	21.8	8.5	8.0	0.10	2.82	319	1.0	ND	0.2	0.1	3.7	ND	0.2	0.8	420	ND	20	90
181074	1330	-14.2	33.1	21.8	8.5	8.0	0.07	2.25	303	1.5	ND	0.2	0.1	3.2	ND	0.3	0.9	440	ND	36	120
211074	1330	-14.2	32.3	15.2	7.3	8.0	0.11	1.26	312	1.3	ND	0.3	0.1	2.5	ND	0.1	0.6	620	ND	33	135
211074	1330	-14.2	32.3	15.2	7.3	8.0	0.09	1.73	299	0.9	ND	0.2	0.0	2.6	ND	0.1	0.5	450	ND	17	80
251074	1100	-14.2	32.2	16.4	7.8	8.1	0.11	2.11	308	2.8	ND	0.4	3.3*	1.9	ND	0.2	1.3	280	ND	31	190
251074	1100	-14.2	32.2	16.4	7.8	8.1	0.10	3.12	322	2.9	ND	0.3	0.3	3.1	ND	0.4	0.8	320	ND	46	85
291074	1530	-14.2	32.3	19.1	7.7	8.0	0.14	1.28	374	2.5	ND	0.3	0.2	1.3	ND	0.2	0.6	380	ND	57	175
291074	1530	-14.2	32.3	19.1	7.7	8.0	0.13	1.76	378	2.6	ND	0.3	0.3	1.6	ND	0.1	0.7	350	ND	27	140

Table 20c. Estuary transects, October, 1974.

Date	Time	Km	S ^o /oo	T ^o C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part. mg/g	Cu Part. µg/g	Zn Part. µg/g
301074	0904	6.8	1.1	16.6	8.5	6.5	1.60	ND	91	14.1	ND	0.2	1.5	ND	ND	ND	ND	ND	ND	ND	ND
301074	0904	6.8	1.1	16.6	8.5	6.5	1.60	1.94	80	14.8	ND	0.5	0.2	5.4	ND	0.6	2.8	220	ND	24	115
301074	0931	8.6	0.0	16.4	7.0	6.4	1.60	0.82	69	9.2	ND	0.0	0.0	2.7	ND	0.7	1.9	230	ND	61	165
301074	0931	8.6	0.0	16.4	7.0	6.4	1.60	ND	52	9.8	ND	0.3	0.0	0.9	ND	0.1	0.7	ND	ND	ND	ND
301074	0957	6.3	1.2	17.3	ND	6.8	1.56	0.90	55	15.9	ND	0.3	0.1	3.2	ND	0.9	2.4	200	ND	52	145
301074	0957	6.3	1.2	17.3	ND	6.8	1.56	1.46	102	14.8	ND	0.3	0.3	2.7	ND	0.2	1.4	190	ND	16	95
301074	1020	4.6	4.9	17.7	7.0	7.1	1.44	1.45	119	17.0	ND	0.4	0.3	3.4	ND	0.3	1.6	280	ND	23	130
301074	1020	4.6	4.9	17.7	7.0	7.1	1.44	0.80	66	18.8	ND	0.7	0.3	2.8	ND	0.0	1.1	230	ND	1	90
301074	1036	3.0	7.8	18.0	7.5	7.3	1.24	1.14	78	19.5	ND	0.6	3.6*	3.7	ND	0.2	1.3	260	ND	13	90
301074	1036	3.0	7.8	18.0	7.5	7.3	1.24	1.38	73	18.7	ND	0.5	0.1	5.5	ND	0.2	1.7	290	ND	9	90
301074	1100	1.3	11.4	18.7	7.6	7.4	1.08	0.62	74	18.4	ND	0.7	0.4	2.9	ND	0.1	0.9	350	ND	8	105
301074	1100	1.3	11.4	18.7	7.6	7.4	1.08	0.90	76	16.5	ND	0.7	0.2	4.1	ND	0.1	1.1	340	ND	6	90
301074	1134	0.0	15.4	20.0	6.0	7.5	0.93	0.84	88	11.8	ND	0.5	0.0	3.9	ND	0.1	0.9	410	ND	11	90
301074	1134	0.0	15.4	20.0	6.0	7.5	0.93	0.78	107	16.5	ND	0.6	0.4	3.6	ND	0.1	0.8	490	ND	9	105
301074	1200	-0.9	19.2	20.5	3.8	7.5	0.70	1.32	108	11.0	ND	0.6	0.1	4.5	ND	0.1	0.8	370	ND	11	65
301074	1200	-0.9	19.2	20.5	3.8	7.5	0.70	1.71	169	9.2	ND	0.4	0.2	5.1	ND	0.1	0.8	500	ND	11	80
301074	1224	-2.2	23.1	21.5	6.3	7.8	0.52	1.56	182	6.9	ND	0.5	0.1	3.7	ND	0.1	0.6	440	ND	14	70
301074	1224	-2.2	23.1	21.5	6.3	7.8	0.52	1.00	135	6.9	ND	0.6	0.1	4.7	ND	0.1	0.7	630	ND	11	100
301074	1258	-7.0	26.5	21.1	6.8	8.0	0.36	0.96	198	4.8	ND	0.4	0.1	3.4	ND	0.2	0.6	710	ND	32	120
301074	1258	-7.0	26.5	21.1	6.8	8.0	0.36	2.64	353	4.8	ND	0.3	0.1	5.2	ND	0.1	0.8	690	ND	11	105
301074	1335	-14.2	32.9	20.4	4.8	8.0	0.14	1.80	351	2.2	ND	0.2	0.2	1.9	ND	0.1	0.6	380	ND	24	125
301074	1335	-14.2	32.9	20.4	4.8	8.0	0.14	2.00	322	3.3	ND	0.3	0.6	2.3	ND	0.2	1.1	360	ND	28	175
311074	0915	8.0	0.0	18.8	ND	6.5	1.54	1.26	96	9.9	ND	0.2	0.5	3.1	ND	0.2	1.9	240	ND	13	150
311074	0915	8.0	0.0	18.8	ND	6.5	1.54	1.25	79	11.0	ND	0.5	1.3	3.7	ND	0.2	1.6	230	ND	11	105
311074	0940	7.0	0.7	18.8	ND	6.4	1.61	0.79	72	12.5	ND	0.7	0.4	2.5	ND	0.2	1.4	230	ND	22	130
311074	0940	7.0	0.7	18.8	ND	6.4	1.61	1.36	65	14.2	ND	0.9	0.3	4.0	ND	0.3	1.8	190	ND	15	90
311074	1000	6.0	2.0	19.0	ND	6.7	1.54	1.44	88	14.5	ND	0.8	0.5	4.2	ND	0.3	1.6	260	ND	17	100
311074	1000	6.0	2.0	19.0	ND	6.7	1.54	1.39	91	17.8	ND	0.6	0.4	3.6	ND	0.2	2.0	240	ND	12	135

Table 20c. Cont.

Date	Time	Km	S _o /∞	T _o °C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part. mg/g	Cu Part. µg/g	Zn Part. µg/g
311074	1015	4.6	3.9	18.2	ND	6.8	1.42	1.56	127	22.5	ND	0.6	0.5	3.5	ND	0.1	1.1	280	ND	10	90
311074	1015	4.6	3.9	18.2	ND	6.8	1.42	0.82	76	19.4	ND	0.8	1.4	2.6	ND	0.1	3.1	240	ND	6	290
311074	1025	2.5	9.8	20.5	ND	7.0	1.13	1.00	92	20.0	ND	0.4	0.3	3.4	ND	0.3	1.4	320	ND	26	125
311074	1025	2.5	9.8	20.5	ND	7.0	1.13	1.66	60	18.5	ND	0.6	0.3	4.5	ND	0.2	1.4	160	ND	8	50
311074	1050	1.3	18.5	20.0	ND	7.3	0.66	1.90	176	10.9	ND	0.5	0.2	6.3	ND	0.1	1.1	580	ND	13	105
311074	1050	1.3	18.5	20.0	ND	7.3	0.66	1.49	101	10.6	ND	0.6	0.3	6.1	ND	0.1	1.5	410	ND	8	105
311074	1105	0.0	19.5	20.5	ND	6.9?	0.76	0.78	101	13.2	ND	0.8	0.3	5.2	ND	0.3	1.0	680	ND	40	130
311074	1105	0.0	19.5	20.5	ND	6.9?	0.76	1.84	135	16.2	ND	0.4	0.5	5.7	ND	0.2	1.2	420	ND	17	90
311074	1125	-0.9	21.0	21.5	ND	7.0?	0.54	1.00	115	11.1	ND	0.6	0.4	4.9	ND	0.1	0.7	560	ND	15	85
311074	1125	-0.9	21.0	21.5	ND	7.0?	0.54	1.64	120	ND	ND	ND	ND	8.2	ND	0.2	1.5	600	ND	11	105
311074	1155	-2.2	24.8	22.3	ND	7.2?	0.38	2.18	229	6.0	ND	0.5	0.2	7.5	ND	0.1	1.1	790	ND	11	120
311074	1155	-2.2	24.8	22.3	ND	7.2?	0.38	1.06	125	6.9	ND	0.6	0.2	6.2	ND	0.1	1.0	730	ND	11	115
311074	1215	-5.0	26.6	21.5	ND	7.8?	0.36	1.54	274	5.5	ND	0.3	0.1	5.2	ND	0.1	0.5	930	ND	10	85
311074	1215	-5.0	26.6	21.5	ND	7.8?	0.36	2.00	339	6.1	ND	0.3	0.2	5.4	ND	0.1	0.5	910	ND	11	85
311074	1250	-14.2	34.0	22.0	ND	7.7?	0.17	1.12	282	3.3	ND	0.3	0.3	1.5	ND	0.1	0.5	380	ND	32	125
311074	1250	-14.2	34.0	22.0	ND	7.7?	0.17	1.36	288	3.3	ND	0.3	0.3	1.5	ND	0.1	0.2	320	ND	29	50

Table 20d. River input, February, 1975.

Date	Time	Km	S ‰	T °C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part. mg/g	Cu Part. µg/g	Zn Part. µg/g
130175	1330	12.0	0.0	13.6	5.0	7.0	2.29	0.28	100	6.7	157	0.4	2.1	0.2	115	BDL	0.8	60	41	BDL	295
130175	1330	12.0	0.0	13.6	5.0	7.0	2.29	0.42	98	6.7	184	0.4	1.9	0.3	133	BDL	2.1	60	31	BDL	490
140175	1030	12.0	0.0	10.2	5.5	6.5	2.26	0.56	73	9.7	242	0.4	1.7	0.3	213	BDL	0.2	40	28	BDL	30
140175	1030	12.0	0.0	10.2	5.5	6.5	2.26	0.56	56	9.0	283	1.0	1.7	0.4	225	BDL	0.5	40	22	BDL	50
150175	1100	12.0	0.0	6.6	7.4	6.6	2.34	0.24	103	7.3	229	0.0	1.7	0.2	ND	ND	ND	70	ND	ND	ND
150175	1100	12.0	0.0	6.6	7.4	6.6	2.34	0.40	109	9.3	232	0.1	1.7	0.1	106	BDL	0.1	30	29	BDL	15
160175	1040	12.0	0.0	8.8	7.8	6.6	2.34	0.46	146	8.3	171	0.1	1.7	0.1	78	BDL	0.1	40	25	BDL	30
160175	1040	12.0	0.0	8.8	7.8	6.6	2.34	0.46	138	8.0	265	0.1	1.7	0.1	71	BDL	0.1	30	21	BDL	25
170175	1100	12.0	0.0	7.3	7.9	6.7	2.33	0.68	80	6.5	200	0.0	1.0	0.3	151	BDL	0.2	30	18	BDL	20
170175	1100	12.0	0.0	7.3	7.9	6.7	2.33	ND	76	9.3	261	0.0	1.0	ND	ND	ND	ND	ND	ND	ND	ND
200175	1055	12.0	0.0	11.1	6.5	6.8	2.19	0.82	80	6.0	212	0.2	1.0	0.3	234	BDL	0.4	30	23	BDL	40
200175	1055	12.0	0.0	11.1	6.5	6.8	2.19	0.55	104	7.5	240	0.1	1.2	0.3	237	BDL	0.3	60	45	BDL	60
210175	1100	12.0	0.0	7.7	6.5	6.6	2.17	0.68	69	6.7	243	0.0	1.1	0.3	158	BDL	0.4	30	16	BDL	40
210175	1100	12.0	0.0	7.7	6.5	6.6	2.17	0.52	104	6.3	241	0.1	1.4	0.4	174	BDL	0.4	80	35	BDL	80
220175	1100	12.0	0.0	6.8	ND	6.6	2.28	0.19	139	6.9	204	0.2	1.2	0.1	75	0.3	0.3	90	55	200	210
220175	1100	12.0	0.0	6.8	ND	6.6	2.28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
230175	1055	12.0	0.0	6.4	7.1	6.5	2.29	ND	177	6.5	214	0.5	1.5	0.0	32	0.0	0.1	ND	ND	ND	ND
230175	1055	12.0	0.0	6.4	7.1	6.5	2.29	0.41	166	7.0	278	0.7	1.6	0.1	59	0.4	0.2	30	24	176	95
240175	1045	12.0	0.0	7.7	7.2	6.1	2.22	ND	182	6.0	303	0.7	1.6	0.1	69	0.1	0.1	ND	ND	ND	ND
240175	1045	12.0	0.0	7.7	7.2	6.1	2.22	0.26	136	6.5	310	0.5	1.4	0.1	74	0.2	0.1	40	39	127	75
270175	1040	12.0	0.0	8.0	6.8	6.4	2.26	0.46	124	5.5	239	0.0	2.1	0.1	79	0.9	0.3	30	21	235	75
270175	1040	12.0	0.0	8.0	6.8	6.4	2.26	0.48	115	6.1	317	1.0	1.6	0.1	85	0.7	0.2	20	20	171	60
280175	1040	12.0	0.0	11.8	6.5	6.2	2.34	0.37	93	4.3	347	0.2	1.3	0.1	71	2.0	0.4	30	18	503	110
280175	1040	12.0	0.0	11.8	6.5	6.2	2.34	1.26	101	7.0	262	0.1	1.4	0.1	59	1.7	0.4	10	5	140	35
290175	1050	12.0	0.0	10.9	7.0	6.6	2.34	ND	100	4.9	255	1.1	1.3	0.2	118	0.3	0.3	ND	ND	ND	ND
290175	1050	12.0	0.0	10.9	7.0	6.6	2.34	0.30	91	5.8	283	2.8	1.6	0.3	253	0.1	0.3	100	77	30	105
300175	1105	12.0	0.0	11.6	6.2	6.3	2.42	ND	116	5.1	286	1.6	1.4	0.0	40	0.1	0.1	ND	ND	ND	ND
300175	1105	12.0	0.0	11.6	6.2	6.3	2.42	ND	127	7.0	246	1.2	1.3	0.2	88	0.1	0.4	ND	ND	ND	ND
310175	1100	12.0	0.0	11.8	6.7	6.4	2.46	ND	154	5.5	381	1.0	1.5	0.1	82	0.1	0.2	ND	ND	ND	ND
310175	1100	12.0	0.0	11.8	6.7	6.4	2.46	ND	121	7.7	299	0.9	1.7	0.1	37	0.3	0.4	ND	ND	ND	ND

Table 20d. Cont.

Date	Time	Km	S ^o /∞	T ^o C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part. mg/g	Cu Part. µg/g	Zn Part. µg/g
010275	1130	12.0	0.0	10.8	5.8	6.1	2.49	0.23	135	7.4	296	0.8	1.7	0.1	91	0.1	0.1	70	53	74	65
010275	1130	12.0	0.0	10.8	5.8	6.1	2.49	0.45	130	7.5	281	1.2	1.8	0.1	84	0.1	0.1	40	24	33	40
020275	1130	12.0	0.0	8.8	6.0	6.2	2.50	0.80	179	9.0	355	0.7	1.3	0.3	112	0.2	0.3	70	25	40	60
020275	1130	12.0	0.0	8.8	6.0	6.2	2.50	0.21	93	9.0	271	1.6	1.8	0.2	116	0.1	0.2	100	51	24	110
030275	1330	12.0	0.0	6.7	6.3	6.1	2.34	0.39	110	6.9	316	1.3	1.6	0.1	86	0.0	0.2	30	24	BDL	45
030275	1330	12.0	0.0	6.7	6.3	6.1	2.34	0.22	136	7.1	349	0.9	1.9	0.1	76	0.1	0.2	70	47	46	130
060275	1520	12.0	0.0	10.3	6.4	6.5	2.05	0.28	50	8.0	218	0.3	1.5	0.4	152	0.3	0.3	70	27	57	55
060275	1520	12.0	0.0	10.3	6.4	6.5	2.05	0.12	50	7.5	223	1.0	2.1	0.4	160	0.5	0.4	180	67	200	150

Table 20e. AEFC dock, February, 1975.

Date	Time	Km	S ^o /∞	T ^o /C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. μg/l	Fe Diss. μg/l	Cu Diss. μg/l	Zn Diss. μg/l	Mn Susp. μg/l	Fe Susp. μg/l	Cu Susp. μg/l	Zn Susp. μg/l	Mn Part. μg/g	Fe Part. mg/g	Cu Part. μg/g	Zn Part. μg/g
140175	0900	-14.2	36.4	12.6	4.3	8.1	0.04	2.16	330	1.0	1.6	0.1	0.2	2.1	274	0.1	0.5	330	4.2	14	75
140175	0900	-14.2	36.4	12.6	4.3	8.1	0.04	2.40	354	0.9	1.0	0.1	0.1	2.2	283	0.2	0.6	330	4.2	24	90
210175	1515	-14.2	27.8	9.6	ND	8.0	0.23	0.46	137	3.2	10.0	0.1	0.2	0.8	156	0.1	0.4	230	4.6	33	130
210175	1515	-14.2	27.8	9.6	ND	8.0	0.23	0.34	112	3.7	10.6	1.0	0.4	0.8	149	0.1	0.5	260	4.9	44	160
240175	1315	-14.2	30.9	9.2	6.6	8.2	0.18	0.54	310	2.5	6.3	0.3	0.4	0.5	79	0.1	0.2	280	4.6	59	100
240175	1315	-14.2	30.9	9.2	6.6	8.2	0.18	0.46	255	1.3	7.1	0.4	0.4	0.5	78	0.1	0.2	260	4.4	46	125
280175	1530	-14.2	29.5	12.0	6.0	8.2	0.15	2.08	231	1.5	5.8	0.2	0.2	1.9	268	0.3	0.6	210	3.0	32	70
280175	1530	-14.2	29.5	12.0	6.0	8.2	0.15	0.82	246	1.6	6.7	0.4	0.3	1.3	174	0.2	0.5	380	5.2	72	160
010275	1445	-14.2	31.4	11.9	5.9	8.2	0.13	1.18	271	0.8	4.5	0.5	0.2	1.7	229	0.1	0.5	390	5.3	24	115
010275	1445	-14.2	31.4	11.9	5.9	8.2	0.13	ND	275	1.0	3.5	0.5	0.2	1.2	163	0.1	0.4	ND	ND	ND	ND
020275	1500	-14.2	32.7	10.6	5.8	8.0	0.16	1.97	264	1.1	4.0	0.2	0.5	1.5	197	0.1	0.4	370	4.8	17	105
020275	1500	-14.2	32.7	10.6	5.8	8.0	0.16	1.86	300	1.2	3.5	0.3	0.4	1.1	147	0.1	0.4	340	4.5	33	110
030275	1515	-14.2	30.5	8.0	4.3	8.0	0.17	1.22	202	1.4	14.4	0.6	0.3	2.0	264	0.2	0.7	330	4.4	31	110
030275	1515	-14.2	30.5	8.0	4.3	8.0	0.17	1.17	208	2.3	7.9	0.3	0.4	1.9	271	0.1	0.5	340	4.8	19	95

Table 20f. Estuary transects, February, 1975.

Date	Time	Km	S ^o /oo	T ^o C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. µg/l	Fe Diss. µg/l	Cu Diss. µg/l	Zn Diss. µg/l	Mn Susp. µg/l	Fe Susp. µg/l	Cu Susp. µg/l	Zn Susp. µg/l	Mn Part. µg/g	Fe Part. mg/g	Cu Part. µg/g	Zn Part. µg/g
040275	1400	11.0	0.1	6.6	7.0	6.4	2.18	ND	122	7.1	230	0.6	1.9	0.1	45	0.1	0.2	ND	ND	ND	ND
040275	1400	11.0	0.1	6.6	7.0	6.4	2.18	ND	112	7.4	303	0.0	1.9	0.3	139	0.2	0.2	ND	ND	ND	ND
040275	1450	1.0	1.8	7.0	ND	6.9	1.83	2.59	62	8.6	247	2.8	1.8	7.8	1707	1.3	1.9	190	41	30	45
040275	1450	1.0	1.6	7.0	ND	6.9	1.83	1.97	57	9.0	252	1.2	0.6	7.5	1625	0.9	3.7	220	47	26	105
040275	1505	2.0	0.8	7.0	7.4	6.8	1.90	1.90	78	9.2	251	2.5	1.2	4.0	985	0.4	1.9	160	41	15	80
040275	1505	2.0	0.9	7.0	7.4	6.8	1.90	ND	69	9.6	287	0.0	0.6	2.2	471	0.3	0.9	ND	ND	ND	ND
040275	1530	-0.2	5.3	6.2	8.5	7.2	1.57	4.68	89	11.9	187	2.1	1.6	13.0	2426	0.8	5.3	250	46	15	100
040275	1530	-0.2	5.0	6.2	8.5	7.2	1.57	4.90	76	11.9	202	0.6	1.4	14.2	2527	1.0	5.9	220	39	15	90
040275	1545	-0.4	5.3	6.1	7.9	7.3	1.54	3.36	46	12.6	180	3.0	3.1	16.9	2913	1.0	5.3	230	40	13	85
040275	1545	-0.4	5.1	6.1	7.9	7.3	1.54	4.75	82	12.3	147	4.6	2.3	13.7	2475	0.6	4.7	240	43	11	80
040275	1605	-2.6	12.1	6.0	8.1	7.5	0.98	3.95	98	15.1	404*	0.6	4.1	9.5	1672	0.4	3.3	240	41	10	80
040275	1605	-2.6	11.6	6.0	8.1	7.5	0.98	4.06	74	9.5	110	2.3	7.1	14.6	2260	0.5	4.5	260	41	11	80
050275	1105	-1.0	0.0	8.3	7.1	6.6	1.81	3.06	62	8.9	287	4.1	1.4	10.9	2089	1.0	4.5	230	42	20	90
050275	1105	-1.0	0.1	8.3	7.1	6.6	1.81	1.94	51	9.4	369	6.1	3.0	8.3	1604	0.3	3.1	220	42	7	80
050275	1135	-1.8	0.4	8.2	7.6	6.6	1.80	2.52	74	8.6	302	4.2	1.4	6.8	1419	0.5	3.5	200	42	16	100
050275	1135	-1.8	0.5	8.2	7.6	6.6	1.80	2.14	58	8.3	305	5.1	1.1	6.9	1493	0.3	3.6	190	41	8	95
050275	1200	-1.7	0.2	8.2	7.6	6.5	1.80	2.58	62	8.6	358	2.6	1.9	8.0	1628	1.5	4.3	190	39	35	105
050275	1200	-1.7	0.2	8.2	7.6	6.5	1.80	2.50	66	8.5	272	3.1	1.7	7.6	1617	0.9	3.7	200	43	23	95
050275	1215	-2.1	0.9	8.9	6.5	6.5	1.78	ND	61	9.1	288	4.2	1.5	2.9	664	0.2	1.2	ND	ND	ND	ND
050275	1215	-2.1	0.4	8.9	6.5	6.5	1.78	1.28	47	8.8	291	4.5	1.5	4.7	1160	1.1	4.3	170	43	41	155
050275	1230	-2.4	11.4	8.5	7.8	7.6	0.85	1.10	67	10.1	77	1.4	5.3	3.2	709	0.1	1.7	190	43	9	105
050275	1230	-2.4	10.9	8.5	7.8	7.6	0.85	0.69	50	11.1	100	0.0	5.5	3.1	710	0.3	1.3	230	51	19	95
050275	1250	-2.3	9.9	8.4	7.6	7.4	1.03	2.47	104	11.0	127	0.8	3.0	4.8	993	0.4	1.9	200	42	18	80
050275	1250	-2.3	11.2	8.4	7.6	7.4	1.03	ND	139	7.7	92	0.8	3.0	2.6	496	0.5	1.3	ND	ND	ND	ND
050275	1320	-7.6	12.0	8.5	7.4	7.7	0.78	1.10	64	8.8	85	0.0	3.8	4.5	795	0.2	2.1	260	46	15	120
050275	1320	-7.6	12.3	8.5	7.4	7.7	0.78	1.76	86	8.7	112	0.1	5.0	5.1	857	0.3	1.9	250	42	16	90

Table 20f. Cont.

Date	Time	Km	S ^o / _∞	T ^o / _C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. μg/l	Fe Diss. μg/l	Cu Diss. μg/l	Zn Diss. μg/l	Mn Susp. μg/l	Fe Susp. μg/l	Cu Susp. μg/l	Zn Susp. μg/l	Mn Part. μg/g	Fe Part. mg/g	Cu Part. μg/g	Zn Part. μg/g
050275	1345	-8.8	18.4	8.9	7.3	8.0	0.34	0.92	121	4.0	23	0.8	4.2	2.6	320	0.2	0.7	340	42	21	90
050275	1345	-8.8	18.2	8.9	7.3	8.0	0.34	0.68	84	5.0	34	0.9	5.2	2.3	288	0.2	0.8	280	35	26	95
050275	1415	-12.0	27.4	9.0	6.7	8.0	0.18	ND	257	0.9	4	0.3	0.4	2.9	335	0.2	0.7	ND	ND	ND	ND
050275	1415	-12.0	27.0	9.0	6.7	8.0	0.18	0.82	157	1.7	7	0.2	0.3	1.9	218	0.1	0.5	300	39	28	90
050275	1430	-14.2	27.5	9.2	6.7	8.0	0.18	ND	201	1.1	6	0.4	0.3	1.9	229	0.1	0.5	ND	ND	ND	ND
050275	1430	-14.2	27.5	9.2	6.7	8.0	0.18	1.37	204	1.2	5	0.3	0.3	2.1	265	0.3	0.9	310	39	46	130

Table 20g. Estuary transect, April, 1975.

Date	Time	Km	S ^o /∞	T ^o C	DO ml/l	pH	UVOrg	Susp. mg	Volume ml	Mn Diss. μg/l	Fe Diss. μg/l	Cu Diss. μg/l	Zn Diss. μg/l	Mn Susp. μg/l	Fe Susp. μg/l	Cu Susp. μg/l	Zn Susp. μg/l	Mn Part. μg/g	Fe Part. mg/g	Cu Part. μg/g	Zn Part. μg/g
041475	1045	11.0	0.1	11.7	6.4	6.4	2.05	0.54	83	8.3	188	1.2	1.6	0.3	18	BDL	ND	40	28	BDL	ND
041475	1045	11.0	0.1	11.7	6.4	6.4	2.05	0.54	101	7.6	218	1.9	1.4	0.7	22	BDL	ND	110	41	BDL	ND
041475	1120	0.5	1.6	12.2	6.2	6.8	1.52	1.77	98	14.8	71	1.1	0.8	4.0	80	BDL	3.6	220	44	BDL	200
041475	1120	0.5	0.9	12.2	6.2	6.8	1.52	2.08	79	12.7	158	2.5	1.1	6.0	104	BDL	6.2	230	40	BDL	240
041475	1130	1.0	0.8	11.8	6.4	6.8	1.69	2.21	89	13.1	254	1.9	1.1	4.8	113	BDL	8.2	190	46	BDL	330
041475	1130	1.0	0.8	11.8	6.4	6.8	1.69	1.59	65	11.5	138	4.1	0.7	5.0	114	BDL	5.6	200	47	BDL	230
041475	1145	0.3	7.9	13.8	5.9	7.2	1.27	3.21	122	18.6	107	2.0	0.4	5.4	103	BDL	8.0	200	39	BDL	300
041475	1145	0.3	6.1	13.8	5.9	7.2	1.27	ND	188	18.3	91	3.4	0.4	6.0	114	BDL	ND	ND	ND	BDL	ND
041475	1155	0.0	11.3	13.4	5.8	7.3	0.99	1.82	77	21.7	59	1.2	0.3	6.4	98	BDL	2.6	270	41	BDL	110
041475	1155	0.0	11.7	13.4	5.8	7.3	0.99	2.06	87	20.4	74	0.6	0.2	4.9	93	BDL	3.4	210	39	BDL	140
041475	1200	-0.3	13.7	13.5	5.8	7.4	0.88	1.30	101	22.0	59	1.2	0.3	3.3	56	BDL	3.2	260	43	BDL	240
041475	1200	-0.3	13.6	13.5	5.8	7.4	0.88	1.76	102	21.5	45	1.4	0.4	4.1	66	BDL	2.3	240	38	BDL	130
041475	1215	-1.9	17.3	13.9	5.7	7.6	0.77	1.53	123	19.9	31	0.5	0.2	3.1	47	BDL	2.1	250	38	BDL	170
041475	1215	-1.9	17.1	13.9	5.7	7.6	0.77	1.63	123	ND	ND	ND	ND	3.6	52	BDL	1.6	270	38	BDL	120
041475	1230	-2.4	18.6	13.9	5.5	7.6	0.62	1.06	94	ND	ND	ND	ND	3.1	49	BDL	1.4	270	44	BDL	120
041475	1230	-2.4	19.0	13.9	5.5	7.6	0.62	1.31	104	21.8	120	1.6	0.7	3.0	52	BDL	1.3	240	41	BDL	110
041475	1245	-5.0	20.5	13.5	5.8	7.7	0.50	1.71	163	15.3	12	0.3	0.2	3.6	42	BDL	1.4	340	40	BDL	140
041475	1245	-5.0	19.4	13.5	5.8	7.7	0.50	0.95	114	ND	ND	ND	ND	5.4	37	BDL	0.7	640	44	BDL	80
041475	1255	-8.8	21.6	13.5	6.1	7.9	0.28	1.06	123	6.5	7	0.3	0.2	3.2	34	BDL	1.2	370	40	BDL	130
041475	1255	-8.8	23.1	13.5	6.1	7.9	0.28	0.63	87	6.3	10	0.7	0.1	3.0	34	BDL	0.9	410	47	BDL	120
041475	1305	-14.2	31.9	13.2	5.5	7.9	0.22	3.24	334	4.0	3	0.4	0.1	2.8	33	BDL	1.4	290	34	BDL	150
041475	1305	-14.2	31.3	13.2	5.5	7.9	0.22	2.46	279	3.0	6	0.4	0.1	2.7	31	BDL	1.4	300	35	BDL	150

APPENDIX C

Table 21 shows complete trace metal data from a cruise aboard R/V Eastward on December 3-6, 1974. Sampling locations are shown in Figure 24. Samples were taken one meter below the surface with a PVC Niskin bottle with internal rubber shock cord closure. No special preparations of the Niskin bottle were made for trace metal analysis. For this reason some contamination might be expected. Samples from station P1 were the first collected, and trace metals leached from the Niskin bottle should be greatest here since subsequent samples would benefit from repeated washing of the bottle by seawater immersion. Station P1 was located in a dredge spoil disposal area. For these reasons, station P2 rather than P1 was chosen to represent primary ocean water mixing in the estuary.

Table 21. Trace metal concentrations in offshore water samples collected from R/V Eastward, December 3-6, 1974. Data are shown for (D) dissolved concentrations as $\mu\text{g/l}$, (S) suspended particulate concentrations as $\mu\text{g/l}$, and (P) concentrations on suspended particulates as $\mu\text{g/g}$ (mg/g for Fe).

Station	Suspended Matter (mg/l)	Mn			Fe			Cu			Zn		
		D	S	P	D	S	P	D	S	P	D	S	P
P1 (S°/oo = 35.86)													
34°38.0'N	4.68	1.33	1.41	300	1.3	109	23	0.9	0.2	40	4.2	1.0	210
76°41.5'W	4.37	0.63	1.03	240	0.6	102	23	0.7	0.3	60	4.8	0.8	190
P2 (S°/oo = 36.48)													
34°25.6'N	3.07	0.34	0.94	310	0.4	73	24	0.1	0.2	60	0.8	0.8	250
76°44.5'W	3.59	0.37	1.10	310	0.4	96	27	0.3	0.3	70	1.0	0.8	230
P3 (S°/oo = 36.56)													
34°16.0'N	0.94	0.37	0.21	220	0.4	23	24	0.1	0.2	180	3.5	0.3	280
76°37.0'W	0.91	0.30	0.25	280	0.3	23	25	0.3	0.2	210	2.9	0.3	300
O (S°/oo = 36.31)													
34°37.9'N	--	0.13	0.01	---	< 0.2	0.4	--	0.2	< 0.1	---	2.1	0.1	---
75°15.0'W	0.19	0.13	0.02	110	0.2	0.5	27	0.2	0.1	750?	2.8	0.1	210
R2 (S°/oo = 36.38)													
34°36.0'N	--	0.16	0.04	---	0.3	4.0	--	0.1	< 0.1	---	0.5	0.1	---
76°16.5'W	0.13	0.13	0.05	390?	< 0.2	5.3	42?	0.2	0.1	860?	0.7	0.1	1200?
R1 (S°/oo = 36.43)													
34°40.6'N	0.32	0.19	0.06	190	< 0.2	4.7	15	0.1	0.1	150	0.5	0.1	220
76°21.0'W	0.35	0.18	0.08	230	< 0.2	5.7	16	0.1	0.1	220	0.5	0.1	290

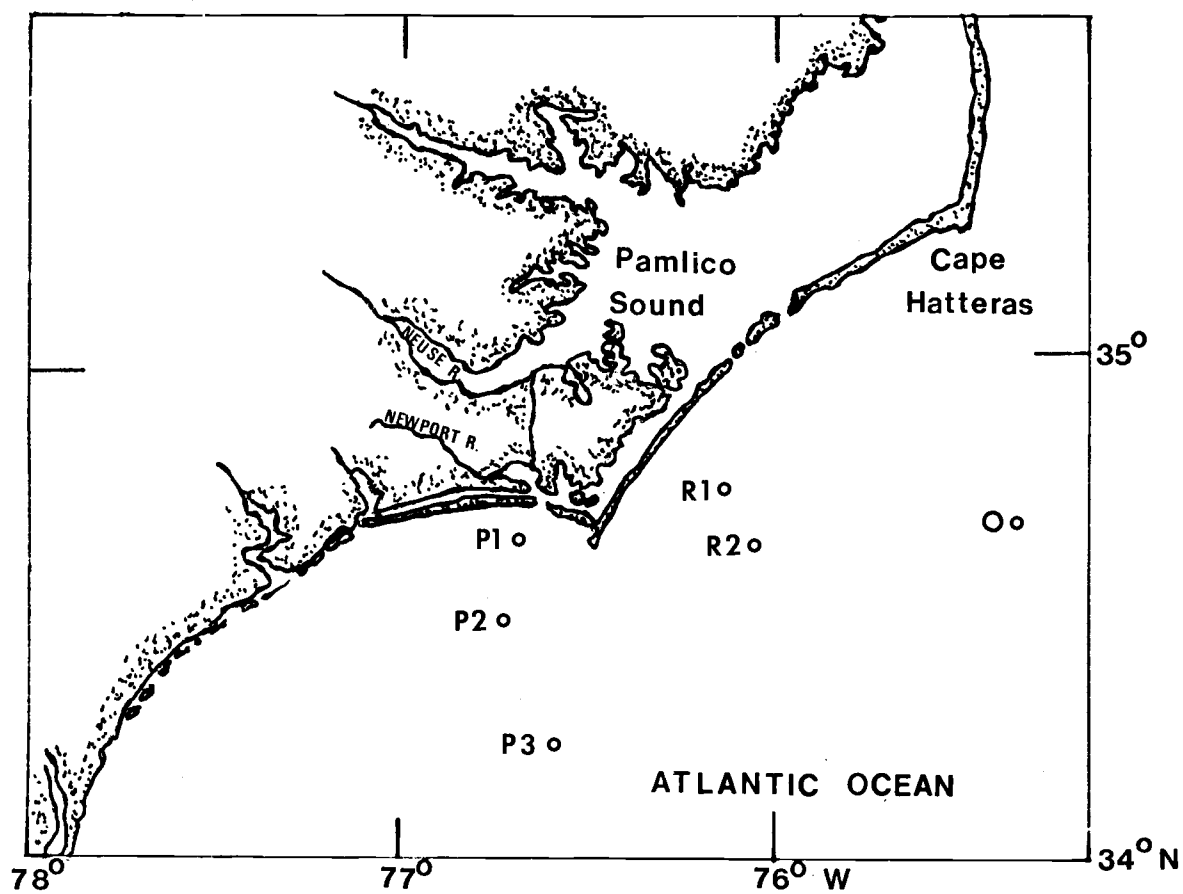


Figure 24. Coastal North Carolina showing sample locations during R/V Eastward cruise, December 3-6, 1974.