# MATHEMATICAL MODELS OF TOXIC SUBSTANCES IN ESTUARIES WITH APPLICATION TO KEPONE IN THE JAMES RIVER

by

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### ABSTRACT

The primary purpose of this research project is to develop the equations for modeling of toxic substances in estuaries and to demonstrate the application of these equations to present and anticipated problem areas. The present structure of the model is two-dimensional (longitudinal-vertical) interacting with lateral embayments which may operate in a steady-state or time-variable mode. The water column is segmented into two vertical layers to incorporate the typical estuarine circulation interacting with a bed which is also segmented into two layers - an active interfacial region and a deeper stationary bed. Adsorption-desorption kinetics are included which, in the case of the Kepone distribution of the James River, are assumed to be at equilibrium. Both steady-state, as well as time-variable, conditions were analyzed to calibrate the model to reproduce presently observed concentrations of Kepone. Sensitivity analyses and projections were conducted to estimate the time required to reduce the present level of contamination.

In order to provide the necessary background for the development of the model, the various factors which affect the kinetic interactions of sorption and which affect the distributions of the suspended and bed solids are discussed in the introductory sections. This is followed by the development of a one-dimensional analysis, similar to the classical estuarine water quality equations in present use. This type of analysis may be used for preliminary assessment of a problem. An example of its application to the James River is included.

A procedure of analysis to address the problem of organic chemicals in estuaries has been structured. The procedure involves a series of analytical and computational steps, relating to the fluid transport, the solids distribution and the concentrations of the organic chemical in the water and the bed. Each step involves the determination or assignment of the appropriate transport, transfer and/or reaction coefficients to analyze a particular constituent of the system. Equally important, each step provides the input for the computation of the next element, for which an additional coefficient is required. The analysis proceeds in a sequence of increasing complexity, each element yielding a calibration or validation of an essential constituent. The final output is the temporal or spatial distribution of the organic chemical.

Specific recommendations are presented relating to further calibration and validation of these models in other estuaries. Particular attention should be directed to an assessment of the inputs, characterization of bed conditions and evaluation of kinetic interactions. It is planned to incorporate these factors in ongoing research.

iii

# CONTENTS

Abstract Figures. Tables Acknowledg		
1.	Introduction       1         Overview and Purpose.       1         Basic Principles.       3         Classification of Analyses and Models       6         Basic Elements of Estuarine Model       9	
2.	Adsorption-Desorption.       16         Equilibrium.       16         Adsorption Models.       16         Kinetics of Kepone Adsorption       24         References.       25	
3.	Characteristics of Suspended Solids and Bed Sediment 31 Settling, Sedimentation and Compaction	
4.	One-Dimensional Estuarine Analysis	
5.	Two-Dimensional Estuarine Models       65         Hydrodynamic Analysis       65         Transport-Salinity Distribution       72         Solids Distributions       74         Organic Chemicals Distributions       79         Procedure of Analysis       81         Numerical Solution of Equations       87         References       94	
6.	Application to Kepone Distribution in the James River.	
7.	Conclusions and Recommendations	
THE PERGIN		

iv

## FIGURES

Number		Page
1-1 1-2 1-3 1-4 1-5	Transport-Kinetics Routes and Food Chain	12 13 14 14 15
2-1 2-2 2-3 2-4 2-5	Equilibrium Concentrations of Kepone	26 27 28 29 30
3-1 3-2 3-3 3-4 3-5	Distribution of Pb <sup>210</sup> in Sediments	43 44 45 46
4-1	Kepone Calculation for the James River Estuary (1976)	64
5-1 5-2 5-3 5-4 5-5 5-6 5-7 5-8 5-9	Schematic Diagram of Two-Dimensional Estuarine Circulation Sequence of Steps in Kepone Analysis	98 99 100 101 102 103 104 105 106
6-1 6-2 6-3 6-4 6-5	Location Map	134 135 136 137
6-6 6-7 6-8 6-9	Sectional Area	138 139 140 141 142

v

## FIGURES (cont'd)

Number		Page
6-12	Distribution of Net Flows (1000 cfs)	145
6-13	Salinity Calculation $(Q = 1000 \text{ cfs})$ .	146
6-14	Salinity Calculation for Various James River Flows	147
6-15	Transport and Solids Distributions	148
6-16	Salinity, Solids and Entrainment (1000 cfs)	149
6-17	Salinity, Solids and Entrainment (7000 cfs)	150
6-18	Salinity, Solids and Entrainment (18500 cfs)	151
6-19	Entrainment and Sedimentation Rates (1000 cfs)	152
6-20	Entrainment and Sedimentation Rates (7000 cfs)	153
6-21	Entrainment and Sedimentation Rates (18500 cfs)	154
6-22	Sedimentation Rates for Embayments	155
6-23	Kepone Distributions in the Water Column (Q = 1000 cfs)	156
6-24	Kepone Distributions in the Water Column (4380 cfs)	157
6-25	Kepone Distributions in the Water Column (18500 cfs)	158
6-26	Annual Kepone Production	1.59
6-27	Kepone Distribution in Bed-Constant Flow Analysis	
	(1000 cfs, ¶ = 500)	160
6-28	Kepone Distributions in Stationary Bed for Constant	
	Flow Analysis	161
6-29	Monthly Average Flow Hydrograph of James River	162
6-30	Kepone Distributions - Time Variable Flow Analysis	163
6-31	Sensitivity of Bed Kepone Concentration to Vertical	
	Diffusion	164
6-32	Sensitivity of Bed Kepone Concentration to Transport Layer	
	Solids Concentration	165
6-33	Sensitivity of Bed Kepone Concentrations to Thickness of	
	Transport Layer	166
634	Sensitivity of Bed Kepone Concentrations to Movement of	
	Transport Laver	167

vi

TABLES

Number		Page
1-1	Classification of Models	11
5-1	Coefficients of Simultaneous Equations for $c^{n+1}$ and $p^{n+1}$	96
6-1 6-2 6-3 6-4 6-5 6-6 6-7	Production Levels of Kepone.	127 128 129 130 131 132 133

vii

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### SECTION 1

## INTRODUCTION

## OVERVIEW AND PURPOSE

Toxic substances are present in varying degrees in all phases of the environment - air, water and land. They are transferred between and among these media, undergo transformation within each and accumulate in viable and non-viable constituents. The magnitude and significance of the problem has become increasingly evident, particularly in the accumulation of toxic substances in both the terrestrial and aquatic food chains and in the release of these substances from land and water disposal areas. In this regard, the impact on the health and activities of man is more direct and significant than in the case of pollutants which the field has classically addressed. This concern led to the formulation of the Toxic Substances Control Act, enacted by Congress in 1976, and, in turn, to the subsequent promulgation of priority pollutants by the Environmental Protection Agency. The latter is under continuous review and periodic updating both by EPA and interested scientific groups in industry, research laboratory and environmental organizations.

A total ban on all organic chemicals is neither desirable nor practical. The benefits derived from the use of these substances are evident in many facets of our society - particularly with respect to the increased food production. The demand for these materials, more specifically the benefits derived from their use, continuously increases. A balance must therefore be sought between the extreme positions - complete ban and no control. Such a balance leads to the use of certain chemicals, which may be safely assimilated in the environment to such levels as to yield the benefits without deleterious effects. This goal necessitates the development of assessment methods which permit an evaluation and ultimately a prediction of environmental concentrations.

Quantitative methods of assessment are mathematical equations, derived from basic principles which define the spatial and temperal distributions of organic chemicals in natural water systems. The development of such models with specific emphasis on estuarine systems is the overall purpose of the research project to which this report is addressed. The original objective of this project was to quantify the inter-relationships among the various physical, chemical and biological variables which affect the fate of pollutants in estuarine systems. The initial schedule envisioned an effort which included a structuring of a two-dimensional estuarine model with subsequent application to an appropriate East or Gulf Coast estuary. The initial emphasis was to be on phytoplankton population dynamics with later parallel efforts directed towards the development of basic equations for modeling the

- 1 -

fate of hazardous materials in estuaries. Early in the project period, it became clear, however, that a redirection of effort was necessary in order to be responsive to the Agency's concern over the contamination of the waters and sediment of the James River Estuary with the pesticide Kepone. Thus, development and application was solely directed to the James and the focus of the project was shifted from analysis of estuarine phytoplankton dynamics to the development of a model to define the spatial and temporal distribution of organic chemicals in estuarine systems with a specific focus on Kepone in the James River Estuary.

The initial phase of the project was directed to a review of the basic factors which affect the transport, transfer and reactions of organic chemicals in natural systems, which is summarized in this introductory section. This section lays out the basic principles involved, presents a general classification of analyses and model types, and details the basic elements of the estuarine model developed under this project.

One of the most distinguishing characteristics of toxic substances is the partitioning between the dissolved and particulate components. Thus equations are developed for each of these components and in addition for those solids which provide sites for the adsorption of the substance. The analysis involves, therefore, the solution of all the interactive simultaneous equations, defining the concentration of the components in the water column. Furthermore, for those water systems which interact with the bed, additional sets of equations are developed to account for distribution in the benthal layer and its effect on water column concentrations. Given these concentrations, the dissolved and the particulate in the water column and in the bed, the distribution through the food chain is then considered.

The purposes of the modeling framework are twofold: the first relates to an evaluation of the distribution of proposed or existing chemicals which, in turn, may provide the basis for waste-load allocation procedures. Such analyses may usually be accomplished by means of the spatial steadystate distributions. The second general purpose relates to the time-variable aspects of the problem. Such analyses apply to the effects of a short-term release of a toxic, such as an accidental spill or a storm overflow discharge. An equally important application in this regard is directed to the time required to build up to the steady and perhaps more significant the time required to cleanse a system from existing contamination. Both the time-variable and steady-state analysis are necessary elements of a general methodology to assess the potential impact of proposed chemicals, which may be introduced into the environment.

Field surveys undoubtedly provide much insight into the analysis of the problem, but this approach is evidently limited in broad application, particularly with respect to the analysis of the more important question of assessment of proposed chemicals. In addition, the costliness and time factor of field surveys impose further disadvantages. Theoretical analysis, in conjunction with controlled laboratory experiments, is the preferred approach. The emphasis in the project was therefore directed to a review of the basic knowledge of the various phenomena and of the application of laboratory data to the analysis. This approach, which is less costly and time-

- 2 -

consuming, lends itself to greater understanding of the problem and broader application to a variety of similar problems. Ultimately, however, the equations developed in this fashion may only be fully validated and tested by prototype data. Case histories and data on presently affected water systems should be fully documented and utilized for this purpose.

The various phenomena, which affect the transport, transformation and accumulation of organic chemicals and heavy metals in the various phases of the aquatic environment, are addressed. Taken into account is the exchange of these materials between the water and the other phases of the environment, air and land. However, the primary emphasis is directed to aquatic systems - specifically to the spatial and temporal distribution of these materials in the various types of natural water bodies - rivers, lakes, estuaries and the coastal zone. The approach taken is similar to that defining the distribution of substances which are natural components of biochemical and ecological cycles - oxygen, nutrients, minerals, dissolved and suspended solids and the basic elements of the food chain - bacteria and phytoplankton. While these constituents influence water quality and man's use of water, they do not have the potentially profound effect of toxic substances, which may impact directly the health and well-being of man. The basis of the determination of the hazardous assessment lies in our ability to define the distribution of these substances in the aquatic environment. While recognizing distinction between the effects and fate, it is important to appreciate their interrelationship in that any reliable hazard assessment is based fundamentally on a realistic and valid definition of the fate of toxic substances. In order to provide a perspective of the overall approach, the basic concepts which are employed in the analysis are first presented.

## BASIC PRINCIPLES

## Mass Balance

Organic chemicals may exist in all phases of the aquatic environment in solution, in suspension, in the bed and air boundaries, and in the various levels of the food chain. The interrelationships between and among these phases are shown diagrammatically in Figure 1-1.

The equations describing the spatial and temporal distribution of organic chemicals are developed using the principle of mass conservation, including the inputs with the transport, transfer and reactions components, as presented in Figure 1-1. The general expression for the mass balance equation about a specified volume, V, is:

$$V \frac{1}{dt} = J_{i} + \Sigma R_{i} + \Sigma T_{i} + \Sigma W$$
 (1-1)

in which

 $c_i = concentration of the chemical in compartment, i.$ 

J = transport through the system

R = reactions within the system

dc.

- 3 -

T = transfer from one phase to another

W = inputs

Equation (1-1) describes the mass rate of change of the substance due to the net effect of the various fluxes and transformations. The purpose of expressing the transfer rate (T), distinct from the transport (J) and reaction (R), is to provide a basis for the development of the equations, which describe more fully the relevant phenomena.

The general term "compartment" refers to each phase of the physiochemical regime - the dissolved and particulate in the water, atmosphere and bed - as well as to each element of the food chain - the phytoplankton, zooplankton, fish and detrital material. The transport, reaction and transfer terms may be positive or negative depending on the direction of kinetic routes between the chemical in compartment i and its concentration in other compartments with which it reacts or exchanges. The pathways are determined by the hydrodynamic and geophysical features of the natural water systems and by the physical, chemical and biological characteristics of both the system and the chemical. The hydrodynamic components transport material from one spatial location to another by dispersion and advective mechanisms. The physical factors transfer from one phase to another, such as exchange with the atmosphere, adsorption to and desorption from the suspended and bed solids and the settling and scour of these solids. The chemical factors transform the substance by processes such as photo-oxidation, hydrolysis and oxidation reduction reactions. The biological phenomena affect both transference and transformation: the latter primarily by microorganisms which may metabolize the chemical and the former by assimilation and excretion by the various aquatic organisms. Accumulation in the food chain is brought about by both ingestion of the chemical from the water and by predation on contaminated prey.

## General Equations for Various Components

Consider the concentration, c, to be the dissolved component of the chemical in the water. It interacts with the particulate concentration, p. The interaction may be an adsorption-desorption process with the solids or an assimilation-depuration process with the aquatic organisms. In either case the particulate concentration is defined as:

 $p_{i} = r_{i}m_{i} \qquad (1-2)$ 

p = particulate concentration in i compartment M/L<sup>3</sup>

r, = mass of chemical/unit of interacting mass M/M

 $m_i$  = concentration of the interacting species M/L<sup>3</sup>

The mass balance equation for the particulate component, similar to equation (1-1), is then:

- 4 -

$$\frac{dp_{i}}{dt} = J + \Sigma R + \Sigma T + \Sigma W$$
 (1-3)

In view of equation (1-2), the left hand side of equation (1-2) may be expressed as:

$$\frac{\mathrm{d}\mathbf{p}_{\mathbf{i}}}{\mathrm{d}\mathbf{t}} = \mathbf{r}_{\mathbf{l}} \frac{\mathrm{d}\mathbf{m}_{\mathbf{l}}}{\mathrm{d}\mathbf{t}} + \mathbf{m}_{\mathbf{l}} \frac{\mathrm{d}\mathbf{r}_{\mathbf{l}}}{\mathrm{d}\mathbf{t}}$$

from which it is apparent that an equivalent expression must be written for the concentration of the interacting compartment,  $\mathbf{m}_{i}$ . In principle, the

analysis of the problem requires the simultaneous solution of the three equations: the concentration of the chemical dissolved in the water, c, the mass concentration of the chemical per unit mass of interacting species, r, and the concentration of the species itself, m. Since this compartment may be further subdivided (inorganic and organic solids, multiple species of fish), equation (1-2) is more generally expressed as a summation of the individual components of the interacting substances:

$$\mathbf{p}_{\mathbf{i}} = \sum_{1}^{n} \mathbf{r}_{\mathbf{i}} \mathbf{m}_{\mathbf{i}}$$
(1-4)

The specific conditions for which the analysis is performed frequently permit simplifying assumptions to be made. In laboratory batch reactors and in certain prototype situations, the rate of change of the interacting species may be zero - i.e. a constant concentration of suspended solids or biomass. Thus  $\frac{dm}{dt} = 0$ , from which an equilibrium concentration of solids or biomass follows, resulting in two simultaneous equations to be solved, instead of three.

## Dynamic Equilibrium

As may be evident from the above discussion, one of the essential properties of the analysis of this water quality problem is the interaction between the dissolved and particulate states of the constituent, which, in time, leads to a dynamic equilibrium between the two components. Consider the most simplified conditions of a batch reactor in which the mixing is of sufficient magnitude to maintain a uniform concentration throughout the vol-

ume of fluid. Assume the concentration of absorbing solids, m  $({\rm M/L}^3)$  is

constant. Let c and p be the concentrations  $(M/L^3)$  of the dissolved and particulate components. If there is neither transfer nor decay of the chemical, the total concentration,  $c_T$ , remains constant in time and is équal to the sum of the dissolved and particulate;

 $c_{\rm p} = c + p \tag{1-5}$ 

The latter is related to the concentration of suspended solids, m, as shown by equation (1-2):

p = rm

The equilibrium between the dissolved concentration in the water and the mass concentration of the solids is usually expressed in terms of a partition

- 5 -

$$=\frac{r}{c}=\frac{P}{mc}$$
 (1-6)

or 
$$\P m = \frac{p}{c}$$

Equation (1-6) is the linear portion of the Langmuir isotherm. Although not always representative of actual conditions, it is a reasonable approximation when the solid phase concentration, r, is much less than the ultimate absorbing capacity of the solids. Combining equations (1-5) and (1-6), the total concentration may be expressed as:

$$c(1 + Sm) = p(1 + \frac{1}{Sm})$$
 (1-7)

The product, m, is a convenient dimensionless parameter, characteristic of a particular system under equilibrium conditions. For a specified value of m, the equilibrium distribution between the dissolved and particulate concentrations is established by equation (1-7).

The distribution between the dissolved concentration and the particulate concentration in the various levels of the food chain may be expressed in an identical fashion. Accounting for the distribution for various types of adsorbing solids and various levels of the food chain, each with its characteristic partition coefficient, equation (1-7) may be more generally expressed:

$$c_{T} = c[1 + \Sigma \P_{i} n_{i}]$$
 (1-8)

The distribution may thus be categorized in accordance with the adsorbing solids (organics, clays, silts and sands) or the accumulating biomass (phytoplankton, zooplankton, fish and macrophytes). Since the total biomass mass in most natural water systems is usually an order of magnitude less than that of the non-viable solids, the equations defining each category may be decoupled and the former may be solved independently. Under those conditions in which it may be significant, it may be readily incorporated as shown in the above equation.

## CLASSIFICATION OF ANALYSES AND MODELS

Equation (1-1) is the most general expression to define the distribution of a toxic substance in a natural water body. Given the characteristics of the drainage area and water system and the nature of the substance, it takes on a more definitive form. As described above, the distribution between the dissolved and particulate components of the toxic material and the kinetic interactions are the essential factors, which are common to all types of models. What distinguishes the various models are the transport components of a specific water system and the characteristics of the bed, with which it interacts. Thus, the basis of the classification lies, to some

- 6 -

degree, in the transport regimes of the general types of water systems lakes, streams and estuaries, but more significantly rests on the transport characteristics of the bed itself, and the magnitude of the water-bed interaction. The kinetic and transfer routes are common to all types. Each of these factors are discussed in this section, concluding with the proposed classification.

## 1. Kinetic and Transfer Routes

The components and their interactions are shown diagrammatically in Figure 1-2. The concentrations of the toxic substances are presented in both the water column and the bed. The distribution between the dissolved, c, and particulate, p, components is determined by the magnitude of the adsorption and desorption coefficients,  $K_1$  and  $K_2$ , and the concentration of the

adsorbing solids, m. Each of these components may be susceptible to decay and exchange, as shown. For conservative, non-volatile toxics these transform routes are negligible but the settling-resuspension transfers are potentially important for any substance, regardless of its other characteristics. These are the characteristics of the system and the substance which essentially determine the complexity of the analysis.

#### 2. Transport Regimes

Each of the general types of natural water systems may be classified in accordance with characteristic fluid transport regime and the interaction of the water with the bed. The components of the transport field are the advective (U) and dispersive (E) elements which, in general, are expressed in three-dimensional space. Each of the systems to be considered - streams, estuaries, lakes and coastal waters - are usually characterized by a predominating component, in one or more dimensions. The transport in streams may be frequently approximated by a one-dimensional longitudinal analysis (B), in lakes by one or two dimensions (A), in which the vertical is the major component and in estuaries by a two-dimensional scheme (C) (longitudinal and vertical). A spatially uniform condition (completely mixed) is type D whose transport coefficient is the detention time. (Figure 1-3).

#### 3. Bed Conditions

The bed conditions, which are relevant to the analysis are shown in Figure 1-4. They may be classified as inactive or stationary, and active or mixed. The latter may be further subdivided: without and with horizontal transport. A further characteristic of bed conditions relates to the phenomenon of sedimentation. All natural water bodies accumulate, in varying degrees, materials which settle from the water column above. In freshwater systems, reservoirs and lakes are repositories of much of the suspended solids which are discharged by the tributary streams and direct drainage. In marine systems, estuaries and embayments accumulate solids in similar fashion and the coastal zones to a lesser degree. In flowing freshwater streams and tidal rivers, suspended solids may settle or scour depending on the magnitude of the velocity and shear associated with the flow. Bed conditions in these systems are therefore subject to seasonal and daily variations, while the beds of estuaries and lakes which are also subject to such variations, tend to accumulate material over long time scales. The increase

- 7 -

in bed depth and concentration is expressed in terms of a sedimentation velocity, measured in terms of months or years, by contrast to the settling velocity of the various solids in suspension, measured in terms of hours or days.

### 4. Classification of Models

The classification, suggested herein, is essentially based on the types of bed conditions, in conjunction with one of the three types of fluid transport shown in Figure 1-3. The three general types are enumerated in a progressive fashion from the simpler to the more complex, as presented in Table 1 and described below. The final form of the equations is based essentially on one of the three types, in conjunction with the kinetic interactions shown in Figure 1-2.

#### TYPE I - STATIONARY BED

A stationary bed is basically characterized by zero to negligible horizontal motion. This condition is most commonly encountered in lakes and reservoirs of relatively great depth, with minimal winds. It also occurs in freshwater streams under low flow conditions and in marine systems with little tidal mixing. It may therefore be associated with any one of the three transport systems discussed above.

The essential characteristic of this type of system is a relatively low degree of vertical mixing in the fluid. The hydrodynamic environment is one which permits the gravitational force to predominate and suspended particles of density greater than that of water to settle. The accumulation of this material in the bed causes an increase in the thickness of the benthal layer, the rate of increase being referred to as a sedimentation velocity. The bed is also characterized by minimal or zero mixing in the layer in contact with the water.

#### TYPE II - MIXED LAYER

This condition, which is probably more common, is characterized by some degree of mixing in the contact layer of the bed. The mixing may be due to either physical or biological factors - increased levels of shear, associated with horizontal or vertical velocities and gradients or bioturbation, attributable to the activity of benthal organisms. It exists, therefore, in lakes where the wind effects extend to the bottom and in streams and rivers under moderate flow conditions.

In each of these cases, the shear exerted on the bed is sufficient to bring about mixing in interfacial layer, but not sufficient to cause significant erosion and bed motion. The net flux of material to the bed is the difference between the settling flux and that returned by the exchange due to the mixing. Thus, the bed thickness may increase or decrease and the sedimentation velocity may be positive or negative. The mixed layer interacts with a stationary bed beneath, as shown. This type of bed condition may also be associated with any of the three fluid transport types, but is more usually associated with type B and in the littoral zone of lakes, where the water depths are sufficiently shallow to permit wind effects to be transmitted to the bed.

- 8 -

### TYPE III - BED TRANSPORT

This bed condition possesses both mixing and advective characteristics. The shearing stress exerted by the fluid is of sufficient intensity to cause erosion and resuspension of the bed and the fluid velocity of sufficient magnitude to induce horizontal motion of either or both the resuspended material and the interfacial bed layer. This phenomenon involves the complex field of sediment transport, which has been greatly developed in streams, but much less in estuaries and lakes. The bed system may now be envisioned as three distinct segments: a moving interfacial layer, a mixed zone and a stationary bed beneath. There is vertical exchange between the moving and mixed layers and the vertical transport in the bed is characterized by the sedimentation velocity.

This type of bed regime is associated only with types B and C fluid transport system. The direction of horizontal motion of the bed is in accordance with velocity vector of the fluid in contact with the bed surface. In freshwater streams and rivers, the bed transport is downstream in the direction of flow, while in estuaries, the net bed transport is upstream in the saline zone due to the tidally averaged motion as shown in Figure 1-3.

#### BASIC ELEMENTS OF ESTUARINE MODELS

In accordance with equation (1-1), the primary components of the mass balance equations are the transport, the transfer and the relevant reactions. Reference is made to Figure 1-2 which describes schematically the reaction and transfer routes, which take place in the water and the bed. It is evident from the discussion of estuarine transport that the fluid motion may be envisioned as a two-layer flow system, the upper layer seaward and the lower landward with a vertical flow to maintain continuity. In addition, turbulent exchange occurs between the two layers. These transport and transfer routes are shown diagrammatically in Figure 1-5, for the fluid, the solids and the two components of the chemical, the dissolved and the particulate. For the solids, the additional terms representing settling and scour are shown. Also represented are transport and transfer elements in the bed. Due to the nature of the water-bed exchange, allowance is made for the motion induced in the layer in contact with the landward moving fluid. This motion is re-stricted to a few centimeters of the upper layers of the bed, which is dissipated at greater depths. Thus a lower stationary bed region is incorporated in the model, into which the particulate components of the chemical is introduced by sedimentation and the dissolved components by diffusion.

The basic elements of an organic chemical model in an estuarine environment are thus represented in Figures 1-2 and 1-5, the former indicating the kinetic and transfer routes and the latter the transport and transfer routes. These patterns describe most completely the overall distribution vertically and longitudinally in both the water and the bed and they are incorporated in the overall model developed in this project. In order to proceed with the development of this model, it is informative to analyze separately the various characteristics of suspended and bed solids and the individual kinetics relevant to organic chemical, specifically to Kepone. Accordingly, the

- 9 -

following sections first describe the kinetic interactions of the modeling framework with particular emphasis on adsorption/desorption processes (Section 2) - the phenomena which, with their characteristic mechanisms and rates, play significant roles in determining the ultimate fate of materials in estuarine systems. The characteristics of solids, both suspended and in the estuary bed, are examined in Section 3. In particular, settling, sedimentation, compaction, solids entrainment and sediment transport are dis-cussed with respect to the interaction of solids with Kepone in the bed and suspension. Given these factors, the one-dimensional analysis of salinity, suspended solids and the organic chemical are presented in Section 4 which is used for a preliminary analysis of the problem. Section 5 presents the two-dimensional (longitudinal-vertical) analysis of these constituents, in which the equations describe more realistically the distribution of the constituents. Exchange between lateral embayments are incorporated. These equations are applied to the analysis of Kepone in the James River in Section 6 for both steady-state and time-variable conditions. The model is calibrated with two sets of survey data. The time history of the Kepone from its initial discharge to the cessation of production and the subsequent fifteen years is simulated. Sensitivity analysis and projections are described in Section 6 and conclusions and recommendations in Section 7.

- 10 -

		BED C	ONDITION	1
		I STATIONARY BED	II MIXED LAYER WITH BED	III SEDIMENT TRANSPORT WITH LAYER & BED
	υ <sub>b</sub> ε <sub>b</sub>	0 ≽0	0 > 0	· >0 >0
FLUID TRANSPORT REGIME	A LAKES RESERVOIRS COASTAL ZONE	DEEP, MINIMAL WINDS	MODERATE DEPTH, WINDS	LITTORAL ZONES
	B STREAMS & RIVERS	LOW FLOW	MODERATE FLOW	HIGH Flow
	C ESTUARIES EMBAYMENTS	ENCLOSED BAYS MINIMAL TIDES	LITTORAL ZONES MAIN CHANNEL LOW FLOW	MAIN CHANNEL MODERATE FLOWS
	D COMPLETELY MIXED	APPLICABLE PARTICULARL RESERVOIRS	TO ALL TYPES, Y TO LAKES & EMBAYMENTS	- -
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## SECTION 2

## ADSORPTION-DESORPTION

The process of adsorption-desorption is an important transfer route of many constituents in natural water systems. The majority of radionuclides, heavy metals and organic chemicals are usually susceptible to adsorption. Bacteria and algae also have a similar tendency. The surfaces to which these constituents adhere are provided by the solids, either in suspension or in the bed. The clay, silica and organic content of the solids are the effective adsorbents by contrast to the sand and silt components.

The substance, in the adsorbed form may be then affected by additional processes such as flocculation and settling. If the flux due to the latter force is greater than that of the vertical mixing, the particulate species deposit on the bed. In streams or rivers, they may then be subjected to resuspension during periods of high flow or intense winds and be transported to a reservoir or estuary. Since the hydrodynamic regime of each of these systems is more conducive to sedimentation than is that of a flowing stream, the ultimate repository of the particulate species frequently is in the bed of the reservoir or estuary. Furthermore, the physiochemical characteristics of the estuary tend to promote desorption and constituent may be released to be recirculated with the estuarine system or transported to the ocean. Therefore, in analyzing the distribution of substances which are subject to adsorption, it may be necessary to take into account a sequence of events both with respect to the hydrologic and hydrodynamic transport through various systems, as well as the kinetic aspects of the transfer processes of adsorption-desorption and settling-scour within these systems.

The following describe the various factors which affect the adsorptiondesorption processes and, based on these, present the development of the relevant equilibrium relations and transfer equations.

### EQUILIBRIUM

Adsorption is a process in which a soluble constituent in the water phase is transferred to and accumulates at the surface of the solids. The adsorptive capacity of a two-phase system depends on the solubility of the constituent and the affinity of the constituent for the solid. The greater the degree of solubility the less is the tendency to be adsorbed. A number of organic compounds have both hydrophylic as well as hydrophobic groups resulting in the orientation of the molecule at the interface. The hydrophylic component tends to remain in solution while the hydrophobic part adheres to the surface.

- 16 -

The molecular characteristics of a compound - its size and weight are related to adsorption capacity, in a fashion consistent with solubility. For a given homologous series, the solubility is inversely proportional to molecular weight and it has been observed that the adsorption capacity increases with increasing molecular weight.

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The affinity of the solute for the solid may be due to an attraction or interaction of an ionic, physical (van der Walls forces) or chemical nature. Most adsorption phenomena consist of combinations of three forms and it is generally difficult to distinguish between them. The more general term "sorption" is used to describe the overall process.

In any case, one notable characteristic of the phenomenon is the dynamic equilibrium which is achieved between the concentration of solute remaining in solution and that on the surface of the adsorbent solid. At equilibrium, the rate of adsorption equals the rate of desorption. The equilibrium relationship, at constant temperature, between the concentration of solute and the amount adsorbed per unit mass of adsorbent is known as an adsorption isotherm. The amount adsorbed per unit mass increases with increasing concentration of solute and usually approaches a limit as the capacity of the solid to accumulate is reached.

Equilibrium exists when the rates of adsorption and desorption are equal. The rate of adsorption depends on the concentration of the solute and the available sites on the adsorbing solid. The latter is proportional to the adsorptive capacity of the solid minus the amount of solute adsorbed. The rate of desorption is proportional to the amount of solute adsorbed:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \mathrm{K}_{1}\mathrm{c}[\mathrm{p}_{c}-\mathrm{p}] - \mathrm{K}_{2}\mathrm{p} \tag{2-1}$$

in which

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=	dissolved	concentration	of	solute	(M/L)	
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- = particulate concentration (M/L)
- = capacity of the adsorbent solids (M/L) P<sub>c</sub>
- = adsorption coefficient  $\left(\frac{1}{TM/L}\right)$ <sup>K</sup>1
- K.2 = desorption coefficient (1/T)

The overall reaction is second order with respect to adsorption and firstorder with respect to desorption. The particulate concentration is a product of the concentration of adsorbing solids in the water, m, and the mass of the solute per unit mass of the adsorbent, r. Equation (2-1) may be expressed:

$$\frac{dc}{dt} = K_1 c m[r_c - r] - K_2 rm \qquad (2-2)$$

At equilibrium, the rate of change of concentration is zero and equation (2-2) becomes after rearranging:

- 17 -

in which  $b = \frac{K_1}{K_2}$ 

Equation (2-3) is known as the Langmuir isotherm in which the parameter, b, is related to energy of adsorption. At  $r = r_c/2$ , the concentration equals 1/b. The parameters,  $r_c$  and 1/b may be evaluated graphically by a linear plot of 1/c versus 1/r. The intercept equals 1/r\_c and the slope 1/br\_c.

The capacity r depends on the nature, size and characteristics of the

adsorbing solids. The various types of clays have greater capacities than silts and sands. The adsorption capacity is, thus, inversely proportional to the size of the particle, specifically to the ratio of its surface area to volume. Furthermore, the capacity is directly proportional to the organic content of the solids. In general, solids composed primarily of organic material have greater capacities than the inorganic components. These materials include detrital matter, and various forms of viable organic substances, such as bacteria, plankton and macrophytes in natural systems and biological solids in treatment systems.

The Langmuir isotherm is based on the assumption that maximum adsorption occurs when the surface of the adsorbent is saturated with a single layer of solute molecules. If one assumes that a number of adsorbate layers may form, the equilibrium condition may have various points of inflection. Essentially an additional degree of freedom is introduced which reflects a greater degree of realism. The resulting relationships fit certain experimental data . better than the Langmuir, particularly at the higher concentrations of solute. At lower concentrations the two isotherms may be approximately equivalent. In addition to the monolayer assumption, there are other conditions for which the Langmuir isotherm may not be appropriate. A semi-empirical relationship, known as the Fruendlich isotherm, which has been found to be more satisfactory in certain cases, is as follows:

$$\mathbf{r} = \mathbf{K}\mathbf{c}^{1/\mathbf{n}} \tag{2-4}$$

The value of the exponent n is usually less than unity. This isotherm has been widely used in the correlation of experimental data, particularly with respect to the adsorption by activated carbon in water and wastewater treatment processes.

If the rates of adsorption and desorption are rapid, with respect to other kinetic and transfer mechanisms, equilibrium between the dissolved and particulate species, expressed by equations 2-3 or 2-4 may be assumed to be established instantaneously.

- 18 -

The above isotherms appear to be particularly appropriate for the analysis of a singular adsorbate or those cases where one is predominant, such as kepone in the James River. When there are a number of compounds present, preferential adsorption and displacement may occur. Present research efforts are directed to the analysis of this problem. A competitive Langmuir isotherm and ideal solution theory are being applied in these cases. For very low concentrations of solute, c << 1/b, the Langmuir isotherm is linear:

#### r = ¶c

The parameter, 1, is termed the partition coefficient. It is the ratio of the mass of substance adsorbed per unit mass of adsorbent solids and the dissolved concentration of solute in the linear range of the Langmuir and Fruendlich isotherms.

The constant K in the Fruendlich isotherm is comparable to the partition coefficient. As the exponent n approaches unity, the isotherms are identical. Since the concentrations of organic chemicals in natural systems are generally low and, thus, well below the capacity of solids in these systems, the linear assumption is a reasonable approximation in many cases.

The partition coefficient incorporates the capacity parameter r.

Therefore, the same factors which influence its magnitude have a comparable effect on the partition coefficient. Large values are characteristic of organic material and clays, by contrast to silts and sands. A typical example is found in data of Garnas, et al. (1), which presents the equilibrium between solid phase concentration and dissolved concentration of Kepone for various types of solids (Fig. 2-1). The slope of one on the logarithmic coordinates is an indication of the appropriateness of the linear portion of the Langmuir isotherm in the region in which the adsorption capacity, r<sub>c</sub>, is

much greater than the solid phase concentration, r (equation 2-5). The influence of the type of adsorbing solids is apparent: the highest partitioning occurring with sediment from Range Point Salt Marsh off Santa Rosa Sound, Florida, which is primarily clay with a high percentage of organic matter. As the organic content decreases, the partition coefficient decreases, the lowest values being associated with material that is primarily sand.

Under equilibrium conditons, the distribution of constituent mass between the dissolved and particulate fraction is established by the partition coefficient and the concentration of the adsorbing solids. The solids may be suspended in the flowing water or relatively fixed in the bed of the system. Under extremely high flow in rivers or winds in lakes, the bed may be scoured and the solids are introduced into the overlying water for a brief period of time, after which they settle to the bed. In any case, assuming sufficient time has elapsed to establish adsorption equilibrium, the total concentration of organic chemical or metal,  $c_{\tau}$ , is the sum of dissolved and particulate:

## $c_T = c + p$

(2-6)

(2-5)

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The dissolved component may be expressed in terms of the particulate frac-

- 19 -

tion, r, and the partition coefficient, while the particulate concentration as a product of the concentration of adsorbing solids, m, and the particulate fraction:

$$c_{\rm m} = \frac{r}{\eta} + rm \tag{2-7}$$

An additional control on the dissolved-particulate distribution is the dependence of the partition coefficient on the concentration of the adsorbing solids (2). The results of a number of laboratory studies demonstrated an inverse relationship between the concentration of adsorbing solids and the partition coefficient (Fig. 2-2). The data were correlated using the functional form:

$$1 = 1_{\infty} + \frac{\beta}{m^{\alpha}}$$
(2-8)

where:

 ${\P}_{\alpha}$  = limiting partition coefficient at high sediment concentration

 $\alpha, \beta$  = empirical constants.

Although no fundamental basis for the relationship has been shown, a vast amount of experimental data is available to substantiate its validity.

The relationship is particularly significant in determining the time required to flush the Kepone from the James River. It implies that the period required is greater than that for a constant-partition condition. This assessment is based on the following reasoning. The material is now concentrated in the bed. When scoured, the contaminated solids are transported vertically into the flowing waters, diluting the concentration by at least one and, more likely, two or three orders of magnitude. Assuming equilibrium is achieved rapidly, these solids accumulate more of the metal or chemical, due to the increase in partitioning. Upon subsequent settling, the solids re-establish the previous equilibrium by releasing dissolved material to the interstitial waters. The subsequent diffusion of the dissolved material is a relatively slow process, thus retaining the constituent in the system longer than if it remained in the flowing waters.

## Kepone Partition Function

The adsorption of Kepone has been extensively studied by Connolly (3), Equilibrium and kinetic behavior were determined using sediments from both the James River and Range Point Salt Marsh, located on Santa Rosa Island, Florida. At constant sediment concentration and equilibrium dissolved Kepone concentrations as high as  $500 \ \mu g/l$ , the Kepone adsorption isotherm is linear and is thus described by the partition coefficient. Consistent with equation (2-8), the partition coefficient was found to vary inversely with sediment concentration (Figure 2-3). This variability was significant, the partition coefficient decreasing by more than an order of magnitude as sediment concentration increased from 10 to 10,000 mg/l.

- 20 -

For the James River sediment, the functional correlation of the partition coefficient and sediment concentration (Eq. 2-8) is:

$$= 1000 + \frac{259,000}{m^{1.2}}$$

(2-9)

with a coefficient of determination of 0.877. It was also shown that hysteresis is not significant, partition coefficients being similar for adsorption and desorption tests at similar sediment concentrations.

### Transfer Rates

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The discussion above concerned equilibrium conditions. The time required to achieve this condition involves the transfer and kinetic mechanisms between adsorbate and adsorbent. The sequence of processes, which characterize the transfer of a substance from solution to a material which has an adsorptive capacity, may be grouped in the following three steps: The first is the transfer of adsorbate through a liquid film to the surface of the adsorbent; and the third is the fixation of the adsorbate on the interior pore or capillary surfaces of the adsorbent. The last step is usually assumed to be very rapid and equilibrium exists at this location. In some cases, the transfer of solute through the surface film or boundary layer is the ratelimiting step. If there is sufficient mixing due to the turbulence of the flowing water, the second step, that of diffusion within the porous material controls the rate.

The very dilute solution of both species, the frequency with which the solute comes in contact with the adsorbent may determine the rate-limiting step. In some cases, adsorption may be occurring on contact of the solute with the bed material and the control may then localize in transfer through surface film on the exterior surface of the bed solids. The situation is comparable to the biological oxidation of organic matter, which takes place in the flowing water by the planktonic bacteria and in the channel bed by the benthic organisms. Both reactions occur simultaneously in natural systems, but in many cases, one or the other controls depending on the depth of the flow, the nature of bed and materials contained in each.

A review of adsorption models and their applicability has been presented by Connolly (3), from which the following discussion is abstracted. Three models were considered: a Langmuir kinetic expression, a surface diffusion model including liquid film transfer, and a model considering a series of mass transfer steps to the particle interior.

#### ADSORPTION MODELS

## Langmuir Kinetic Expression

The Langmuir Kinetic Expression is essentially Eq. 2-2. The simplicity of this equation makes it useful in describing adsorption kinetics. Values for the adsorptive capacity and the ratio of the adsorption and desorption

- 21 -

rate constants may be obtained directly from isotherm data. The model considers adsorption as a single step process. There is no explicit specification of mass transport steps that may be important to the overall adsorption process. While it is true that the rate constants are implicitly related to mass transfer, the model cannot distringuish multiple steps nor handle changes in mass transfer rates due to changes in hydraulic conditions. Consequently, it is applicable only to cases where adsorption rate is controlled by a single mechanism throughout the adsorption process, by Weber and Crittenden (4).

## Surface Diffusion Model

The surface diffusion model was originally presented by Matthews and Weber (5). Three mechanisms are considered in representing the adsorption process: diffusion from the bulk fluid to the particle surface, adsorption at the surface, and diffusion of sorbed compound on the particle. Local surface kinetics are assumed to be much faster than diffusive transport and local equilibrium is applied at the particle surface.

The basic differential equation results from conservation of mass expressed in spherical coordinates:

$$r^{2}d\Theta^{2}dr \frac{\partial q}{\partial t} = -r^{2}d\Theta^{2}D \frac{\partial q}{\partial r} - (-r^{2}d\Theta^{2}D \frac{\partial q}{\partial r} + (\frac{\partial}{\partial r}(-r^{2}d\Theta^{2}D \frac{\partial q}{\partial r}))$$
$$\frac{\partial q}{\partial t} = \frac{1}{r^{2}}\frac{\partial}{\partial r}(r^{2}D \frac{\partial q}{\partial r}) \qquad (2-10)$$

A flux equality condition stating that the rate of flux through the laminar boundary layer surrounding the particle is equal to the rate of flux into the particle is used as the surface boundary condition, or

$$\rho_b D_{\partial r}^{\partial q} = \frac{k_f}{1000} (c - c_s)$$
(2-11)

where

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D = surface diffusion coefficient (cm<sup>2</sup>/sec)

- q = sorbed concentration (µg/gm adsorbant)
- ${\bf k}_{\rm f}$  = film (laminar boundary layer) mass transfer coefficient (cm/sec)

 $\rho_{b}^{-}$  = particle density (gm/cm<sup>3</sup>)

c = bulk liquid dissolved phase concentration ( $\mu g/l$ )

- $c_{g}^{}$  = near surface dissolved phase concentration (µg/l)
- r = particle radial coordinate
- R = particle radius (cm)

A zero flux condition at the particle center is employed as:

$$\frac{\partial q}{\partial r} = 0 @ r = 0$$

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$$(2-12)$$

The dissolved phase and sorbed phase are coupled through a kinetic equilibrium expression relating the near surface dissolved concentration  $c_{\rm g}$ 

to the particulate surface sorbed concentration  $q_g (q_g = q @ r = R)$ . Any of the isotherm equations mentioned previously or any equilibrium equation may be used.

### Series Mass Transfer Model

The third model was developed by Famularo, Pannu and Mueller (6). Three mass transfer steps are considered. Solute is transported from the bulk liquid through the laminar boundary layer to the particle surface. Instantaneous equilibrium between the solid phase and liquid phase at the particle surface is assumed. Sorbed solute is transported from the particle surface into the large pores or "macroshell" of the particle. Finally, sorbed solute is transported from the macroshell into the small pores or "microcore". In each step the rate of transport is expressed as the product of a mass transfer coefficient and a linear concentration driving force.

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The microcore/macroshell concept is envisioned as a sample representation of solute transport into an adsorbent with a bi-modal pore size distribution. The model was developed for adsorption to activated carbon which exhibits such a pore size distribution. In the conceptualization of the model, the particle is assumed to be a sphere of radius R that is divided into two regions; the macroshell and the microcore. Each region is assumed to be of uniform-state (completely mixed) and thus represented by a single concentration. The distribution of particle volume between the two regions is an empirical parameter determined through fitting the model to adsorption data.

A modified version of the model was employed in analysis of Kepone in which the particle surface-macroshell transport step is eliminated. The surface dissolved phase concentration is assumed to be in equilibrium with adsorption sites on the particle surface and in the large pores. This modification was performed because simulation capability was not affected and a degree of freedom was eliminated from the model.

The rate of mass transport, n (µg/sec), is given by the following equations. Transport from bulk liquid to particle surface is given by:

$$n = \frac{k_f a_s}{1000} (c_s - c_s)$$
(2-13)

and transport to interior of the particle is represented by:

 $n = k_{c} a_{c} \rho_{b} (q_{s} - q_{c})$ (2-14)

where

 $a_s = total particle surface area (cm<sup>2</sup>)$ 

- 23 -

 $a_{_{\rm C}}$  = total interfacial area between exterior and interior sections (cm  $^2)$ 

 $q_{_{\rm S}}$  = solid phase concentration in exterior section (µg/gm)

 $\boldsymbol{q}_{_{\rm C}}$  = solid phase concentration in interior section (µg/gm)

## KINETICS OF KEPONE ADSORPTION

Kepone adsorption experiments show a rapid decrease of dissolved Kepone for approximately 5 minutes followed by a slower rate of decrease to equilibrium. Typical experimental results are shown in Figure 2-4. The majority of total adsorption (70 to 80 percent) occurs in the first 5 minutes. Equilibrium is reached in 1 to 2 hours. The three models fit the data reasonably well, as shown in Figure 2-5. The Surface Diffusion and the Series Mass Transfer models fit the initial high rate better than the Langmuir, indicating that the multi-step kinetic analysis is a more valid description of the phenomenon than the single-step. These kinetics suggest that for the time scale considered in this work an assumption of instantaneous equilibrium is valid. Such an assumption may not be valid, however, if an intratidal time scale is important to the problem.

- 24 -

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## SECTION 3

### CHARACTERISTICS OF SUSPENDED SOLIDS AND BED SEDIMENT

The distribution of an organic chemical or a heavy metal is highly dependent on the physical characteristics of the solids and the hydrodynamic regime which affect the solids both in suspension and the bed. Accordingly, this section of the report is directed to a discussion of the relevant features of suspended and bed solids. Solids in suspension are characterized by concentrations in order of  $10-100 \text{ mg/}\ell$  for the low to moderate freshwater flows encountered in many coastal plain estuaries, such as the James River, and up to concentrations of many hundreds for the higher flood flows. The concentration of bed solids, on the other hand, is in the order of some hundred thousands, while the interfacial zone may have values in intermediate range of 10,000 mg/ $\ell$  to 10,000 mg/ $\ell$ . The interfacial region is highly dynamic due to shearing stresses and velocity gradients which are most intense in this zone. It is furthermore affected by the tidal action, the magnitude of freshwater flow and, to some degree, by the intensity of the winds. It is the hydrodynamic structure of this region and its associated concentration which are most indicative of the distribution of solids and the adsorbed material in suspension and the bed. The flux of solids through this zone may be negative or positive, characterizing a region of estuary as sedimenting or eroding.

## SETTLING, SEDIMENTATION AND COMPACTION

Sedimentation occurs when the net vertical flux of solids is downward from the water column to the bed. In suspensions of relatively low concentrations ( $\sim 100 \text{ mg/k}$ ), the particles settle individually, discounting any flocculation effects. As the concentration increases ( $\sim 1000 \text{ mg/k}$ ) the hindering of the settling process is initiated. In suspensions with concentrations in order of 10,000 mg/k or less, the mass tends to settle as a unit, very comparable to settling of biological sludges in wastewater treatment processes. As the mass settles and compacts into beds of higher concentration, water is displaced upward through the voids and the process of sedimentation takes place. The limit of this process produces concentrations in the order of some hundreds of thousands mg/k, at which levels it is customary to express the characteristic concentrations in terms of porosity or voids ratio.

Investigations of estuaries, in which detailed measurements of the mechanisms were studied, indicate that two characteristic consolidations occurred. One is associated with flocculated silt, which is formed relatively rapidly and is much more stable than that of the soft silt. The water between the particles is essentially pressed out under the weight of the overlying mass. The density of the consolidated material increases and at about  $1300 \text{ kg/m}^3$ .

- 31 -

the mixture is no longer fluid but has become more solid, a so-called "hard mud".

The consolidation of the soft silt takes some appreciable times and one of the most important features of a bed of this material is the duration of time over which it retains its relative mobility. This material is more readily eroded and also may be displaced by the flowing water, comparable to sediment transport in rivers. It is extremely difficult to measure consolidation under prototype conditions. Laboratory investigations on the density of the representative areas of the bed should be a routine element in an estuarine sampling program for toxic substances. Regardless of the initial

density (1050 - 1150 kg/m<sup>3</sup>), the equilibrium value in the order of 1300 kg/m<sup>3</sup> appears to be achieved. The vertical distribution of density within the bed varies in a typical fashion, increasing asumptotically in an exponential manner to an equilibrium density:

 $\phi = \phi_e [1 - e^{-gz}]$ 

 $\phi$  = porosity at z

 $\phi_e$  = equilibrium porosity

 $g = coefficient - L^{-1}$ 

Soft silt which remains in place for some weeks gradually changes into a more compact and consolidated material. In addition, the strength of the material increases and thus is less susceptible to erosion. Whether or not the material was fully thixotropic - i.e., regains its structure after deformation has stopped - has not been determined.

In general, when sedimentation takes place at relatively slow rates, the consolidation process of the deposited solids more or less keeps pace with the supply of new material. When however, a massive deposition occurs, conditions lend themselves to the formation of soft silts which are more susceptible to erosion. The conclusions to be drawn from these studies, as applicable to the Kepone analysis of James are two-fold:

- Depending on the nature of the solids, the bed may compact and tend to retain any substances adsorbed to its surface or if sufficient time is not available for consolidation, it will form a less dense more erodible bed, which is susceptible to erosion.
- 2. Depending on the seasonal and annual inflow of solids and the local hydrodynamic condition, the bed material may progressively be covered and buried or be characterized by a highly interactive system in which the adsorbed material will be concentrated in the upper layers of the bed.

All estuaries are characterized by both these conditions in some degree and tend, on annual balance and a large scale, to be sedimenting and accumulating systems in which solids and the adsorbed material are retained. The fraction which is stored within the estuarine fluid and bed system, as contrasted to that transported to the ocean, depends on the relative magnitude of rate of supply of fresh solids and the rate of sedimentation and consoli-

- 32 -

dation. It is likely that these factors and the associated fluxes establish the nature of characteristics of the estuarine bed. These in concert with the tidal and fresh water hydrodynamics determine the degree of water-bed interaction. The James River Estuary includes areas which are characterized by highly inactive bed water exchange, as well as those which are primarily sedimenting and compacting.

There are various procedures which have been employed in the field to measure sedimentation rates: rate of change of elevation, radioactive traces and stratographic markers. Rates of sedimentation and erosion may be approximately calculated by depth changes which occur over extended time periods  $\sim$  decades. This has been done in the James River Estuary (1). The main site of deposition is apparently in the middle estuary, where the salinity ranges from 5 to 14 parts per thousand. It also occurs at the upstream end of the salinity, but to a lesser degree. While sedimentation rates up to 3 cm/yr have been noted, average estuary-wide values appear to be in the order of tenths to one centimeter per year.

The second, more commonly used method at the present time, involves the measurement of certain radionuclides from specific sources: Global fallout from atmospheric bomb tests and low-level releases of local nuclear reactors. Elements which are typically utilized for such purposes in sediments are nuclides such as plutonium, lead, cesium and cobalt, among others. The vertical distribution of these substances indicate not only their natural decay rates, but more important, sedimentation rates of the deposited fine-grains sediments. (Stratographic markers, commonly used in oceanographic sedimentation has not been applied to estuaries). An example from the Savannah River estuary (2) is shown in Figure 3-1 which displays the logarithm of the radio-activity against a linear scale of depth. The semi-logarithmic slope is the ratio of the decay rate of the isotope to the sedimentation velocity of sediment. Since the former is known for each isotope, the latter is readily determined from the slope of the fine fit through the observations.

## MECHANISM OF ENTRAINMENT

The fundamental hydrodynamic factors which bring about transport of bed material, also are effective in the entrainment mechanism. The problem of sediment movement and entrainment is so complex that it has not yet been subject to completely rational and analytical solution. The major emphasis in the past has been concerned with transport in rivers, and relatively little has been done in estuaries. The most fruitful analysis has proceeded on the basis of qualitative reasoning and dimensional analysis, confirmed and supplemented by laboratory experiments and field observations in freshwater streams. The majority of the analytical treatments involve general relationship between dimensionless parameters of the flow and the characteristics of the particles. All involve consideration of the force inducing notion and that resisting: the former expressed as a function of the particle diameter and shear velocity and the latter related to the form of the bed and the immersed weight of the particle.

- 33 -

The motivating forces are the drag parallel to and the lift normal to the bed. The resisting forces may be categorized by the size and nature of the particle: for coarse sediments, such as sand and gravels, the resistance is due to submerged weight of the particles and for fine sediments, such as silt and clay, cohesion, rather than weight, is the more important factor. Furthermore, the coarser particles move as individual units while the finer sediments are entrained as agglomerates of a number of individual particles. A comparison may be drawn in this respect to the discrete and flocculent phases of settling.

The finer particles have a much greater tendency to attract and adsorb other substances such as organic chemicals, heavy metals and nutrients. Consequently, these finer solids - the clays and the organic particulates - are usually of much greater importance in water quality than are the sands and gravel. However the entrainment and transport of the finer particles has received much less attention than those of the coarser particles. The following sections present first, a brief review of the latter to indicate the general development of the field and, second, the possible application to the more important problems associated with the finer particles, with a description of their important characteristics.

#### Coarse Solids

Although both lift and drag are recognized as forces which tend to produce bed movement, most of the theoretical developments have considered only drag. Since both mechanisms are functions of the density and velocity of the fluid, the omission of the lift effect is not critical at this stage of development. It is automatically taken into account by the coefficients, which are determined experimentally.

When bed motion is impending, the shear stress attains a critical value,  $\tau_c$ . The shear or drag force is a product of this bed stress and the surface area, which is expressed in terms of the equivalent diameter of the particles composing the bed - i.e.,  $\tau_c c_1 d^2$ , in which  $c_1$  is an areal shape factor which permits expressing the surface area in terms of an equivalent diameter, d. This force is resisted by the gravity force, the submerged weight of the particle in the fluid - i.e.  $c_2 g[\rho_s - \rho] d^3$ , in which  $c_2$  is a volumetric shape factor.  $\rho_s$  and  $\rho$  are the densities of the solid and the fluid, respectively. The frictional resistance is taken into account by the nature of the material (clay, silt, sand) and form of the bed (ripples, flat, dunes). Bed motion is incipient when the drag force equals the resisting force. Thus,

$$\tau_{c} = C \rho g[s_{s}-1]d \qquad (3-1)$$

in which  $s_s$  = specific gravity of the particle. The coefficient, C, is combined effect of the shape factors of the particles and the characteristic nature and form of the bed.

- 34 -

Confirmation of this general relation and further insight into the mechanism of bed motion is obtained from a dimensional analysis of the relevant variables,  $\tau_c$ ,  $\rho$ ,  $\rho_c$ , d,  $\mu$  and g, which yields

 $\frac{T_{c}}{\rho g[s-1]d} = \phi \left[\frac{U_{*}d}{\nu}\right]$ 

(3-2)

in which

$$U_{\star} = \left[\frac{\tau}{\rho}\right]^2$$
 = shearing velocity  
 $v = \mu/\rho$  = kinematic viscosity

1.

It is apparent from equation (3-2) that the right-hand side is a bed Reynolds number, which defines the coefficient, C, of equation (3-1), and that the left-hand side is a form of the Froude number, since  $\frac{T}{c}$  may be replaced by

 $U_{\star}^{2}$ . Equation (3-2) was first developed by Shields (3). Figure 3-2 presents a graph of this function, based on experimental data measured in flumes with artificially flattened beds of noncohesive sediments. Noteworthy is the similarity between the function presented in Figure 3-2 and those defining fluid flow of water and air over surfaces of increasing roughness. This type of function, relating a Froude and Reynolds number, has been used by many investigators to correlate and compare various sets of experimental data. A coordinate above the correlation line represents movement, saltation and ultimately suspension while that below, a stationary condition. At low values of the Reynolds number, the sediment particles are completely encompassed by the viscous sublayer and the motion characterized by viscous action. A minimum in the function is usually encountered, beyond which the function approaches a horizontal line. In this regime, the sublayer is completely disrupted by virtue of the roughness induced by the particles and the motion involves boundary turbulence.

Additional experimental investigations, notably by Taylor and Vanoni (4), indicated that the pattern shown in Figure 3-2 is affected by the sediment discharge. For a given Reynolds number, the critical shear decreases as the sediment discharge, but retains the general shape of the function as expressed by the above equation.

The function shown in Figure 3-2 may be re-expressed more directly in terms of the critical shear necessary to initiate motion of a particulate of various sizes. A more practical relationship may be developed by expressing the critical shear in terms of a flow velocity. Converting the shear to a mean velocity, the resulting relationship with the particle diameter is presented in Figure 3-3. The relationships are based on the analysis of Hjulstrom (5), who employed the data of several workers. The range represents data for depth of flows greater than 1 meter, which should reflect the more realistic conditions encountered in natural systems. The data for mean sediment sizes less than 0.01 mm are taken from the original work of Fortier and Scobey. Individual data points represent those studies in which the solids were partially composed of clays. In general, these fine materials have

- 35 -

physical and chemical properties, quite different from the coarser materials.

#### Fine Solids

These particles consist of the clays and smaller silts and are generally referred to as the wash load in sediment transport in streams. In estuaries, the major portion of the solids transport is composed of the fine solids, which are much more readily held in suspension. Smaller scale agitation, both thermal and fluid, are effective in this regard. In general, these fine materials have physical and chemical properties quite different from the coarser materials.

Many of these particles have electrical charges, which in fresh water systems are repelled by like charges on other particles. Particles of kaolinite, a clay of hydrous silicates of aluminum having calcium and magnesium bases, repel each in fresh water. In a water containing a high percentage of dissolved salts, as encountered in estuaries, the sodium ions of the chlorides exchange with the calcium or magnesium ions from the particles. On the loss of the charge, particles attract each other, grow in size and form flocs. The settling velocity of the agglomerates is greater than that of the individual particles.

Many of these fines form soil-water complexes which possess definitive physical and chemical characteristics. Electro-chemical forces frequently control the behavior of these particles, which in large measure is determined by the structure and composition of the elemental particle and the chemistry of the pore water. As may be inferred from the previous discussion, the state and history of the compaction are formative factors. While many investigators agree that it is likely the fundamental electro-chemical properties have a bearing on soil-erodibility, few studies have been conducted to eludicate the relation. Most investigators have approached the problem from the viewpoint of the physical properties of the clays.

In alluvial soils the threshold of sediment motion was defined in terms of the entrainment function,  $\frac{\tau}{\rho g d}$ , which has definite discrete values for

various size grains. In cohesive soils, the assignment of equivalent grain size in a comparable manner is nebulous. The value in general is increased by cohesion, but there is no general relation between cohesion and grain size. The cohesive or shear strength of clay soils is expressed in terms of its physical characterisitics such as normal stress on the rupture plane and the angle of friction. Although shear strength is frequently used to describe clay soils, no definitive correlation has been found between this property and erodibility. The same comment may also be applied to the Atterberg limits which define the consistency of clay materials: liquid limit, plastic limit and plasticity Index. It appears to be accepted that erosion rates and the associated critical shearing stresses are related to some measure of moisture content.

A correlation, frequently referenced (5) is also shown in Figure 3-3 which follows the general dimensionless Shields relation. The percent water is the additional variable which permits some assessment to be made of the

- 36 -

critical velocity for various clay compositions. The critical erosion velocity diminishes with decreasing grain size down to about 150 microns - a value in the order of the silt-sand delineation. For smaller grain sizes, the critical velocity increases and the finer the size, the greater the range. For clays, the range is primarily affected but the state of consolidation or water fraction, as shown.

It is apparent from this brief review that there are a number of factors which affect the distribution and transport of cohesive particles in estuaries, which play the dominant role in estuarine shoaling. More recent work has been directed to a better understanding of the fine sediment in the flow field. Krone (6) conducted a series of studies on the deposition of San Francisco Bay salty clay (commonly referred to as bay mud), investigating such factors as the apparent settling velocity of the sediment, the bed shear stress and the critical shear below which no sediment remains in suspension. Partheniades (7) used a recirculating flume to study the erosion and deposition of the same sediment as Krone.

Figure 3-4 presents the erosion rates of the silty clay sediment as a function of the shearing stress of the fluid on the bed. Below a threshold value, U  $\sim$  15cm/s, a rapid deposition of practically all the solids occurred. Greater than this, scour commences and increases rapidly in the vicinty of 30-40 cm/sec depending on the condition of the bed. The two types of sediment investigated refer to a loose compaction formed from resuspended (I) and a more dense consolidation representative of the deeper cores (II). Type I is presumably representative of the surficial sediment, which interacts with the water, while Type II is characteristic of the consolidated deeper sediment. Also shown in Figure 3-4 are the data of Ariathurai and Arulanandan (8) who investigated the shear and erosion in a rotating cylinder, similar to Krone's original setup. Among the number of factors, study the temperature effect was most evident as indicated by the plotted data. It was also shown that the composition and concentration of the pore water influenced the erosion rates.

#### SEDIMENT TRANSPORT

The above discussion related to the entrainment of solids from or close to the water bed interface a mechanism which enhances the transport of solids in suspension. The total solids transport includes not only the suspended load, but also the bed load. The former includes the small, fine clays and some silts which are maintained primarily in suspension while the heavier silts and sands are incorporated in the latter. In tidal systems, it is apparent that the periodic variation of current is reflected in a comparable variation of solids concentration and composition over the tidal cycle and thus in the suspended load. The increase in the larger and more dense clays and silts at maximum tidal currents is due to the enhanced shearing stress active over the bed during these times, entraining particles which under lower fluid velocities and shear, would remain in the bed. The mechanism of entrainment increases the suspended load and promotes more exchange not only between the bed and suspended particles, but also the increases the possibility of exchange of organic chemicals and heavy metals adsorbed to these par-

- 37 -

ticles. The bed transport carries the heavier particles within the bed itself or in a layer very close to the bed during periods of tidal motion.

Sediment transport in estuaries, has been relatively little studied and is poorly understood. The knowledge gained of the phenomenon in fresh water streams provides at least some basis and a point of departure for an analysis in estuaries. The majority of sediment transport equations are of the following general form:

$$G_{s} = K[\tau_{o} - \tau_{c}] U^{m}$$
(3-3)

in which

 $G_s = sediment transport rate$ 

K = constant description of the characteristics of the particles

 $\tau_{0}$  = shearing stress

 $\tau_{c}$  = critical shear inducing motion

U = a measure of the flow velocity

Since the shearing stress is equivalent to a velocity squared, the above equation may be simply expressed as:

$$G_{s} = \phi U^{n}$$
(3-4)

(3-5)

The power n has values in the range of 3 to 5, borne out by some semi-theoretical analysis, but more significantly by experiments in the field and laboratory. The various sediment transport functions of the above form are based on the classical Du Boys relationship. Later developments, notably by Einstein, Kalinske, Englelund-Hansen, Laursen and Bagnold (3), incorporated the more fundamental turbulence parameters of the flow field and the interaction with the solid particle. The basic concepts of initiation of motion of the solids within the bed and the entrainment of the particles in the flowing water are the primary factors involved in the transport analysis. The effective factors are the applied and resisting forces, the former due to the fluid drag and the latter to the submerged weight of the particle as discussed above. Einstein, who was the first to develop the more rational approach, introduced the concept of the probability of motion of a particle and postulated that a given particle moves in a series of steps, the size and frequency of which are functions of the particle characteristics (diameter, density, fall velocity). His relationship is:

φ :

in which:

 $\phi = \frac{g}{\gamma s} \cdot \frac{\rho}{\rho_s - \rho} \cdot \frac{1}{gd^3}$ 

- 38 -

$$v = \frac{U_{\star}^2}{(2 - 1)}$$

(S<sub>s</sub>-1)gd

g = bed transport per unit width of stream

 $\rho = density$ 

 $\gamma$  = specific weight of water

d = diameter of particle

U = shear velocity

Kalinske included relationships between the bed shear and turbulence of the flow field; and developed the following:

$$\frac{g}{U_{\star}d} = f(\psi)$$
(3-6)

The approaches of the other investigators referenced above incorporated various features of the process, yielding various degrees of agreement with observations.

The difficulty in applying any of these relations to sediment transport in estuarine systems, is due to the fact they were developed considering discrete non-cohesive larger particles, such as sands. Furthermore, the fluid transport systems considered were exclusively fresh water rivers. Comparable developments for flocculent cohesive materials, such as clays, in estuarine systems is lacking. Although there has been a great amount of interest and activity in this regard, quantitative relationships have not been developed and field and laboratory data are scarce. There have been a number of excellent studies on the characteristics and distribution of solids in estuarine beds, but very few on bed and solids transport.

Using the information gained from sediment transport in rivers and the empirical observations of solids in various estuarine systems, the important factors may be envisioned as follows over a typical tidal cycle: During slack conditions, the solids remaining in suspension comprise the wash load, composed primarily of clays and the smaller sized salt particles. The interfacial bed layer is approximately stationary with little or no horizontal motion. As the tidal velocities increase entrainment is initiated and, also, motion is induced in bed in the direction of the current. With further rise in the velocity more erosion of the interfacial layer occurs and the concentration of solids throughout the water column increases markedly. Horizontal transport of solids is therefore taking place by two distinct mechanisms: one by the shear-induced motion of the bed (bed-load) and secondly by flow velocity containing the resuspended solids (suspended load). As the tidal velocity decreases, the heavier solids again settle to the bed, leaving the lighter flocculent material. As the tide reverses, the same phenomenon occurs, but now in the opposite direction, the difference between the ebb and the flood reflecting the magnitude of the fresh water flow, the type of tide and the geometry of the channel.

- 39 -

On a tidally averaged basis, the net fluid motion in the lower layer is landward, in accordance with the previous discussion, and this ocean derived material is transported upstream. Some of this material is dispersed into the upper layer, whose net motion is seaward. The magnitude of the vertical dispersive transport depends on the density stratification and the fresh water flow. The vertical flux of solids is also enhanced by the vertical fluid velocity which usually achieves a maximum value downstream of the salinity intrusion giving rise to the turbidity maximum. At the tail of the salinity intrusion, a zone of minimum horizontal and vertical velocities occurs, generally resulting in shoaling.

The locations of these regions depend on the fresh water flow and the magnitude of the tide. Solids transport, whether it be a movement of a bed layer or the result of a saltation process, is of great importance, particularly in estuarine systems. Averaging over the tidal cycle, this motion, as controlled by the fluid immediately overlying the sediments, tends to move sediments toward the null zone, i.e.downstream in the fresh water regions and upstream in the saline zone. The relative magnitude of this motion will then play an important role in determining sedimentation in the estuary.

The larger and heavier of the land derived solids also tend to accumulate in the bed at the null zone while the light solids are washed downstream where they may settle to the lower layer to be transported back to the null zone or settle to the bed. Thus, most coastal plane estuaries are generally sediment traps for both land and ocean solids, as reservoirs are for solids transported by tributary streams. While this is the overall pattern observed in most coastal plain estuaries, localized areas within any estuary may be either a sedimenting or eroding depending on channel and flow characteristics.

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#### BED VELOCITIES

The movement of the interfacial sediment layer has been measured in some rivers and estuaries. More extensive work has been performed in the laboratory in this regard. The more limited prototype measurements are in general accord with the laboratory results as shown in Figure 3-5. Data from both river and a few estuarine systems are highlighted. The correlation lines, which are sketched by eyes indicate slopes of 3 to 5 in accord with the limited theoretical analysis. While most of these data are for transport of sands, there are a few cases in which the motion of silts and clays was measured. The latter are most applicable to the Kepone analysis in the James.

One of the most notable field experiments on sediment transport in estuarine systems was conducted in Galveston Bay (9). Sediment was tagged with a radioactive tracer, released as a delta function and followed over a number of tidal cycles. About 5 curies of the isotope gold were thoroughly mixed with sediment taken from the ship channel. The activated sediment was then deposited at two locations and numerous samples of sediment were then measured daily for radioactivity for approximately 1 week. The

- 40 -

conclusions drawn from the study, as shown in this figure, are that in both channel reaches sediment moves upstream at a measurable and progressive rate. The only downstream movement appears to take place immediately following the tracer releases. Most of the sediment moved along the center-line of the ship channel, with little lateral dispersion onto the shoulders on tributary streams. Ships navigating the channel appear to contribute to resuspension of the deposited sediment. When resuspended, the sediment moves progressively upstream under the influence of the predominantly upstream currents in the vicinity of the channel bed.

Since the motion of the sediments may be related to the shear at the water-sediment interface, the net tidal effect of this action is important. Consider an idealized estuarine velocity distribution in which the net tidal velocity is in the upstream direction in the lower layer in contact with the bed. This horizontal velocity may be expressed as:

$$u_{b} = \overline{u}_{b} + C \cos x \qquad (3-7)$$

where  $\overline{u}_{b}$  is the net tidal velocity at the water-sediment interface, C is the

amplitude of the tidal variation taken as a constant with respect to depth. Assuming the classic shear function as the square of the average velocity, the mean value of the bottom shear averaged over the tidal cycle may be shown to be:

$$\frac{\overline{\tau}}{\rho} = \frac{C_d}{\pi} [4u_b C]$$

The sediment flux rate,  ${\bf g}_{_{\rm S}}$  expressed in mass per unit width of sediment per unit time may be approximated as:

$$g_s \alpha 4 \frac{k}{\pi} \overline{u}_b C h_b m_b$$

where  $h_{\rm b}$  is the depth of the moving sediment layer and  $m_{\rm b}$  is the solids concentration associated with this layer. By further assuming that the tidal amplitudes are approximately constant in space and time, the term 4 k C/\pi, along with the constant of proportionality may be expressed as a bulk coefficient,  $\zeta$ , yielding:

$$g_{s} = \zeta h_{b} m_{b} \overline{u}_{b}$$
(3-8)

where  $\zeta$  is dimensionless.

- 41 -

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- 42 -

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- 44 -





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#### SECTION 4

# ONE-DIMENSIONAL ESTUARINE ANALYSIS

This section and the following section of the report deal with the general and basic equations which define the distribution of organic chemicals in estuaries. The predominant transport features of estuarine systems are the tidal forces and salinity intrusion, which give rise to a characteristic circulation pattern. The transport regime is composed of both advective and dispersive components. In the saline regions, the latter is frequently of much greater significance and, in some cases, of such a magnitude that the advective component may be neglected without introducing appreciable errors. In the tidal, but nonsaline stretches, the two components are approximately of comparable magnitude.

The circulation pattern is induced by the salinity intrusion, which, with the tidal currents emanating from the mouth and the freshwater flow from upstream, produce a characteristic circulation. On a tidally averaged basis, there exists a net landward flow in the lower layer and a seaward flow in the upper layer. These horizontal flows are balanced by dispersion and velocity in the vertical, which transfers momentum and mass from the lower to the upper layer over large sections of the estuary. The magnitude of these transport vectors is a function of the salinity gradients, tidal amplitudes and freshwater flow.

During low flow periods, the vertical mixing is frequently of sufficient intensity to overcome stratification and one-dimensional longitudinal analysis is appropriate. As the flow increases and higher tides occur, the stratification becomes progressively more pronounced and a two-dimensional, longitudinal and vertical, analysis is necessary to define adequately the distribution of various substances. For those constituents, which are susceptible to settling, the two-dimensional analysis is usually necessary. In the case of suspended solids, the phenomenon of the "turbidity maximum" is the result of these transport patterns.

Accordingly, more attention is devoted to the two-dimensional transport in the saline zone, since the distribution of organic chemicals may be markedly influenced by the concentration of suspended solids. For the nonsaline region, the one-dimensional is frequently satisfactory. Therefore, this case is first addressed, followed by a presentation of the two-dimensional case. For each, the various types of bed conditions are addressed. The solutions for the idealized estuary of constant cross-section and freshwater flow are developed and presented for the purpose of insight and understanding. For a specific application, numerical solutions are recommended, which procedures permit a more realistic definition of the spatial and temporal distributions.

- 47 -

#### LONGITUDINAL ANALYSIS

#### 1. Transport

The one-dimensional transport in estuaries has been typically addressed by a simple advective-dispersive model. The application of this model has yielded a vast empirical data base of dispersion coefficients, which have been successfully employed in a broad spectrum of water quality studies. Analysis of the dissolved solids (salinity) associated with the ocean source permits determination of the dispersion coefficient. The basic differential equation which is used in this steady state analysis is:

$$0 = \frac{1}{A} \frac{d}{dx} (EA \frac{ds}{dx}) - \frac{Q}{A} \frac{ds}{dx}$$
(4-1)

in which s = salinity

A = cross-sectional area

E = dispersion coefficient

## Q = freshwater flow

in which the functional form of the variations of the cross-sectional area, freshwater flow and dispersion coefficient are not yet specified. The vast majority of tidal rivers and estuaries have variable areas and some also are characterized by a longitudinal variation in flow and dispersion. For the most general case, therefore, the dispersion coefficient can be evaluated using equation (4-1) which is re-expressed as follows:

$$E(x) = \frac{Q(x)}{A(x)} \frac{s(x)}{\frac{ds(x)}{dx}}$$
(4-2)

The flow, Q, the cross-sectional area A, and the concentration, s, of salinity are readily established for the given location. The concentration gradient, however, is more difficult to evaluate. Extensive data are required to accurately describe the spatial profile and their gradients. This is a disadvantage of the method. The advantage in using equation (4-2) lies in the fact that no assumptions have to be made about the spatial variation of A, E, and Q. Results of such analysis have produced two general observations regarding the variation of the dispersion coefficient. In many estuaries a constant value reasonably defines the distribution of chlorides; while in others, an increasing value of the coefficient in the seaward direction appears to be a more realistic description.

For those reaches of an estuary where geometry and flow are reasonably constant, solution of equation (4-1) is straightforward, yielding an exponential function, whose parameter is the ratio of the advective and dispersive coefficients:

$$S(x) = S \exp(Ux/E)$$
(4-3)

- 48 -

 $S_0 = Salinity at x = 0$ 

# U = Q/A = advective component

Note that the velocity (U) used in equation (4-3) is the freshwater velocity - the seaward transport parameter which opposes landward dispersion of ocean salinity.

It has been observed that an exponential function increasing in the seaward direction provides a good fit of cross-sectional area data in many cases. Assuming this dependency, the salinity distribution is given by the equation:

$$S(x) = S_{o} \exp \{-\frac{U_{o}}{E_{o}a}(e^{ax}-1)\}$$
 (4-4)

a = exponent of areal increase

where  $U_0 = Q_0/A_0$ . For convenience, the ocean boundary is located at  $x_0 = 0$  and the distance along the estuary, x, is taken as positive upstream. This equation can be used directly to analyze salinity or chlorinity data in order to evaluate the dispersion coefficient.

## 2. Type I Analysis - Stationary, Non-Interactive Bed

The basic equations of suspended solids and organic chemicals in onedimensional estuaries for this bed condition may be written directly. The equation for solids distribution is first presented, for which the solution is readily available. Given this distribution, the equations for the dissolved and particulate components of the organic chemicals are developed incorporating this result.

# a) Suspended Solids

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The solids equation includes the dispersion, advection and settling terms as follows:

$$D = E \frac{d^{2}m_{1}}{dx^{2}} - U \frac{dm_{1}}{dx} - K_{s}m_{1}$$
(4-5)

in which the coefficient,  $K_s$ , represents the settling, equal to the settling velocity divided by the average depth. The solution is direct:

$n_{1g} = \frac{W}{Qm} e^{gx}$	for x < o	(4-6a)
$n_{1h} = \frac{W}{Qm} e^{hx}$	for x > o	(4-6b)
$g = \frac{U}{2E} [1 + n]$		
$h = \frac{U}{2E} [1 - n]$		
- 49 -		

$$n = \sqrt{1 + \frac{4K_{E}E}{U^2}}$$

W = mass input at x = o

## Q = freshwater flow

The above equations may also apply to the downstream boundary condition to represent the landward transport of the ocean solids and the upstream boundary condition to represent the solids inflow of the freshwater.

# b. Organic Chemical

The dissolved component of the organic chemical includes the transport components indicated above, with adsorptive-desorptive interaction with the particulate fraction and allows for a decay:

$$0 = E \frac{d^2 c}{dx^2} - U \frac{d c}{dx} - K_{o} mc + K_{2} p - K_{a} c$$
(4-7)

The particulate component is described in a comparable fashion, but includes a settling term:

$$0 = E \frac{d^2 p}{dx^2} - U \frac{d p}{dx} + K_0 mc - K_2 p - K_s p$$
(4-8)

in which

K<sub>o</sub> = adsorption coefficient

 $K_2 = desorption coefficient$ 

 $\tilde{K_a}$  = decay coefficient for dissolved component

K<sub>s</sub> ≈ settling coefficient of particulate coefficient

The coefficient,  $K_a$ , may be thought of as an evaporative loss or whatever decay or transfer processes is applicable. Addition of the above equation yields the equation for the total concentration:

$$0 = E \frac{d^2 c_T}{dx^2} - U \frac{d c_T}{dx} - K_a c - K_s p$$
 (4-9)

Substituting for the dissolved and particulate components the respective fractions of the total gives:

$$0 = E \frac{d^{2}c_{T}}{dx^{2}} - U \frac{dc_{T}}{dx} - [f_{d}K_{a} + f_{p}K_{s}] c_{T}$$
(4-10)

- 50 -

in which

$$f_{d} = \frac{1}{1 + \Im m}$$
$$f_{p} = \frac{\Im m}{1 + \Im m}$$

The solution is direct for a condition of uniform spatial concentrations of solids:

$$E_{\rm T} = \frac{W_{\rm T}}{Qn} e \qquad x < o \qquad (4-11a)$$

$$c_{T} = \frac{w_{T}}{Qn} e \qquad x > o \qquad (4-11b)$$

in which

$$g = \frac{U}{2E} [1 + n]$$

$$h = \frac{U}{2E} [1 - n]$$

$$n = \left[1 + \frac{4E(f_{d}K_{a} + f_{p}K_{s})}{U^{2}}\right]^{1/2}$$

x = o is defined as the location of the toxic mass input,  $W_{\rm T}.$ 

Since the expressions for  $f_{\rm d}$  and  $f_{\rm p}$  contain the solids concentration, the estuary is segmented such that the solids concentration may be assumed constant in each segment, but varying from one to another in accordance with the solids distribution.

3. Type II Analysis - Mixed, Interactive Bed

The equations for this condition follow directly from the above.

a. Suspended Solids

The solids analysis is written as in the previous case and, in addition, includes a resuspension term:

$$0 = E \frac{d^2 m_1}{dx^2} - U \frac{d m_1}{dx} - K_s m_1 + K_u m_2$$
(4-12)

in which

 $K_u = resuspension coefficient$ 

 $m_2 = \text{concentrations of bed solids}$ 

2

- 51 -

Assume this equation applies from x = o seaward (region h) and upstream (region g), equation (4-1) applies. The solutions for the respective regions are:

$$m_{1g} = \frac{\frac{K_{m}m_{2}}{m_{2n}}}{K_{s}} \left[\frac{n-1}{2n}\right] e^{gx} \qquad x < 0 \qquad (4-13a)$$

$$m_{1h} = \frac{K_u m_2}{K_s} [1 - \frac{n+1}{2n}] e^{-1K_s}$$
 (4-13b)

in which

 $g = \frac{U}{2E}[1 + n]$   $h = \frac{U}{2E}[1 - n]$  $n = [1 + \frac{4K_{s}E}{U^{2}}]^{1}2$ 

....

For large x, equilibrium is achieved downstream at  $m_{le} = \frac{K_u m_2}{K_s}$ 

# b. Organic Chemicals

The basic equation for the total concentration may be written directly allowing for evaporative transfer of the dissolved and settling for the particulate:

$$0 = E \frac{d^2 c_T}{dx^2} - U \frac{d c_T}{dx} - [f_d K_a + f_p K_s] c_T + K_u r_2 m_2$$
(4-14)

 ${\rm r}_2$  = solid-phase concentration of chemical in bed and the other terms as defined previously.

For the condition of constant solids concentration in equilibrium with the bed, the solution for each region is:

$$c_{\text{Tlg}} = \frac{r_2^{\text{m}} e_1}{f_p + f_d \frac{K}{K_s}} e^{gx} \qquad \text{for } x < o \qquad (4-15a)$$

$$c_{T1h} = \frac{r_2^{m}e_1}{f_p + f_a \frac{K_g}{K_g}} [1 - \frac{2n}{1+n} e^{hx}] \quad \text{for } x > o \quad (4-15b)$$

- 52 -

in which

$$g = \frac{U}{2E}[1 + n]$$

$$h = \frac{U}{2E}[1 - n]$$

$$n = [1 + \frac{4E(f_{d}K_{a} + f_{p}K_{s})}{U^{2}}]^{1}2$$

These equations define the concentration in the water as a result of interaction with the bed. If, in addition, a point source of organic chemicals is located within the region, the equations of the previous section, in which this situation is analyzed, are simply added to the appropriate equations above. The direct addition is valid due to the linearity of the system.

## VERTICAL DISTRIBUTIONS

The previous sections indicated the importance of the concentration of the solids to which the organic chemical adsorbs and of the interaction of water and the bed with respect to both the solids and the chemical. This section is directed to the development of the equations which relate to these issues - specifically the vertical distribution of solids and chemicals in water column and bed layers. The transport mechanisms, which are effective in the vertical are common to all types of natural water systems. In lakes and coastal waters, they are the predominant factors which determine the distribution of solids and toxics. In streams and estuaries, there is no doubt that the horizontal transport may be equally significant. The fact remains, however, that the vertical parameters provide the fundamental insight to the relevant phenomena. Accordingly, the following discussion addresses the issue of the vertical distribution exclusively, from which analysis the basis is provided to structure the more detailed model.

### 1. Basic Factors

The spatial distribution of suspended solids in a natural water body depends on the transport, deposition and entrainment mechanisms of the system - more specifically on the physical properties of the suspended and bed solids and the hydrodynamic characteristics of the flow.

The solids properties may be related to an individual particle, to the distribution of the particles and to the bulk sediment. With respect to the individual particle, the most important are the size, density and shape, since these, in conjunction with the fluid properties of viscosity and density, determine the settling velocity of the individual particle in the fluid medium. All natural systems are characterized by a distribution of particle properties - most commonly classified as sands, silts and clays. The frequency distributions of the particle properties are usually reduced

- 53 -

to one or more statistical parameters, reflecting the aggregrate behavior of the suspension. The bulk properties of the sediment are in contrast to the characteristics of the suspension. In this regard porosity and bulk and solid densities are important.

The hydrodynamic factors which determine the vertical distribution of solids are the turbulent velocities and the associated dispersion effects. In the bulk of the fluid, this mechanism transfers solids upward in the direction of decreasing concentration, which is counteracted by the downward flux, due to settling velocity of the particles or of the suspension. In the vicinity of the water-bed interface, the vertical dispersion decreases and approaches zero. At this point the intensity of turbulence, as measured by the turbulent velocity, takes on more importance. The ratio of the turbulent velocity and the fall velocity is the relevant parameter which dictates the relative degree of entrainment or settling. The characteristics and transport of the bed layer are likewise influenced by the shear velocity at the interface. In this region, and in the deeper bed layer, the porosity and specific weight of the material are controlling factors, with respect to both the solids and the organic chemical.

It should be apparent from the proceeding, that the most fundamental approach to the analytical treatment of the problem lies in treating the system in its totality - i.e. - analyzing the water and bed as a continuum with the solids and associated chemical. It is more fruitful however, at this point to examine the component elements as a preliminary step. Thus the suspended solids analysis, as well as that of toxic substances in the water, may be decoupled from the bed sediment, with each system providing a necessary boundary condition for the other. While realizing that the holistic approach must ultimately be addressed, the following developments relate to the individual components with the view of eventual coupling.

The analyses of the water column concentrations are therefore first presented, followed by the development of comparable relations for the bed. In each case, the equations of the solids and the chemical distributions are presented.

2. Distributions in Water Column

#### a. Suspended Solids

(1)

The basic equation of the solids distribution is derived from the mass balance principle. Restricting the analysis to the vertical distribution, the steady-state form is:

$$0 = \varepsilon(z) \frac{d^2 m_1}{dz^2} - w_s \frac{dm_1}{dz}$$
(4-16).

The subscript, 1, indicates the water column and  $\varepsilon(z)$  = vertical dispersion coefficient. This equation expresses the equilibrium which exists between the rate at which particles settle downward and the rate at which they are diffused upward. The settling is due to the weight and size of the particle,

- 54 -

tending to increase the concentration in the direction of the bed. This flux is counteracted by the dispersion which by virtue of the gradient tends to transfer particles in the opposite direction. The solution of the above is straightforward:

in which  $m_{1i}$  = concentration in the water at the bed interface. This concen-

tration is not necessarily equal to that in the bed at the interface - the ratio between the two being a function of the ratio of the fall velocity to the shear velocity and the characteristic Reynolds of the grains. The inter-facial condition is one of the most critical and least understood in the analysis of the problem.

In streams and rivers, the assumption is usually made that the vertical dispersion is equal to the eddy viscosity of the fluid and this appears to be sufficiently realistic for the analysis of the problem. However, as the concentration of solids increase ( $\sim 10,000 \text{ mg/k}$ ) the value of the vertical eddy dispersion is less than that of the eddy viscosity. A comparable condition occurs in estuaries and lakes, in which the mass dispersion may be much less than the momentum transfer due to the density differences. As the concentration increases an additional order or more, the viscosity effect changes markedly. Thus the motion of bed solids may be characterized by a viscosity less than that of the kinematic viscosity of water.

The solution, shown above, is based on the assumption that the parameter,  $\varepsilon$ , is constant throughout the depth of the water column. However, it does vary from water surface to bed. In rivers, the variation is well-established being essentially zero at each boundary and maximum at approximately middepth. The value used in the above equation may be interpreted as an average over the depth, which assumption has been shown to be a practical approximation. From both of the above equations, it is apparent that

$$\frac{l}{n}\frac{dm_1}{dz} = \frac{w_s}{\varepsilon}$$
(4-18)

a relationship which is useful in the following sections.

b. Organic Chemicals

The basic equation for the organic chemical may be developed directly by considering the dissolved and particulate forms, the latter being subject to settling:

$$0 = \varepsilon \frac{d^2 c_1}{dz^2} - K_0 m_1 c_1 + K_2 p$$
 (4-19)

- 55 -

$$0 = \varepsilon \frac{d^2 p_1}{dz^2} + K_0 m_1 c - K_2 p - w_s \frac{dp}{dz}$$
(4-20)

For the concentrations of suspended solids encountered in natural water systems, the assumption that the dispersion coefficient is the identical for both dissolved and particulate and equal to the eddy viscosity is valid. As noted above, however, as the concentration of solids increases, the dispersion coefficient decreases. Larger concentration of solids, as may exist in the bed, precludes the dispersion effect for the particulate, and the dissolved component in the interstitial water is subject to molecular diffusion.

The total concentration of the organic chemical follows an addition of the above equations, which cancels the adsorption and desorption terms leading to:

$$0 = \varepsilon \frac{d^2 c_{T1}}{dz^2} - w_s \frac{dp_1}{dz}$$
(4-21)

Assuming instantaneous equilibrium the particulate component may be expressed in terms of the total:

$$0 = \varepsilon \frac{d^2 c_{\text{Tl}}}{dz^2} - w_{\text{s}} \frac{d}{dz} (\frac{\$m_1}{1 + \$m_1} c_{\text{Tl}})$$
(4-22)

Expanding the term with the appropriate differentiation and substituting equation (4-18), the final form after simplification is:

 $0 = \frac{d^2 c_{T1}}{dz^2} - f_p \frac{w_s}{\varepsilon} \frac{d c_{T1}}{dz} - (f_p \frac{w_s}{\varepsilon})^2 \frac{c_{T1}}{\eta_{m_1}}$ (4-23)

Since  $m_1$  and  $f_p$  are depth variables, there is no simple analytical solution for this equation. However, by segmenting the depth such that the solids concentration in each element is approximately uniform, this equation may be solved:

$$c_{r_1} \approx c_{r_1} e^{-gz} \qquad (4-24)$$

in which

$$g = f_p \frac{w_s}{2\varepsilon} \left[1 - \left[1 + \frac{4}{\Im m_1}\right]^2\right]$$

The significance of the parameter, 1m, is evident.

For  $\ensuremath{\mathbb{I}}\xspace_n$  much greater or less than unity, the exponent is

- 56 -

44



#### Distributions in the Bed з.

The equations describing the distributions in the bed are similar to those in the water. However, due to the large concentration of bed solids certain modifications must be made - specifically, the distinction between the volumes of the interstitial water and solids. There are a number of quantitative expressions of this ratio. The porosity,  $\phi$ , a commonly accepted definition, is the pore volume (interstitial water) expressed as a fraction of the total volume. The total mass of toxicant in the bed, M is the even of thet in the interstitial water and in the particulate  $M_{\rm T2}^{}$ , is the sum of that in the interstitial water and in the particulate phase. Thus

$$M_{r2} = \phi V_2 c + V_2 p \qquad (4-25)$$

in which

## $\phi = \text{porosity}$

Dividing by the volume and replacing the particulate concentration by the product of the solid-phase and solids concentrations:

$$c_{T2} = \phi c_2 + r_2 m_2$$
 (4-26)

Substituting for the solid phase concentration, its equivalent in terms of the dissolved concentration and partition coefficient

$$\frac{c_2}{c_{T2}} = \frac{1}{\phi + \Im m_2}$$
(4-27a)

and expressing the porosity in terms of the solids concentration:

$$\frac{c_2}{c_{T2}} = \frac{1}{1 + \ln_2 - \frac{m_2}{\rho_c}}$$
(4-27b)

- 57 -

# $\rho_s$ = density of the solid particles

It is apparent from these equations that the correction for porosity has an insignificant effect on the distribution between the dissolved and particulate components. It is further evident that the mass of the toxicant is predominantly in the solid phase for any substance which has a moderate tendency to adsorb (1 > 100) since the concentration of solids,  $\rm m_2^{},$  is great. By

neglecting the dissolved phase in the bed, an error of less than 1% is introduced.

It is emphasized that the above approximation applies only to total mass balances and not necessarily to processes, which depend on concentration differences over long time periods. Consider the case in which a toxicant, which has been discharged for some period of time, is banned. The dissolved concentration in the water column decreases in time due to the flushing action of the flow. The dissolved component in the bed, regardless of its low concentration with respect to the particulate, is greater than that in the water. This differential in concentration from bed to water establishes a transfer route which contributes to the ultimate cleansing of the system. In such a case, the dissolved concentration in the bed must be included in the analysis. It is apparent that, in such an analysis, neglecting the dissolved component in the bed not only introduces a significant error, but also eliminates a basic mechanism. With this perspective in mind, the equations for the solids and toxic substances are developed in the following sections.

#### a. Solids

As noted above, the effect of dispersion decreases with increasing concentration of solids. In the vicinity of the bed, it may be greatly reduced and in the bed, itself, it may be entirely dissipated due to concentration of The extent to which the mixing extends into the bed is a function solids. of the fluid velocity and particularly the shear velocity. Under low flow conditions, the mixing in the interfacial bed layer may be so negligible as to characterize the bed as stationary. A mixed bed, on the other hand, is one in which the dispersion effect is felt to some degree due either to the hydraulic shearing stress or a bioturbation effect. A form of equation (4-23) is appropriate for this case. The depth to which the mixing extends is, of course, limited, probably in the orders of 1 or 10 centimeters, below which quiescent conditions prevail. Thus, the stationary bed is the limiting condition, in which the mass rate of change is due solely to compaction of the solids. The compression displaces the interstitial water upward, thus increasing the solids concentration. As the sediment becomes more compressed, the porosity further decreases and consequently the interstitial velocity of the displaced fluid, the permeability being the order of the limiting velocity.

The equation for the mass rate of change of solids for the mixed bed includes both dispersive and advective terms, while that for the stationary

- 58 -

bed contains only the advective component.

$$\frac{\partial m_2}{\partial t} = \frac{\partial}{\partial z} (\varepsilon_2 \ \frac{\partial m_2}{\partial z}) - \frac{\partial}{\partial z} (w_1 m_2)$$
(4-28a)

and

$$\frac{\partial m_3}{\partial t} = -\frac{\partial}{\partial z} (w_1 m_3)$$
 (4-28b)

in which

 $m_2$  = concentration in mixed layer of bed  $m_3$  = concentration in deep bed  $\epsilon_2$  = dispersion coefficient  $w_i$  = interstitial velocity

The effect of the solids settling from the water column is introduced as a boundary condition at the interface, where the fluxes are equated.

Expanding the right-hand side of equation (4-28b) and re-expressing the left-hand side:

$$w_{d} \frac{\partial m_{2}}{\partial z} = -w_{i} \frac{\partial m_{2}}{\partial z} - m_{2} \frac{\partial w_{i}}{\partial z}$$
(4-29)

in which  $w_d = \frac{dz}{dt} =$  the sedimentation velocity

In the limit, when the change of velocity is zero, the interstitial velocity is in the order of the permeability, which in turn equals the sedimentation velocity - i.e., the depth of the bed is decreasing at a rate proportional to the interstitial velocity or the permeability assuming there is no flux from solids settling from the water column. Admittedly, these equations only provide some insight, rather than practical utility.

A more practical approach is to consider a depth-averaged concentration taking into account both the flux of settling solids and compaction. In this regard, it is informative to develop the volumetric balance of the bed. The volumetric rate of change is due to the net effect of the two phenomena. Thus,

$$\frac{dV_2}{dt} = -\left(\frac{dV}{dt}\right)_{D} + \left(\frac{dV}{dt}\right)$$

in which the subscripts p and s refer to the compaction and settling, respectively. Substituting for each term on the right-hand:

s

- 59. -

$$\frac{dV_2}{dt} = -\phi Aw_i + \frac{w_s Am_1}{\rho_b}$$
(4-30)

in which

2

$$\phi = \text{porosity} \rho_{\text{b}} = \text{bulk density} - (\text{M/L}^3) = \phi \rho + (1 - \phi) \rho_{\text{s}} \rho = \text{fluid density} \rho_{\text{s}} = \text{solid density}$$

The porosity is the fractional volume of pores and is related to the concentration:

$$m_2 = (1 - \phi)\rho_s$$
 (4-31)

Substituting and simplifying, the above reduces to after dividing by the area:

$$\frac{dz}{dt} = -(1 - \frac{m_2}{\rho_2}) w_1 + \frac{w_s m_1}{\rho + m_2 (1 - \frac{\rho}{\rho_s})}$$
(4-32)

Equation (4-32) is an expression for the sedimentation velocity which may be either positive or negative depending on the magnitude of the settling and compaction. For most natural systems, the net effect is positive yielding values in the order of 1 cm per year.

Since the settling flux is the only term producing a mass change (assuming no resuspension) the mass balance is

$$\frac{d(\mathbb{V}_{2}m_{2})}{dt} = w_{s}Am_{1}$$
(4-33)

Expanding the right-hand side and transposing these results

$$\frac{\partial z}{\partial t} = w_{\rm s} \frac{m_1}{m_2} - \frac{z}{m_2} \frac{\partial m_2}{\partial t}$$
(4-34)

The approach given above has not been generally employed in analyzing bed distributions. Rather, the sedimentation velocity is introduced directly in the mass balance equation, and includes the compaction rate. Since  $\frac{dz}{dt}$  is taken as the sedimentation velocity  $w_d$ , equation (4-34) at steady-state reduces directly to

$$w_{s}m_{1} = w_{d}m_{2}$$
 (4-35)

If resuspension of bed occurs, an additional term is introduced

$$w_{s1} = (w_d - w_u)m_2$$
 (4-36)

in which

 $w_{u}$  = resuspension velocity.

# b. Organic Chemical

The equations for the chemical follow directly from the above. In the mixed layer, the dissolved and particulate equations are

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial z} \left[ (c_2 + D_L) \frac{\partial c_2}{\partial z} \right] - \frac{\partial}{\partial z} (w_1 c_2) - K_0 m_2 c_2 + K_2 p_2$$
(4-37)

$$\frac{\partial \mathbf{p}_2}{\partial \mathbf{t}} = \frac{\partial}{\partial z} \left[ \epsilon_2 \frac{\partial \mathbf{p}_2}{\partial z} \right] + \mathbf{K}_0 \mathbf{m}_2 \mathbf{c}_2 - \mathbf{K}_2 \mathbf{p}_2$$
(4-38)

At steady-state - i.e. a constant rate of change of the bed depth, these equations may be expressed, after introducing equation (4-29).

$$0 = \frac{d}{dz} \left[ \left( \varepsilon_2 + D_L \right) \frac{\partial c_2}{\partial z} \right] - \frac{d}{dz} \left[ \left( w_1 + w_d \right) c_2 \right] - K_0 m_2 c_2 + K_2 p_2$$
(4-39)

$$0 = \frac{d}{dz} \left[ \epsilon_2 \frac{dp_2}{dz} \right] - \frac{d}{dz} \left[ (w_1 + w_d) p_2 \right] + K_0 m_2 c_2 - K_2 p_2$$
(4-40)

In the stationary bed, the physical and/or biological mixing is negligible and the coefficient,  $\epsilon$ , is zero. Thus the particulate equation contains only velocity terms.

The recommended procedure of analysis for these conditions tracks the particulate form, first, since the vast majority of the mass is contained therein. Having established the distribution of the particulate concentration, the solid phase and dissolved concentrations follow directly. Knowing the dissolved distribution, the flux across the water-bed and the mixed-stationary bed interfaces may be determined. Alternately, each of the above sets of equations may be added, from which the total concentration is evaluated which may then be fractionated into its components. In the stationary bed the equation is:

$$\mathbf{0} = \frac{\mathrm{d}}{\mathrm{d}z} \left[ \frac{\mathrm{D}_{\mathrm{L}}}{\mathrm{M}_{2}} \frac{\mathrm{d}c_{\mathrm{T2}}}{\mathrm{d}z} \right] - \frac{\mathrm{d}}{\mathrm{d}z} \left[ (\mathrm{w}_{\mathrm{i}} + \mathrm{w}_{\mathrm{d}}) c_{\mathrm{T2}} \right]$$
(4-41)

APPLICATION TO KEPONE DISTRIBUTION IN THE JAMES RIVER

The James River is a tributary of the Chesapeake Bay. The region of concern extends approximately 120 KM upstream from the mouth of the river to Hopewell, Virginia, the location of the source of Kepone. The input of Kepone to the river occurred through the discharge from the waste treatment plant, from surface drainage and runoff from the production site and through leaching of ground water through the contaminated areas. The river is dredged for navigation purposes and the deep channel is bordered by shallow littoral areas some of which are productive fishery zones. The cross-sectional area of the channel increases in the downstream direction and broadens perceptively at a number of locations. The James is a coastal plane estuary, with a typical estuarine circulation, the result of the combined effects of the freshwater flow and tidal action, in conjunction with the vertical and horizontal salinity gradients inducing a density-driven flow pattern. This circulation pattern exists in the saline region of the estuary. Upstream in the non-saline zone, tidal currents persist to Hopewell without the density effects and the transport may be readily defined by the one-dimensional advective-dispersive equation.

The source of the Kepone input is located in the non-saline, tidal region of the James River estuary, and consequently, the concentration was most evident in the immediate vicinity of and downstream from the source. A preliminary analysis of the Kepone distribution was performed employing the one-dimensional longitudinal model, described above. The kinetic form of the equations, defining the dissolved and particulate concentrations individually, rather than the total, was utilized. The purpose of this analysis was two-fold: first, to determine the general applicability of the advective-dispersive model and secondly, to assess the kinetic interactions of adsorption and desorption.

The results of the analysis are shown in Figure 4-1. The transport coefficients were readily determined. The advective components form the hydraulic continuity equation knowing the freshwater flow and the cross-sectional area. The dispersive coefficient was assigned in the range of 2 to 5 square miles per day (5-7.5 square kilometers per day) as typical for tidal, non-saline systems. The distribution was relatively insensitive to this range of dispersion coefficient.

This preliminary analysis was simplified by various assumptions - subject to verification by the ongoing field and laboratory studies. The bed solids concentration,  $m_2$ , were much greater than the suspended solids concentration,  $m_1$ ; the evaporative transfer coefficient,  $K_a$ , was taken to be negligible; and the solids adsorptive capacity,  $r_c$ , was assumed to be much greater than either of the Kepone concentrations on the solids,  $r_1$  and  $r_2$ . The kinetic coefficients -  $K_o$ ,  $K_d$ ,  $K_s$ , and  $K_u$ , were assigned from the lim-

- 62 -
ited data available. Finally, the Kepone concentrations on the bed solids,  $r_2$ , were assigned from data; these concentrations were in turn utilized as forcing functions to calculate the Kepone water column concentrations.

Based on these assignments of coefficients, the longitudinal distribution of total and dissolved Kepone in the water column is presented in the figure, with the 1976 Kepone data. The calculated total Kepone concentration fits the data quite well and although the dissolved fraction of Kepone is high, this concentration is merely a function of Kepone kinetic coefficients,  $K_{o}$  and  $K_{d}$  - values which were obtained from a minimal amount of kinetic data.

A range of the kinetic coefficients were assigned to test the sensitivity of the response to the adsorption-desorption exchange. Based on the tidally average analysis, it was concluded that the instantaneous equilibrium assumption was applicable. This condition greatly simplifies the computational procedures: it is only necessary to calculate the total concentration, in accordance with the equations developed in the previous section, from which the dissolved and particulate components may be readily determined by means of the partition coefficient. Furthermore, the model runs investigated under this phase of the project, established the analytical procedure for the more complex analyses, involving bed-interaction in both saline and non-saline regions. The first and critical step in the analysis of such organic chemicals involves assessment of the water concentrations, based on the assignment of observed bed concentrations. This step calibrates the water phase of the model and establishes the flux between the water and bed, an important element for the model of the bed, as described in subsequent sections.

- 63 -



# SECTION 5

### TWO-DIMENSIONAL ESTUARINE MODELS

#### HYDRODYNAMIC ANALYSIS

The circulation within the saline zone of estuaries is due to the interaction of a number of factors - tidal action, density differentials, freshwater flow, winds and the characteristics of the channel. On a tidally averaged basis, the circulation is characterized by a horizontal seaward velocity in the upper layer and a landward velocity in the lower layer, with a compensating vertical velocity pattern to maintain hydraulic continuity. A simplified analytical solution is developed from the equations of momentum, continuity, and state, which defines the vertical distribution of horizontal velocity. It is based on the condition that the salinity distribution in both the longitudinal and vertical planes are known or may be assigned.

The most fundamental approach to the analysis of this type of estuarine circulation is based on the simultaneous solutions of the fundamental equations of momentum, continuity and state. It involves a numerical solution of the basic equations, which is generally quite complex. Due to the small time and space steps, which are necessary to insure numerical stability, the procedure usually requires a substantial amount of time and effort. The output which defines the velocity variation in time and space, are averaged vertically and tidally to yield the net circulation. By contrast, the method of analysis described herein, which is based on decoupling the equations of motion and salt balance, is relatively straightforward. It is therefore computationally simple and rapid and offers a definite advantage as an analytical tool.

The characteristic estuarine pattern of seaward velocity in the upper layer and a landward velocity in the lower layer, which is evident after the longitudinal velocities at various depths are averaged over a tidal cycle, was first observed by Pritchard (1) in the James River Estuary. Following this work, a series of papers were presented clarifying many of the salient features of this type of estuarine circulation for a variety of conditions (Pritchard, (2); Pritchard and Kent, (3).

The general nature of this circulation and the effect of freshwater flow was further borne out by a series of experiments in hydraulic models constructed by the Army Corps of Engineers at the Waterway Experiment Station. From these experiments and additional field measurements, Simmons (4) suggested the term of "flow predominance" to describe the circulation and indicated its significance in the shoaling of estuaries. Harleman <u>et al</u> (5) conducted a series of experimental investigations in a laboratory flume, in which the mixing was induced by grids oscillating vertically to simulate pro-

- 65 -

totype observations. They also analyzed a detailed set of salinity and current measurements under controlled laboratory conditions which were conducted in the Waterways Experiment Station (Harlemen and Ippen, (5), (6). Subsequent field measurements provided further evidence of this typical circulation (Harlemen and Ippen, (5), (6).

One of the first analytical approaches was developed by Defant (7) in defining the two-dimensional currents in tidal straights. Rattray and Hansen (8) demonstrated the similarity solution techniques by decoupling the fluid motion and salt transport equations. By postulating logarithmic functions for the channel geometry, direct solutions for the velocity profiles were developed. Bowden (9), extended this general approach with more detailed measurements and further analysis, and presented an excellent summary of the state of the art, as of 1962. In a recent text, Officer (10) further developed a number of simplified analytical solutions and thus provided a great deal of insight into the phenomenon. More complex numerical solutions have been presented by Leenderstee et al. (11), Hamilton (12), Blumberg (13,14), Boericke and Hogan (15) among others to describe more completely the tidal circulation patterns from which the tidally averaged velocities have been abstracted. The approach taken in this paper follows the path laid out by these investigators and presents a practical engineering method to analyze this type of circulation in estuaries in a simplified and synthetic manner.

The laterally-averaged form of the equation of motion for the horizontal velocity is:

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + w \frac{\partial u}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial x}$$
(5-1)

in which u and w are the horizontal and vertical velocities, p is pressure; and  $\rho = \rho(x,z)$  is density of water. The molecular diffusion of momentum is normally considered negligible in the natural environment. The vertical component of the equation of motion (the hydrostatic assumption) becomes:

$$\frac{1}{\rho} \frac{\partial p}{\partial z} = g$$
 (5-2)

in which g is acceleration of gravity. In order to take into account tidal currents as well as the turbulent character of the flow, the velocity components u and w are divided into three terms, which are uncorrelated with one another.

$$u = \overline{u} + u_{t} + u'$$
$$w = \overline{w} + w_{t} + w'$$

where  $\bar{u}$  is the mean velocity averaged over one or more tidal periods,  $u_t$  is the tidal component and u' the turbulent component. Introducing these velocity terms into Eq. 5-1 and taking the time mean over one or more tidal

- 66 -

yield the turbulent stress terms  $\overline{u'u'}$  and  $\overline{u'w'}$ . Relating the stress terms to the mean velocity gradients through the eddy viscosities, the time mean of Eq. 5-1 for the tidally averaged steady state is given by:

$$\overline{u} \frac{\partial \overline{u}}{\partial x} + \overline{w} \frac{\partial \overline{u}}{\partial z} + u_{to} \frac{\partial u_{to}}{\partial x} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \frac{\partial}{\partial x} (N_x \frac{\partial \overline{u}}{\partial x}) + \frac{\partial}{\partial z} (N_z \frac{\partial \overline{u}}{\partial z})$$
(5-3)

The last two terms in Eq. 5-3 are the turbulent nonadvective flux of momentum, and are represented by the product of the eddy viscosities, N<sub>x</sub> and N<sub>z</sub> and the associated velocity gradients. The term,  $u_{to} \partial u_{to} / \partial x$  is a field acceleration resulting from  $\partial (u_t^2) / \partial x$  since  $u_t = u_{to} \cos \sigma$  ( $\sigma$  represents the sum of an angular time argument of tidal period plus a phase angle). The pressure gradient term in Eq. 5-3 is the mean value of  $\frac{1}{\rho} \frac{\partial p}{\partial x}$  in Eq. 5-1 with respect to time.

Pritchard (2) demonstrated that the horizontal component of the turbulent flux of momentum  $\frac{\partial}{\partial x} (N_x \frac{\partial \bar{u}}{\partial x})$  and the non-linear acceleration terms were negligible, compared to other terms in Eq. 5-3, for selected stations in the James River. In some cases, the field acceleration term  $u_{to}(\partial u_{to}/\partial x)$  may also be small and can be neglected. In the present analysis,  $N_z$  is assumed constant with respect to depth in order to make the equation mathematically tractable. Admittedly, the last two assumptions may be crude approximations. However, subsequent development indicates the practical utility of the approach. The final working equation, therefore, involves two terms: the longitudinal pressure gradient and internal friction.

$$\frac{1}{\rho} \frac{\partial p}{\partial x} = N \frac{\partial^2 \bar{u}}{\partial z^2}$$
(5-4)

The coordinates for Eq. 5-4 are shown in Fig. 5-1 in which the longitudinal x-axis is positive toward the ocean and the vertical z-axis is positive toward the bed of the estuary.

The boundary conditions for Eq. 5-4 are: at the free surface  $(z = -\eta)$ ,  $\partial \bar{u}/\partial z = 0$ , i.e., no wind effect; and at the bottom (z = h),

$$\mathbb{E}\left(\frac{\partial \overline{u}}{\partial z}\right)\Big|_{z=h} = C_{d} |u_{b}|u_{b}$$
(5-5)

in which  $\mathbf{C}_{\mathbf{d}}$  is a dimensionless friction coefficient and  $\mathbf{u}_{\mathbf{b}}$  is the velocity at the bed.

In order to solve Eq. 5-4, the hydrostatic pressure in Eq. 5-2 is expressed in terms of the horizontal and vertical distributions of salinity and the equation of state which specifies the density as a function of salinity

- 67 -

is given by:

$$\rho = \rho_{f} (1 + \alpha \overline{C})$$
 (5-6)

in which  $\rho_f$  is the density at zero salt content and  $\alpha = 0.000757$  (parts per thousand)<sup>-1</sup>. The pressure force is then evaluated in terms of the salinity gradients and freshwater flow, which are assumed known from measurement. Integration of Eq. 5-2 yields:

$$\int_{-\eta}^{z} \frac{\partial p}{\partial z} dz = g \int_{-\eta}^{z} \rho dz$$

and substitution of Eq. 5-6 gives:

$$p - p_a = g \int_{-n}^{z} \rho_f (1 + \alpha \overline{C}) dz \qquad (5-7)$$

where  $p_a = \text{constant atmospheric pressure.}$  Expressing the vertical salinity distribution in general as  $\overline{C} = \overline{C}_{s} \phi(z)$  in which  $\overline{C}_{s}$  is the surface salinity, Eq. 5-7 becomes:

$$p - p_{a} = g \int_{-\pi}^{z} \rho_{f} (1 + \alpha \overline{C}_{s} \phi(z)) dz$$
$$= g \rho_{f} (z + \eta) + g \rho_{f} \overline{C}_{s} \alpha \int_{-\pi}^{z} \phi(z) dz$$
(5-8)

Differentiating Eq. 5-8 yields:

$$\frac{\partial \mathbf{p}}{\partial \mathbf{x}} = \mathbf{g} \rho_{f} \frac{d\mathbf{n}}{d\mathbf{x}} + \mathbf{g} \rho_{f} \alpha \frac{\partial}{\partial \mathbf{x}} (\overline{\mathbf{C}}_{g} \int_{-\infty}^{z} \phi(z) dz$$

from which it is evident that the longitudinal pressure gradient is essentially composed of two components: the slope of the water surface and the gradient of the product of the horizontal and the vertical distributions of salinity. Expanding the derivative of the product in the latter term and substituting the entire expression into Eq. 5-4 results in:

$$N \frac{\partial^2 \overline{u}}{\partial z^2} = g s + g \alpha \frac{d\overline{C}_s}{dx} \int \phi(z) dz + g \alpha \overline{C}_s \frac{\partial}{\partial x} \int \phi(z) dz \qquad (5-9)$$

in which s = dn/dx, the surface gradient where the quotient  $\rho_{\rm f}/\rho$  is assumed to be subsumed into the eddy viscosity N (approximate range of  $\rho_{\rm f}/\rho$  is 1.00 freshwater to 0.97 seawater) and any effects of the vertical variability of the density  $\rho$  on subsequent depthwise integrations are assumed negligible.

- 68 -

Integrating Eq. 5-9 and applying the boundary condition  $N(\partial \overline{u}/\partial z) = 0$  at z = -n yields:

$$N \frac{\partial \widetilde{u}}{\partial z} = gs(\eta + z) + g\alpha \frac{dC_s}{dx} \int_{-\eta}^{z} \int_{-\eta}^{z} \phi(z) (dz)^2 + g\alpha \widetilde{C}_s \int_{-\eta}^{z} (\frac{\partial}{\partial x} \int_{-\eta}^{z} \phi(z) dz) dz$$
(5-10)

Applying the second boundary condition (Eq. 5-5) in the next integration gives the horizontal velocity:

The last term in Eq. 5-11 is the bottom velocity,  $u_{\rm b}$ . Note that, for convenience, it is assumed that the origin of the coordinate system is at the location of interest (i.e. n = 0).

The surface slope, s, may be now evaluated by applying the continuity condition to Eq. 5-11:

$$\begin{array}{c} h \\ Q = b \int \overline{u} \, dz \\ -\eta \end{array}$$

in which Q is the freshwater flow; and b is the depth-averaged width. Equation 5-11 becomes:

$$\frac{Q}{bh} + \frac{gsh^2}{3N} + \frac{g\alpha}{hN} \frac{d\overline{C}_s}{dx} \int_{-\eta}^{h} f \int_{z-\eta}^{h} \frac{\varphi(z)(dz)^4}{(z-\eta)^4} + \frac{g\alpha}{hN} \overline{C}_s \int_{-\eta}^{h} \frac{f}{z-\eta} \int_{-\eta}^{z-\eta} \frac{z}{(z-\eta)^4} + \frac{g\alpha}{hN} \overline{C}_s \int_{-\eta}^{h} \frac{f}{z-\eta} \int_{-\eta}^{z-\eta} \frac{\varphi(z)(dz)(dz)^3}{(z-\eta)^4} + \left[ \frac{gsh}{C_d} + \frac{g\alpha}{C_d} \frac{d\overline{C}_s}{dx} \int_{-\eta}^{h} \frac{f}{\varphi(z)(dz)^2} + \frac{g\alpha}{C_d} \overline{C}_s \int_{-\eta}^{h} \frac{\varphi(z)(dz)(dz)^2}{(dz)^4} + \frac{g\alpha}{C_d} \frac{\overline{C}_s}{(d-\eta)^4} \int_{-\eta}^{h} \frac{\varphi(z)(dz)(dz)^2}{(d-\eta)^4} + \frac{g\alpha}{C_d} \frac{\overline{C}_s}{(d-\eta)^4} \int_{-\eta}^{h} \frac{\varphi(z)(dz)(dz)^4}{(d-\eta)^4} = 0 \quad (5-12)$$

Equation 5-12 is a quadratic expression for s, since it appears as a first power in the second term and a half-power in the last term. It, therefore,

- 69 -

has two roots, one of which can be discarded because it yields a seaward bottom velocity. The appropriate root is then substituted into Eq. 5-11 to yield the solution of the horizontal velocity as a function of depth. Equation 5-11 indicates that local conditions rather than boundary conditions, control the magnitude and gradient of horizontal velocity at a particular location. Because of this local control, the velocity calculation at one location is relatively independent of those at other locations. This condition occurs as a result of decoupling the equations of motion and salt transport through use of field salt measurements to obtain the mean water surface salinity  $(\tilde{C}_{\rm g})$ , the horizontal surface salinity gradient  $(\partial \tilde{C}_{\rm g}/\partial x)$  and the

vertical salt gradient ( $\phi(z)$ ) at a specified location in the estuary. The vertical variation  $\phi(z)$  is often described by a polynomial,  $\phi(z) = 1 + a_1 z_2$ 

 $+a_2z^2 + a_3z^3$  to characterize its non-linear nature. The linear approximation, involving the first two terms, has been found to be adequate to define the horizontal velocity distribution in several estuaries.

#### Plane of No Net Motion

The depth at which the net horizontal velocity is zero may be determined by Eq. 5-11. Solving for this depth at a number of stations and interpolating for others delineates the plane of no net motion for the saline intrusion zone of the estuary (Fig. 5-1). At the tail of the salinity intrusion, this plane meets the bed of the estuary. Upstream of this area, the horizontal velocity in the whole water column is in the seaward direction.

It is convenient to divide the estuary into a surface and bottom layer by the plane of no net motion as shown in Fig. 5-1, so that the horizontal flow is downstream in the surface layer and upstream in the bottom layer. The average horizontal velocity in the surface layer is:

$$[\vec{u}] = \frac{1}{h_0 + n} \int_{-n}^{n_0} \vec{u} \, dz$$
 (5-13)

where  $h_o$  is the vertical distance from the surface to the plane of no net motion. The horizontal velocity,  $\bar{u}$ , therefore, is comprised of a layer mean value  $[\bar{u}]$  and the deviation from this mean  $\bar{u}'$ , (Fig. 5-1), so that:

$$\overline{u} = [\overline{u}] + \overline{u}^{\dagger}$$

×.,

Vertical Velocity

Given the horizontal velocity at various locations, the vertical velocity may be evaluated by means of the continuity equation:

$$\frac{\partial}{\partial x}(b\bar{u}) + \frac{\partial}{\partial z}(b\bar{w}) = 0$$
 (5-14)

- 70 -

Differentiating Eq. 5-11 with respect to distance, substituting into Eq. 5-14 and integrating with respect to depth yields:

$$\vec{w}(x,z) - \vec{w}(x, -\eta) = \int_{-\eta}^{z} \frac{\partial \vec{w}}{\partial z} dz = -\frac{1}{b} \int_{-\eta}^{z} \frac{\partial}{\partial x} (b\vec{u}) dz = -\frac{1}{b} \frac{\partial}{\partial x} (b \int_{-\eta}^{z} \vec{u} dz)$$
  
and  $\vec{w}(x,z) = -\frac{1}{b} \frac{\partial}{\partial x} (b \int_{-\eta}^{z} \vec{u} dz)$ , where  $\vec{w}(x, -\eta) = 0$ 

Thus, the vertical velocity at the plane of no net motion is,

$$\overline{w}(\mathbf{x},\mathbf{h}_{o}) = -\frac{1}{b} \frac{\partial}{\partial \mathbf{x}} (\mathbf{b} \int_{-\pi}^{\pi} \overline{u} dz) = -\frac{1}{b} \frac{\partial}{\partial \mathbf{x}} (\mathbf{b}(\mathbf{h}_{o} + \pi) [\overline{u}])$$
(5-15)

# Null Zone

One of the important features in the two-dimensional estuarine circulation is the null zone, which is characterized by a zero bottom stress. Thus, by means of Eq. 5-5, the bottom velocity becomes zero. As a result, the last term in Eq. 5-11 is zero and consequently, Eq. 5-12 becomes:

$$\frac{Q}{bh} + \frac{gsh^2}{3N_0} + \frac{g\alpha}{hN_0} \frac{d\overline{c}}{dx} + \frac{g\alpha}{h} + \frac{d\overline{c}}{dx} + \frac{g\alpha}{h} + \frac{d\overline{c}}{dx} + \frac{g\alpha}{h} + \frac$$

where N is the vertical eddy viscosity in the null zone. For  $\phi(z) = 1 + a_1 z$ , Eq. 5-16 reduces to:

$$N_{o} = -\frac{gsh^{2}}{u_{f}} \left\{ \frac{1}{3} + \frac{\alpha}{sh^{3}} - \frac{d\bar{c}_{s}}{dx} \left( \frac{h^{4}}{8} + \frac{a_{1}h^{5}}{30} \right) \right\}$$
(5-17)

where  $u_f = Q/(bh)$ . As an approximation, the salinity gradient  $d\overline{C}_s/dx$  approaches zero at the null zone, and therefore, Eq. 5-17 becomes:

$$N_{o} = \frac{-gsh^{2}}{3u_{f}} = \frac{u_{\star}^{2}h}{3u_{f}}$$
(5-18)

- 71 -

in which  $u_{\star} = \sqrt{-gsh}$ , the shear velocity.

#### Modification

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The previous analysis may be modified to incorporate the non-rectilinear nature characteristic of many estuarine cross-sections. For this purpose, the width of a particular cross-section may be expressed as  $b = b_S \zeta(z)$ , where  $\zeta(z)$  is the vertical variation of width. The continuity condition is then expressed as:

$$Q = b \int_{S} \zeta(z) \, \overline{u} dz$$

with subsequent revisions in equations 5-12 through 5-18. Under most circumstances, a linear approximation is adequate to express the vertical variation  $\zeta(z)$  such that  $\zeta(z) = 1 - \beta z$ , i.e. cross-sections may be represented by trapezoidal geometries.

## TRANSPORT - SALINITY DISTRIBUTION

The steady state mass transport equation for salinity in a two-dimensional estuary on a tidally averaged basis may be written as:

$$\frac{\partial}{\partial x}(\bar{u}\ \bar{s}) + \frac{\partial}{\partial z}(\bar{w}\ \bar{s}) + \frac{\partial}{\partial x}(u_t\ s_t) = \frac{\partial}{\partial z}(\varepsilon_z\ \frac{\partial\bar{s}}{\partial z})$$
(5-19)

in which  $\bar{s}$  is the tidally averaged concentration of salinity;  $\varepsilon_z$  is the vertical eddy diffusion coefficient; and  $u_t$  and  $s_t$  are the tidal components of

horizontal velocity and salt concentration, respectively. Longitudinal turbulent diffusion is neglected because its effect is relatively insignificant compared to the terms in Equation 5-19.

The estuary is divided into two vertical layers with the interface normally positioned at the plane of no net motion, i.e. the vertical location at which the horizontal velocity is zero. After vertical averaging, Equation 5-19 becomes:

$$\frac{\partial}{\partial x}(\langle \bar{u} \rangle \langle \bar{s} \rangle) + \frac{\partial}{\partial x}(\langle u_{t} \rangle \langle s_{t} \rangle) + \frac{\partial}{\partial x}(\bar{u}' \bar{s}') + \frac{\partial}{\partial z}(\bar{w} \bar{s})_{0}$$

$$- \frac{\partial}{\partial z}(\epsilon_{z} \frac{\partial \bar{s}}{\partial z})_{0} = 0$$
(5-20)

for each layer. The terms  $<\!\bar{u}\!>$  and  $<\!\bar{s}\!>$  are layer averages of the velocity and salinity concentration, respectively, such that:

$$\overline{u} = \langle \overline{u} \rangle + \overline{u}'$$
$$\overline{s} = \langle \overline{s} \rangle + \overline{s}'$$

where  $\bar{u}'$  and  $\bar{s}'$  are the tidally averaged deviations from the mean values in each layer. The subscript 'o' in the last two terms of Eq. 5-20 represents

- 72 -

the plane of no net motion.

Each term in Equation 5-20 represents a distinct transport mechanism. The first term,  $\langle \bar{u} \rangle \langle \bar{s} \rangle$ , defines the contribution to the flux of salinity by the advective flow in each layer. The second term,  $\langle u_t \rangle \langle s_t \rangle$ , is referred to as tidal diffusion. The third term,  $\bar{u}'\bar{s}'$ , arises from the layer-averaging

process and represents the shear effect in each layer. For the James River, the net effect of tidal diffusion and shear effect is not significant. They are briefly discussed for completeness and for their potential importance in other applications. The last two terms in Equation 5-20 are the vertical and dispersive fluxes of salinity across the plane of no net motion.

The final equation of salinity applicable to each layer of a two-dimensional estuary is:

$$\frac{\partial}{\partial x}(\langle \overline{u} \rangle \langle \overline{s} \rangle) + \frac{\partial}{\partial z}(\overline{w} \ \overline{s})_{0} = \frac{\partial}{\partial z}(\varepsilon_{z} \ \frac{\partial \overline{s}}{\partial z})_{0}$$
(5-21)

The solution is based on a finite difference approximation of Equation 5-21. A central difference scheme is used in the numerical calculation. The estuarine system is divided into 2 vertical layers. The upper flow is net seaward and the lower is net landward. The longitudinal boundary conditions of salinity are the concentrations associated with the freshwater inflow at the upstream limit and with the saline waters in the lower layer at the downstream location.

Inspection of Equation 5-21 indicates that the salinity distribution is dependent on three transport coefficients. Two of these coefficients, the horizontal and vertical velocities, have been determined in the previous section, Equation 5-18, by employing the equations of momentum, continuity and state. An initial estimate of the final coefficient, the vertical dispersion term, may be obtained from the empirical relationship with the vertical eddy viscosity,  $N_z$ , such that,

$$\varepsilon_z = \frac{N_z}{1 + R_f}$$
(5-22)

(5-23)

in which  $R_1$  is the Richardson number defined as:

$$R_{1} = \frac{g \frac{\partial \rho}{\partial z}}{\rho [\frac{\partial u}{\partial z}]}$$

In some instances, minor adjustments of this coefficient are necessary to achieve suitable agreement with observed salinities.

- 73 -

# SOLIDS DISTRIBUTIONS

1. Water Column

Since the concentration of solid material is an important factor as an accumulation site for Kepone, the temporal and spatial distribution of suspended solids within the estuarine system is a necessary element in the overall analysis. The solids distribution, in turn, is related to estuarine circulation. Some finegrained material, such as clays, remain primarily in suspension and follow the residual tidally averaged flow. The silts will also be maintained in suspension but also subject to deposition at slack water and erosion at maximum current. The coarser grained sands will be primarily in the bed and if eroded will travel along the bed, being less susceptible to alternate erosion and deposition. It is evident that solids eroded from the bed move upstream if retained in the lower layer and downstream if they are dispersed to the upper layer.

Particles in the range of 1 to 5  $\mu$ m in diameter or smaller are primarily made up of clay mineral complexes - montmorillonite, kaolinite and illite. They are susceptible to flocculation when they encounter seawater. The probability of coagulation occurring is a function of the particle number and electrolytic concentration. The size of the agglomerated particles is regulated by the intensity of the shearing stress of the flow regime. With sufficiently high concentrations, turbulence may be dampened, and with reduced shear, the particles will fall as a unit, with concentrations in the order of as much as 100,000 mg/k or more moving as a "fluid mud". This phenomenon, however, is not characteristic of the James River, although solids concentrations in the bed material are of this order.

The coarse sediments are composed of sand and gravel; which do not flocculate. The distribution of the former is particularly informative in the analysis of the transport with the bed itself. Some concentrations of sand may deposit in the null zone if such material is present in the incoming freshwater flow. In general, the concentration in inflow is minimal and the major source of the sand is from the ocean boundary condition.

There can be significant lateral variations also - at bends, junctions and bays. Most evident is the difference the dredged ship channel and shallow littoral sections. In the coastal plain estuaries of the eastern region of the United States, the landward residual flow near the bed, in conjunction with the solids load brought in by the freshwater flow causes a net accumulation of solids within the estuary. This accumulation is referred to as the sedimentation velocity whose order is tenths or units of centimeters per year. There is in general very little sediment from the rivers reaching the continental shelf and most of the solid material is accumulated with the estuary proper. Flood loads will with its associated solids load flush out some of this material, but significant fractions are retained.

The spatial distribution of this material, as observed in many partially mixed estuaries, such as the James, is characterized, in the vicinity of the salinity intrusion limit, by a peak concentration higher than that of either

- 74 -

the river source or the oceanic waters. This phenomenon, usually referred to as the "turbidity maximum", decreases with decreasing river flow and may be washed out under relatively high flow conditions. Other factors, which include dependencies on the settling velocity (particle size) of the sediment, the amount of sediment introduced at both the ocean and river sources, the strength of the estuarine circulation, flocculation and deflocculation regulated by salinity variation, and local resuspension by tidal currents or waves, may also be effective in this regard.

A steady state mass transport equation for suspended sediment, analogous to that for salinity, Equation (5-19), may be written for a tidally averaged, two dimensional estuary of constant width:

$$\frac{\partial}{\partial x}(\bar{u}\ \bar{m}) + \frac{\partial}{\partial z}[(\bar{w}\ + \bar{w}_{s})\bar{m}] + \frac{\partial}{\partial x}(u_{t}m_{t}) = \frac{\partial}{\partial z}(\varepsilon_{z}\ \frac{\partial\bar{m}}{\partial z})$$
(5-24)

in which  $\bar{m}$  is the tidally averaged concentration of suspended sediment;  $\bar{w}_s$  is the averaged settling velocities of suspended particles; and  $u_t$ ,  $m_t$  are the

tidal components of horizontal velocity and suspended sediment concentration. The longitudinal turbulent diffusion is neglected because its effect is relatively insignificant compared to the terms in Equation (5-24).

Vertical averaging of Equation (5-24) about the plane of no net motion yields the expression,

$$\frac{\partial}{\partial \mathbf{x}}(\langle \vec{\mathbf{u}} \rangle \langle \vec{\mathbf{m}} \rangle) + \frac{\partial}{\partial \mathbf{x}}(\langle \mathbf{u}_{t} \rangle \langle \mathbf{m}_{t} \rangle) + \frac{\partial}{\partial \mathbf{x}}(\vec{\mathbf{u}} \cdot \vec{\mathbf{m}}) + \frac{\partial}{\partial z}[(\vec{\mathbf{w}} + \vec{\mathbf{w}}_{s})\vec{\mathbf{m}}]_{o} - \frac{\partial}{\partial z}(\varepsilon_{z} \frac{\partial \vec{\mathbf{m}}}{\partial z})_{o} = 0$$
(5-25)

applicable for each layer. The terms  $\langle u \rangle$  and  $\langle m \rangle$  are layer averages of the velocity and suspended sediment concentration, respectively, such that:

 $\bar{u} = \langle \bar{u} \rangle + \bar{u}^{\dagger}$  $\bar{m} = \langle \bar{m} \rangle + \bar{m}'$ 

where  $\bar{u}'$  and  $\bar{m}'$  are the tidally averaged deviations from the mean values in each layer. The subscript 'o' in the last two terms of Equation (5-25) represent the plane of no net motion.

Each term in Equation (5-25) represents a distinct transport mechanism. The first term,  $\langle u_{1} \rangle \langle m \rangle$ , defines the contribution to the flux of suspended sediment by the advective flow in each layer. The second term,  $\langle u_{+} \rangle \langle m_{+} \rangle$ , is

referred to as the tidal diffusion. The third term,  $\bar{u'm'}$ , arises from the layer-averaging process and represents the shear effect in each layer. By assigning the temporal distributions of current velocities to sine functions and approximating that the distributions of suspended sediments are symmetri-

- 75 ~

cal about slack water, i.e. the distributions show a mirror image for periods of flood and ebb, the net effect of tidal diffusion is not significant. The last two terms in Equation (5-25) are the vertical advective and dispersive fluxes of suspended sediment across the plane of no net motion.

114 W

The final equation of suspended sediment applicable to each layer of a two-dimensional estuary is:

$$\frac{\partial}{\partial x}(\overline{\langle u \rangle \langle \overline{m} \rangle}) + \frac{\partial}{\partial z}[(\overline{w} - \overline{w}_{g})\overline{m}] = \frac{\partial}{\partial z}(\varepsilon_{z} \ \frac{\partial \overline{m}}{\partial z})$$
(5-26)

This equation reflects the effect of superimposing the settling velocity of particles onto the tidally averaged estuarine circulation pattern in determining the distribution of suspended sediment. The effects of flocculation and deflocculation may also be introduced into this framework by expanding the settling velocity term to include these physio-chemical processes. The equations developed above represent an estuary of constant width. In most coastal plane estuaries, the width varies in the longitudinal direction:

$$\frac{1}{B}\frac{\partial}{\partial x}(uBm) + \frac{\partial}{\partial z}[(w-w_s)m] = \frac{\partial}{\partial z}(\varepsilon_z \frac{\partial m}{\partial z})$$

in which

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B = width of the estuary

The bracket and bar symbols are not included henceforth.

The longitudinal boundary conditions specified for the evaluation of Equation (5-26) are the concentrations of suspended sediment associated with the freshwater inflow at the upstream limit and with the oceanic waters in the lower layer at the downstream location. In addition, a vertical boundary condition is established by the interaction at the water-sediment interface. The resulting flux of this interaction, which is the net effect of settling of particles from the water to the bed and entrainment of particles from the sediment layer, is expressed as:

$$J_{\bar{b}} = w_{\bar{b}}m + w_{\bar{u}}m_{\bar{b}}$$
(5-27)

in which  $m_b$  is the concentration of particles in the sediment layer, and  $w_u$  is the tidally averaged entrainment velocity of these sediment particles across the interface. A net flux from the water to the sediment layer implies that the mean settling is greater than the resuspension of particles and conversely a net flux from the sediment layer to the water stipulates that uplift is greater than settling.

Inspection of Equation (5-26) indicates that the suspended sediment distribution is dependent on four transport coefficients. The horizontal and vertical velocities are determined by employing the equations of momentum, continuity and state, and the vertical dispersion is calculated from an

- 76 -

empirical relation involving the eddy viscosity and the Richardson number. Validation of these parameters has previously been performed in examining the mass transport of salinity.

The last coefficient required in this evaluation is the settling velocity which is a function of the size, shape and density of the suspended particles. Furthermore, the density of cohesive sediments depends on the water content and nature of the particle. Recent work on marine particles from various sources provides a basis to relate particle density to inorganic composition and to particle size. The correlation, originally proposed by McCave (16), is based on a 60-40 ratio of inorganic-organic composition. Subsequent analysis on the solids in the Sacramento-San Joaquin Delta (17) indicated an inorganic-organic composition of 85-15. This ratio is much more in line with that observed in the James. The relationship between particle density and particle size for this composition is derived as follows:

$$p_{2} = 2.0 d^{-0.15}$$
 (5-28)

in which  $\rho_{\rm s}$  is the density of the particle in gm/cm  $^3$  and d is the particle diameter in  $\mu m$ . The settling velocity is then estimated by substituting this expression into Stokes' equation, yielding the distribution of settling velocities for the range of the observed particle sizes.

2. Bed Conditions

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The transport components of the bed consist of a longitudinal advection and a vertical dispersion or mixing. The advective component of transport in the bed is induced by shearing stress of the overlying flowing water, with which it is in contact. The horizontal velocity of bed is a maximum at the water interface and diminishes in depth to a point at which the bed may be regarded as stationary. The vertical dispersion follows a similar pattern. A mass balance about an elemental volume within the bed results in the following equation defining the solids distribution:

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial z} (\varepsilon(x) \ \frac{\partial m}{\partial z}) + \frac{u(z)}{B(x)} \ \frac{\partial Bm}{\partial x}$$
(5-29)

in which

 $\varepsilon$  = vertical mixing coefficient

u = horizontal velocity

B = width of the bed

The boundary condition in the vertical planes are specified at the water-bed interface and at that depth of zero horizontal velocity, which is the interface between the transport layer and the stationary bed. The former is the net flux due to the settling of suspended solids from the overlying water and the resuspension of the bed from the transport layer in accordance with Equation (5-27). The net effect of this flux is a change in the elevation of the water-bed interface, which rises or falls depending on the rela-

- 77 -

tive magnitude of the two terms in the above equation.

Assuming vertical uniformity over the transport layer, the vertical dispersive term in the bed equation is replaced by the boundary conditions as described. Furthermore, since this flux produces a volumetric change in the bed, this factor must be taken into account in the mass balance. Thus, the mass rate of change per unit length of estuary bed is:

$$\frac{\partial m_b}{\partial t} = \frac{\partial}{\partial t} (Am_b) = w_s Bm_w - w_u Bm_b + uH \frac{\partial}{\partial x} (Bm_b)$$
(5-30)

Expanding the left-hand side of this equation and dividing through by the cross-sectional area of the bed:

$$\frac{\partial m_{\rm b}}{\partial t} + \frac{m_{\rm b}}{A} \frac{\partial A}{\partial t} = \frac{w_{\rm s}}{H} m_{\rm w} - \frac{w_{\rm u}}{H} m_{\rm b} + \frac{u}{B} \frac{\partial}{\partial x} (Bm_{\rm b})$$
(5-31)

in which

$$\frac{1}{A}\frac{\partial A}{\partial t} = \frac{1}{H}\frac{dz}{dt} = \frac{w_d}{H}$$
(5-32)

# $\frac{dz}{dt}$ = $\frac{dz}{dt}$ = the rate of change of the bed elevation

The rate of change of the bed elevation is referred to as a sedimentation velocity. It may be envisioned as the velocity at which the water-bed interface approaches the stationary bed if erosion is predominant or at which the interface moves away from that datum if settling is the significant term.

Assuming the concentration of the bed,  $m_b$ , is approximately constant, the above reduces to, under steady-state:

$$0 = \frac{\mathbf{w}_{a}^{m}\mathbf{w}}{H} - \frac{\mathbf{m}_{b}}{H} (\mathbf{w}_{u} + \mathbf{w}_{d}) + \mathbf{u}_{b}\mathbf{b}$$
(5-33)

in which

 $b = \frac{1}{B} \frac{dB}{dx}$ 

Interpreting the bed elevation change as described, the flux about the stationary bed is:

$$w_b^m b = w_d^m s$$

(5-34)

in which

 $m_s = average$  concentration of the solids in the stationary bed.

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# ORGANIC CHEMICALS DISTRIBUTIONS

The longitudinal and vertical distributions of the dissolved and particulate components of an organic chemical, in an estuary under steady-state, tidally averaged conditions may be written as follows:

$$0 = \frac{\partial}{\partial z} (\varepsilon) \frac{\partial c}{\partial z} - u \frac{\partial c}{\partial x} - w \frac{\partial c}{\partial z} - K_{o}mc + K_{2}p \qquad (5-35)$$

$$0 = \frac{\partial}{\partial z} (\varepsilon) \frac{\partial p}{\partial z} - u \frac{\partial p}{\partial x} - (w - w_s) \frac{\partial p}{\partial z} + K_o mc - K_2 p \qquad (5-36)$$

in which

c = concentration of dissolved

p = concentration of particulate component

 $\varepsilon$  = vertical dispersion coefficient

u = horizontal velocity

w = vertical velocity

w = settling velocity

K = Adsorption coefficient

K<sub>2</sub>= Desorption coefficient

The first two terms in each of the equations represent the vertical dispersion and horizontal advection. The third term is the vertical advection, which includes the settling velocity of the particulate component in equation (5-36). The remaining two terms define the rates of adsorption and desorption, respectively.

The vertical boundary conditions are assigned at the air-water and water-bed interfaces, at which concentration and flux conditions are specified. The flux may be negative or positive, representing net deposition or scour at the bed, respectively, or gas-liquid exchange at the air-water surface. An additional source due to precipitation may be effective under certain conditions. A zero-flux condition indicates equilibrium. To be noted is on the fact that, although the suspended and bed solids may be in equilibrium, the same condition does not necessarily apply to the organic chemical, due to the adsorption-desorption interaction. If the coefficients defining this process are large, the assumption of instantaneous equilibrium may be appropriate.

A comparison between the above equations for the two dimensional case and those of the one-dimensional analysis is informative: In the latter, both evaporation and settling are incorporated in the basic differential equation while on the former, only the settling appears in the basic equation and the evaporation flux is introduced as a boundary condition. The horizontal boundary conditions are assigned at the upstream limit of the model. In the two-layered approximation of the above equations, the downstream lower layer concentration is specified.

- 79 -

Addition of the equations describing the distributions of the dissolved and particulate components yields:

$$0 = \frac{\partial}{\partial z} \left( \varepsilon \ \frac{\partial c_{\rm T}}{\partial z} \right) - u \ \frac{\partial c_{\rm T}}{\partial x} + w \ \frac{\partial c_{\rm T}}{\partial z} - w_{\rm s} \ \frac{\partial p}{\partial z}$$
(5-37)

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Substitution of the total concentration for the particulate fraction, assuming instantaneous equilibrium yields the final form:

$$0 = \frac{\partial}{\partial z} \left( \varepsilon \frac{\partial c_{\mathrm{T}}}{\partial z} \right) - u \frac{\partial c_{\mathrm{T}}}{\partial x} + w \frac{\partial c_{\mathrm{T}}}{\partial z} + w_{\mathrm{s}} \frac{\partial}{\partial z} \left( f_{\mathrm{p}} c_{\mathrm{T}} \right)$$
(5-38)

If the evaporative flux is significant, it is introduced as boundary condition at the air water interface:

$$\varepsilon \frac{\partial^2 \mathbf{T}}{\partial z} \Big|_{z=0}^{z} - \mathbf{K}_{\mathrm{L}}^{c}$$
(5-39)

Expressing the dissolved fraction in terms of the total yields:

$$\varepsilon \frac{\partial}{\partial z} (f_{d} c_{T}) \mid = \frac{k_{L}}{z=0} \frac{k_{T}}{1+f_{m}} c_{T}$$
(5-40)

In the case of Kepone, this flux is insignificant. The flux of the particulate is evidently zero at the air-water interface.

The boundary conditions at the water-bed interface are for the particulate and dissolved components, respectively:

$$j = + E \frac{\partial f_p c_T}{\partial z} \Big|_{z=H} - w_s f_p c_T$$
(5-41)

or

.

$$j_{p} = w_{u} f_{p} c_{Tb} - w_{s} f_{p} c_{Tw}$$

$$j_{d} = -D \frac{\partial c}{\partial z} |_{z=H}$$
(5-42)

The exchange coefficients between the two layers is expressed in terms of entrainment velocity  $w_{\rm u}$ , in finite difference form since the particulate

concentration in the bed is much greater than that in the water due to the solids. The pertinent differential equation is as described in the previous section. At the interface between the moving layer and the stationary bed, the boundary conditions of flux is expressed in terms of the sedimentation velocity,  $w_d$ .

- 80 -

#### PROCEDURE OF ANALYSIS

Application of the principle discussed in the preceding chapters to a prototype estuarine setting involves four steps. First, principles of continuity, momentum and state are employed in a steady-state tidally averaged mode to generate two-layered horizontal flows as well as vertical flows. Secondly, a two-layer steady state model of the water column is used to determine the vertical dispersion coefficient between the two water column layers using ocean salt as a tracer. In addition, the net resuspension rate of suspended solids from the bed to the water is estimated to match observed suspended solids. Finally, using observed kepone concentrations in the surficial sediments as a boundary condition, estimates of the dissolved and particulate kepone fractions in the water column are made. These estimates are compared with available data and - assuming instantaneous equilibrium - the partition coefficient in the water column adjusted to achieve agreement.

In the third step of the procedure, the moving bed and stationary bed sediment layers are added to the model. Net horizontal velocities of the moving layer are then estimated and the flux of sediment between the two sediment layers is determined. With selected values of solids concentrations for both the moving and stationary beds, the net sedimentation rate of the bed is calculated and compared to observed rates in the estuary.

The fourth step involves using the four layer model - two layers in the water column and in the bed (one transport and one stationary) - to generate dissolved and particulate concentrations of kepone in the water and bed phases. The molecular diffusivity of the dissolved kepone in the bed interstitial water and coefficients for all pertinent transfer and decay processes are assigned. Partition coefficients are selected for the water and sediment phases based on the assumption of instantaneous equilibrium.

Using historical inputs of kepone and the appropriate seasonal hydrologic input, a time trace of bed kepone buildup is calculated and values for selected times after the beginning of the discharge are compared with corresponding measurements. With the cessation of Kepone production, the fate of the mass of Kepone in the system can be projected temporally and the time to return the aqueous and sediment phases to acceptable concentrations may be estimated.

A summary of these steps is presented in Fig. 5-2. Note that all coefficients indicated in the figure are used for the final four-layer model analysis. In the sketch of each step, only the additional coefficients selected in that step are shown. More detailed discussion of each of the four steps follows.

# Hydrodynamics

The procedure of analysis for obtaining net tidally averaged horizontal and vertical velocities is, in principle, simple and straightforward. The assignment of input parameters - salinity, longitudinal and vertical gradients, freshwater flow and channel characteristics - is first made. The

- 81 -

sequential computation of horizontal and vertical velocities follows, based on an assumed value of the eddy viscosity. Since only the order of magnitude of the eddy viscosity is known, a few trials may be necessary to achieve the best fit between the observed and calculated velocity. Although the procedure involves a number of steps, it is computationally simple and relatively rapid. The entire process requires about 10 seconds on a CDC 6600 computer. The procedure may be repeated for various combinations of tidal and flow conditions to establish the range of transport patterns for the two-dimensional estuarine circulation.

The first step is to estimate from the runoff records of the nearest upstream gauge the average freshwater flow entering the head of the estuary during a steady state period. If the hydrograph reflects unsteady flow, the period over which the flow is averaged requires some judgment and an average period of a week to month prior to the sampling time is usually representative.

Various locations throughout the saline zone are selected, the number depending on the variation of the average depth of the channel. A trapezoidal schematization of the cross-sections are assigned from the selected stations. The next step involves the assignment of the horizontal surface salinity gradients and the vertical distribution of salinity for each station for mean tide condition. If salinity measurements are taken at slack tide, mean tide salinity is established by spatially translating the observations half of a tidal excursion. If, on the other hand, salinity data are available over the entire tidal period, the average salinity values over the period may be more representative of the mean tide condition. Given these data, the surface salinity ( $\overline{c}_{S}$ ) is assigned as well as the salinity gradient

 $(d\overline{c}_{s}/dx)$  for each station. The vertical variation  $\phi(z)$  is often described by polynomials,  $\phi(z) = 1 + a_{1}z + a_{2}z^{2} + a_{3}z^{3}$  to characterize its non-linear

nature. The linear approximation, involving the first two terms, has been found to be adequate to define the horizontal velocity distribution on several estuaries. Thus, the vertical salinity distribution is expressed as  $\overline{C} = \overline{C}_{s}(1 + a_{1}z)$ , in which  $a_{1}$  may be readily determined from the salinity observations. Using the above data, the horizontal velocities are calculated over the depth and the eddy viscosity (N) adjusted to fit the measured velocities.

The plane of no net motion is determined at each station by determining the depth to zero velocity. By interpolation between stations, the plane is defined for the entire saline region and a two-layered system is constructed. The average horizontal velocity in each layer is then determined from the calculated velocity profiles by integrating above and below the point of no net motion. The average vertical velocity across the plane of no net motion is obtained by flow balance. Thus, with the estuary segmented lontitudinally, the horizontal flow in the surface layer at each vertical cross section is first calculated. The difference in horizontal flow between two adjacent vertical planes gives the vertical flow between the surface and bottom layers. The vertical velocity is obtained subsequently by dividing the vertical flow by the product of the average width of the segment and the

- 82 -

#### length between adjacent vertical planes.

The hydrodynamic output for each freshwater flow analyzed consists of a set of horizontal flows between the longitudinal segments and a set of vertical flows between the upper and lower water layer segments. The plane of no net motion is also defined in this step. Although the location of the plane will vary slightly with the magnitude of the freshwater flow, a single location is selected so that each model segment may be characterized by a constant geometry.

#### Salinity

With the horizontal and vertical flows determined from the hydrodynamic analysis above, the advective component of mass transport is known for any substance. Salinity, a dissolved, conservative constituent, is then used to obtain the second transport component, namely the vertical dispersion coefficient between the two layers of the water column. As noted previously, an initial estimate of the vertical dispersion coefficient, ɛ, is obtained from an empirical relationship involving the vertical eddy viscosity, N, and the local Richardson number. With these initial estimates of the vertical dispersion coefficients for the entire model, the two-layer steady state model is run for a particular freshwater flow with upstream and downstream boundary conditions appropriate for that flow. The initial estimates of the vertical dispersion coefficients are then adjusted so that salinity profiles in both upper and lower water column layers agree with measured values. An increase in the vertical dispersion coefficients will raise the absolute magnitude of the salinity in both upper and lower water column layers and diminish differences between the layers whereas a decrease will amplify the vertical salt gradient.

The advective and dispersive fluxes which enter a mass balance for a finite water segment are graphically shown in Figure (5-3) for an upper and lower water column segment. Thus, for the upper water column layer, the net amount of salt transported out of the segment by the horizontal velocity  $(u_1)$  is equal to the salt transported into the segment by the vertical velocity (w) and the vertical dispersion ( $\epsilon$ ).

#### Suspended Solids

The settling velocity of the suspended solids in the water column (w\_), resuspension rate of bed sediment  $(w_{ij})$  and sedimentation rate of the bed sediment  $(w_d)$  are estimated in the next phase of the analysis procedure. The settling velocity is first estimated, based on the nature and characteristics of the suspended solids in the water column. As a first estimate, the settling velocity may be assumed to be relatively constant throughout the estuarv -- as is presently assumed in the James River model. Spatial variations may be incorporated as information on characteristic settling velocities for the ambient classes of solids becomes available. It may be noted that a single aggregate solids class is utilized in the present model.

- 83 -

Having adopted an aggregate settling velocity, the flux of sediment resuspending into the water column from the moving sediment layer is determined next. A resuspension flux is input to the lower water column layer, upstream and downstream boundary conditions are selected - corresponding to the flow condition being analyzed - and the steady state model is run. The assumed resuspension flux is adjusted until calculated suspended solids profiles for both upper and lower water column layers agree with observed profiles.

Pertinent mechanisms incorporated in this analysis are shown in Figure (5-4). For any steady state period being analyzed, an upper water column segment loses solids due to the longitudinal oceanward velocities  $(u_1)$  and settling  $(w_s)$  of its solids  $(m_1)$  to the lower layer. These losses are balanced by inputs from the lower water segment due to vertical advection (w) and dispersion (c). Vertical advection and dispersion represent losses to the lower water column segment and the settling of the upper layer solids  $(m_1)$  is an input whereas settling of the lower layer solids  $(m_2)$  to the bed is a loss. For the lower water layer, these fluxes are balanced by the loss or gain of solids from the landward lower water layer velocities  $(u_2)$  and the input of solids due to resuspension of the bed sediment.

Computationally, as indicated in Figure (5-4), the resuspension flux is treated as a resuspension velocity  $(w_u)$  associated with the concentration of sediment in the moving sediment layer  $(m_3)$  - the latter value selected on the basis of data from sediment cores. Typically, the resuspension flux varies spatially, with a relatively constant value in the upstream freshwater zone and peak values in the null zone which subsequently decrease downstream. With increasing freshwater flow, the peak values increase and move downstream with the null zone.

With the suspended solids coefficients which affect the water column determined (settling, and resuspension), the analysis proceeds to calculate sedimentation rates for the bed. As indicated in Figure (5-5), the moving active layer of solids is subjected to horizontal transport  $(u_3)$  induced by

the motion of the lower water layer. The motion will be landward provided the net estuarine density circulation on the bottom is landward. Thus, a mass balance around a segment in the moving layer includes the net flux of sediment into the segment due to the induced velocity  $(u_3)$  and the associated

bed sediment concentration  $(m_3)$ . The value of  $m_3$  presently is assumed to be

relatively constant along the estuary and, thus no change in concentration  $(\Delta m_3)$  is shown in Figure (5-5). Additional fluxes include the settling from

the lower water layer, resuspension of bed sediment, all the above balanced by the flux of sediment into the stationary bed  $(w^{T}m_{3})$ .

Below the movable layer, a stationary bed either receives the net flux of solids from the active layer (deposition/sedimentation) or serves as a source of solids for the movable layer (scour). Thus, in Figure (5-5), a final mass balance indicates the incoming flux from the moving layer is

- 84 -

equal to the sedimenting flux  $(w_d^m_4)$ . After selecting a representative value for the sediment concentration in the stationary bed  $(m_4)$  based on data from sediment cores, the long-term sedimentation velocity  $(w_d)$  is calculated. The latter value is then compared to estimated sedimentation rates in the estuary as a validation step.

It may be noted that, at a given location in the estuary, sedimentation may occur for a low flow condition and scour at a higher flow, or vice versa. Since toxicant concentrations in the bed will only build up in sedimenting zones of the estuary, selecting an appropriate long-term hydrology for the river require careful consideration when bed buildup and depuration simulations are being performed.

### Kepone

In this final phase of the analysis procedure, Kepone parameters are evaluated. Based on the assumption that Kepone adsorption-desorption rates are rapid - that is, instantaneous equilibrium exists between the dissolved and particulate components of Kepone, a partition coefficient is stipulated in accordance with the concentration of suspended solids, as described in Section 2 of this report. In the water column, an appropriate partition coefficient can be selected for a given flow condition by means of the two layer steady state model. Thus, by using observed values of particulate Kepone in the surficial bed sediments as a boundary condition, an initial estimate of the partition coefficient is made and adjusted until observed and calculated values of both dissolved and particulate Kepone in the water column are in agreement. Transport components of the mass balance in the two water column layers are shown in Figure (5-6). Note that a molecular diffusion term is indicated between the lower water layer and the moving bed for the dissolved Kepone component. Presently, the diffusion coefficient ( $D_{2-3}$ )

is set to zero and research is continuing to evaluate its importance in transferring Kepone for the bed to the water column. Adsorption and desorption fluxes are not indicated in Figure (5-6) since these fluxes are equal when instantaneous equilibrium is assumed and thus cause no net loss or gain of Kepone.

The four layer time variable Kepone model is then run to predict existing distributions of dissolved and particulate Kepone in the water column and bed. Equilibrium experiments with Kepone provide a basis for selecting partition coefficients in the movable and stationary beds where sediment concentrations are orders of magnitude greater than suspended solids concentrations in the water column layers. Diffusion of dissolved Kepone between the bed layers is assigned at molecular rates  $(D_{3-4})$ . The transport mechanisms assumed for the moving and stationary beds are shown in Figure (5-7). Note that Kepone in the bed is released into the water column through the sole mechanism of resuspension of particulate Kepone when diffusion of the dissolved component is assumed negligible. Also observe that sedimentation  $(w_d)$ 

transfers Kepone from the active bed into the deeper sediment, making this mass unavailable for subsequent resuspension into the overlying waters.

- 85 -

In a buildup calculation, historic discharges of Kepone into the river must be estimated. Since records of these values are generally non-existent, Kepone production records provide the sole basis of evaluating these loadings. If leaching of disposal sites is deemed to contribute significant quantities of the toxicant to the river, an estimate of this non-point source input must be made for the production period and, if production has ceased, for the subsequent period when residual quantities of toxicant in disposal In a buildup calculation, historic discharges of Kepone into the river must be estimated. Since records of these values are generally non-existent, Kepone production records provide the sole basis of evaluating these loadings. If leaching of disposal sites is deemed to contribute significant quantities of the toxicant to the river, an estimate of this non-point source input must be made for the production period and, if production has ceased, for the subsequent period when residual quantities of toxicant in disposal areas may enter the receiving waters.

Using the historic loading estimate, a calculation of bed Kepone concentrations can be made for the corresponding historic hydrology. Comparisons between observed and calculated spatial profiles of Kepone can then be made at field survey periods to assess the reliability of the model. Since water column and moving bed Kepone concentrations respond strongly to the loading function selected, emphasis should be on comparison of stationary bed values which respond less rapidly to the assumed discharge of Kepone.

Assuming discharges have ceased, a forecast of the Kepone concentrations and masses in the water column and bed can be made under an assumed future hydrology. In this instance, the Kepone mass in the bed provides the forcing function to the system. Water column and surficial bed concentrations can be estimated for any point in time, and the time to reach desired aqueous and sediment concentrations can be estimated.

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During the entire hindcast and forecast, the total mass of Kepone discharged can be accounted for in three basic compartments: the mass resident in the water column and bed of the model, the mass exiting the model into Chesapeake Bay and the mass bound up in the deep sediments below the active bed.

- 86 -

### NUMERICAL SOLUTION OF EQUATIONS

# Finite Difference Equations - Theory

The mass balance equations presented in the previous sections are written in terms of continuous spatial and temporal coordinates since they are differential equations. In order to obtain time variable solutions for irregular geometries it is necessary to employ numerical methods. The conventional approach approximates the spatial and temporal derivatives with suitable difference expressions. This transforms the differential equations into difference equations which can be readily solved numerically.

The numerical solution of the differential equations derived in the previous sections is complicated by the presence of spatially and temporally varying transport parameters, and the interactive adsorption-desorption kinetics. The difficulty of solution is increased by the large magnitude of the net non-tidal horizontal advection. In conventional one dimensional estuarine analysis the vertically averaged net non-tidal horizontal velocity is used, which is an order of magnitude smaller.

The reversible adsorption-desorption kinetics also contribute to the difficulty. This reaction is very rapid relative to the time scale of the transport. These large reaction rates can cause unstable behavior in the numerical scheme. In order to illustrate this problem, consider the situation for which only a kinetic reaction affects the dissolved and particulate Kepone:

$$\frac{dc}{dt} = -K_1 mc + K_2 p \tag{5-43}$$

$$\frac{dp}{dt} = -K_2 p + K_1 mc$$
(5-44)

In order to express the particulate concentration equation in finite differences let:

$$p^{n} = p(n\Delta t) \tag{5-45}$$

$$p^{n+1} = p[(n+1)\Delta t]$$
(5-46)

The derivative is replaced by the difference expression and equation (5-44) becomes:

$$\frac{p^{n+1}-p^{n}}{\Delta t} = -K_{2}p^{n} + K_{1}m^{n}c^{n}$$
(5-47)

so that at time  $(n+1) \Delta t$  the solution is:

$$p^{n+1} = p^n (1 - K_2 \Delta t) + \Delta t K_1 m^n c^n$$
 (5-48)

If  $K_2$  is large, so large that  $K_2 \Delta t >> 1$ , then  $p^{n+1}$  can be negative which is physically impossible. One solution to this problem is to keep  $\Delta t$  very small. However this can increase computation time to the point of impracticality.

The source of the difficulty is the right hand side of equation (5-47), where these concentrations are expressed at time level n. This is called an explicit<sup>\*</sup>finite difference scheme since  $p^{n+1}$  is given explicitly by equation (5-48). Although this is a useful feature of explicit schemes, it can lead to unstable behavior as shown above. The solution to this difficulty is to express the right hand side of equation (5-47) at time level n+1. Initially if only p is expressed at time level n+1, equation (5-47) becomes:

$$\frac{p^{n+1} - p^n}{\Delta t} = -K_2 p^{n+1} + K_1 m^n c_n$$
(5-49)

For this illustrative case, the linear equation for  $p^{n+1}$  can be easily solved, the result being:

$$p^{n+1} = \frac{p^n}{1 + K_2 \Delta t} + \Delta t K_1 m_c n$$
 (5-50)

Note that the particulate concentration is now always positive regardless of the magnitude of  $K_2\Delta t$ . Similarly the analogous dissolved concentration finite difference equation for equation (5-43) is:

$$\frac{c^{n+1} - c^n}{\Delta t} = -K_1 m^n c^{n+1} + K_2 p^n$$
 (5-51)

which yields:

$$c^{n+1} = \frac{c^n}{1+K_1m^n\Delta t} + \Delta t \ K_2 p^n$$
(5-52)

Again no problem with positivity occurs for large  $K_1 m^n \Delta t$ .

However there is a problem with accuracy. The kinetic equations (5-43) and (5-44) imply that c(t) + p(t) is constant in time. However, adding eq. (5-50) and eq. (5-52) yields:

$$p^{n+1} + c^{n+1} = \frac{p^n}{1 + K_2 \Delta t} + \Delta t K_1 m^n c^n + \frac{c^n}{1 + K_1 m^n \Delta t} + \Delta t K_2 p^n$$
 (5-53)

which does not equal  $p^n$  +  $c^n,$  unless both  $K_2 \Delta t$  << 1 and  $K_1 m^n \Delta t$  << 1, since in that case:

- 88 -

$$\frac{1}{1 + K_2 \Delta t} \simeq 1 - K_2 \Delta t$$
(5-54)

$$\frac{1}{1 + K_1 m^n \Delta t} \simeq 1 - K_1 m^n \Delta$$
(5-55)

and the appropriate terms cancel. But keeping  $\Delta t$  small is not a practical recourse.

The source of the inaccuracy for this scheme can be seen to be the mixing of time levels at which c and p are evaluated in the right-hand side of the equations. If both p and c are evaluated at time level n+l in the kinetic expression, the result is:

$$\frac{p^{n+1} - p^n}{\Delta t} = -K_2 p^{n+1} + K_1 m^n c^{n+1}$$
(5-56)

$$\frac{c^{n+1} - c^n}{\Delta t} = + K_2 p^{n+1} - K_1 m^n c^{n+1}$$
(5-57)

Adding these equations shows that  $p^{n+1} + c^{n+1} = p^n + c^n$  as required by mass balance so that the finite difference equations conserve mass properly. It can be shown, also, that the solution for  $p^{n+1}$  and  $c^{n+1}$  is positive for positive  $p^n$  and  $c^n$  for any choice of  $\Delta t$ .

The price that is paid for this desirable behavior is that these implicit equations yield simultaneous linear equations for  $p^{n+1}$  and  $c^{n+1}$ :

$$(1 + K_2 \Delta t)p^{n+1} + (1 + K_1 m^n \Delta t)c^{n+1} = p^n$$
 (5-58)

$$- (K_2 \Delta t) p^{n+1} + (1 + K_1 m^n \Delta t) c^{n+1} = c^n$$
(5-59)

which must be solved at each time step of the integration. For this illustrative example, this is not difficult but as shown below, it does lead to complications for larger sets of equations.

A similar difficulty can occur with the advective derivative. Consider the simple case of purely horizontal advection:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = o$$
 (5-60)

In order to maintain positivity for simple schemes at least, it is known

- 89 -

that the advective derivative must be expressed as a backward spatial difference. Letting  $c_i^n = c(i\Delta x, n\Delta t)$  then:

$$\frac{\partial c^{n}}{\partial x} \approx \frac{c^{n}_{1} - c^{n}_{1-1}}{\Delta x}$$
(5-61)

and the explicit difference equation becomes:

$$\frac{c_{1}^{n+1} - c_{1}^{n}}{\Delta t} + u \frac{c_{1}^{n} - c_{1-1}^{n}}{\Delta x} = 0$$
 (5-62)

or:

$$c_{i}^{n+1} = c_{i}^{n} \left(1 - \frac{u\Delta t}{\Delta x}\right) + \frac{u\Delta t}{\Delta x} c_{i-1}^{n}$$
(5-63)

The condition for stability is that  $\Delta x > u\Delta t$  and therefore if u is large and  $\Delta x$  is reasonably small, which is necessary to preserve accuracy, then  $\Delta t$  is required to be very small. For example, if u = 1 mi/d and  $\Delta x = 1 \text{ mi}$ , then  $\Delta t < 1 \text{ day}$ . Similar problems occur for the vertical velocity and dispersion terms if explicit schemes are used.

The problem can be overcome by evaluating the advective derivative at time level n+1 so that eq. (5-62) becomes:

$$\frac{c_{i}^{n+1} - c_{i}^{n}}{\Delta t} + u \frac{c_{i-1}^{n+1} - c_{i-1}^{n+1}}{\Delta x} = 0$$
 (5-64)

which yields a set of simultaneous equations for  $c_{d}^{n}$ :

$$-\lambda c_{i-1}^{n+1} + (1+\lambda)c_{i}^{n+1} = c_{i}^{n}$$
(5-65)

where  $\lambda = u\Delta t / \Delta x$ . Positivity is preserved since:

 $c_{i}^{n+1} = \frac{c_{i}^{n}}{1+\lambda} + \lambda c_{i-1}^{n+1}$ 

which is positive regardless of the magnitude of  $\lambda$ . For this illustration it is again straightforward to solve the implicit linear equations that result.

The conclusion from the above analysis is that expressing the transport and kinetic expressions at the n+1 time level solves the problem of main-taining positivity in spite of the rapid kinetics and large transport magni-

- 90 -

tudes. However it does require that sets of simultaneous linear equations be solved at each time step.

# Finite Difference Equations for Dissolved and Particulate Kepone

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The analysis of the previous section suggests that a fully implicit integration of the mass balance equations is required for the transport and kinetics associated with Kepone fate. Consider the differential equations for dissolved and particulate Kepone:

$$\frac{\partial c}{\partial t} - \frac{\partial}{\partial z} \left( \varepsilon^{d} \frac{\partial c}{\partial z} \right) + \frac{1}{B} \frac{\partial}{\partial x} \left( u^{d} B c \right) + \frac{\partial}{\partial z} \left( w^{d} c \right) = -K_{1} m c + K_{2} p \qquad (5-66)$$

$$\frac{\partial p}{\partial t} - \frac{\partial}{\partial z} \left( \varepsilon^{p} \frac{\partial p}{\partial z} \right) + \frac{1}{B} \frac{\partial}{\partial x} \left( u^{p} B_{p} \right) + \frac{\partial}{\partial z} \left( w^{p} _{p} \right) = K_{1} m c - K_{2} p \qquad (5-67)$$

where the superscripts d and p refer to the transport of dissolved and particulate Kepone.

The finite difference equations for these equations employ the definitions for concentrations illustrated in Fig. (5-8a). The index i denotes the borizontal coordinate; the index j denotes the vertical coordinate. The grid spacing is as indicated. The dispersive and advective transport coefficients are defined in Fig. (5-8b). The one-half index denotes the interface being considered. The spatial finite difference expressions for the derivatives are conventional: backward spatial differences for the velocity terms and centered spatial differences for the dispersion term.

The mass balance equation is constructed by considering the flux of mass into and out of the i,j<sup>th</sup> volume,  $V_{i,j}$ . This procedure is discussed in more detail elsewhere (18). That is for dissolved Kepone concentration  $c_{ij}$ :

$$V_{ij} \frac{c_{ij}^{n+1} - c_{ij}^{n}}{\Delta t} = \frac{\varepsilon_{i,j+k_{2}}^{d} A_{i,j+k_{2}}}{\Delta z_{i,j+k_{2}}} (c_{i,j+1}^{n+1} - c_{i,j}^{n+1})$$
(5-68)  
+  $\frac{\varepsilon_{i,j-k_{2}}^{d} A_{i,j-k_{2}}}{\Delta z_{i,j-k_{2}}} (c_{i,j-1}^{n+1} - c_{i,j}^{n+1})$   
+  $u_{i-k_{2},j}^{d} A_{i-k_{2},j} c_{i-1,j}^{n+1}$   
-  $u_{i+k_{2},j}^{d} A_{i+k_{2},j} c_{i,j}^{n+1}$   
- 91 -

+ 
$$w_{i,j+\frac{1}{2}}^{d} A_{i,j+\frac{1}{2}} c_{i,j+1}^{n+1}$$
  
-  $w_{i,j-\frac{1}{2}}^{d} A_{i,j-\frac{1}{2}} c_{i,j}^{n+1}$   
+  $v_{ij} (- K_{1}m^{n}c_{i,j}^{n+1} + K_{2}p_{i,j}^{n+1})$ 

If the signs of the velocities are negative the associated concentrations are changed to keep the advective derivative a backward difference, i.e. if  $u_{i-l_2,j}^d < 0$  then that term becomes:  $u_{i-l_2,j}^d c_{i,j}^{n+1}$  since the concentration in the backward (or upstream) direction is  $c_{i,j}^{n+1}$ .

The particulate Kepone equation is similar, with  $\varepsilon^p$ ,  $u^p$ , and  $w^p$ , the particulate transport coefficients, replacing  $\varepsilon^d$ ,  $u^d$ , and  $w^d$  and with the signs of the kinetic expression reversed. These two simultaneous equations are listed in table (5-1). For each segment of the grid, analogous finite difference equations are written for dissolved and particulate concentrations.

Since these equations are implicit in  $c^{n+1}$  and  $p^{n+1}$ , a set of simultaneous equations must be solved at each time step. At first glance this may appear to be an unreasonable requirement since, for an N segment model the order of the equations is 2N by 2N which can be quite large. For simple geometries this may not be a problem since the equations have special structures and efficient routines for their solution are available. For example a one-dimensional segmentation for a single concentration produces a banded set of equations. Unfortunately the structure of segmentation for two interacting concentrations in a two dimensional problem is not as regular. Consider the example shown in Fig. (5-9). A three layer model is shown with vertical and horizontal transport of both dissolved and particulate Kepone. The pattern of the non-zero coefficients is also illustrated. The transport coefficients appear in the locations specified by the connectivity of the segmentation. The upper left and lower right quadrant are the transport interactions between segments for dissolved and particulate Kepone respectively. The upper right and lower left quadrants contain the adsorption-desorption interactions between dissolved and particulate Kepone.

Although there is a certain regularity to the pattern the key to an efficient solution technique is the fact that the coefficient matrix is sparse. That is, only a small fraction of the 2N by 2N elements are non-zero and this fraction decreases as the number of segments, N, increases. Whereas for a completely filled coefficient matrix the number of elements

increases as the square of the matrix size  $(2N)^2$ , and the computation time increases as the cube of the size,  $(2N)^3$ , for sparse matrices, the increase in nonzero elements is linear in segment size. Thus it is computationally feasible to integrate the equations with a fairly large number of segments.

- 92 -

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For the James Estuary model the number of segments is 135 and the average number of nonzero coefficients per segment is approximately 5. Hence the total number of non-zero elements is  $\sim (2)(135)(5) = 1350$  which corresponds to a completely filled matrix of order  $\sim 40$ . Since this is a reasonably small matrix, the solution time is acceptable.

The solution of large sets of sparse simultaneous equations is an area of active research and a number of techniques have been developed (19). The most efficient of these are based on the concept of reordering the numbering scheme of the equations in such a way that during the forward elimination step of the Gaussian elimination procedure, the number of new non-zero elements that are created is minimized. This limits the additional computer memory required and also limits the total number of arithmetic operations required for solution. The most reliable reordering schemes also monitor the magnitude of the pivot elements employed in the elimination thereby preserving the numerical stability of the solution by preventing division by small pivot elements. The subroutine package employed in this project was developed by the U.K. Atomic Energy Establishment, Harwell, England (20). A complete description and documentation of the computer program is being prepared as a separate report.

- 93 -

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- 94 -

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$$c_{i,j-1}^{n+1} [-\alpha_{i,j-\frac{1}{2}}^{d}]$$
+  $c_{i,j}^{n+1} [1 + \alpha_{i,j+\frac{1}{2}}^{d} + \alpha_{i,j-\frac{1}{2}}^{d} + \beta_{i+\frac{1}{2},j}^{d} + \gamma_{i,j-\frac{1}{2}}^{d} + K_{ij}^{d}]$ 
+  $c_{i,j+1}^{n+1} [-\alpha_{i,j+\frac{1}{2}}^{d} - \gamma_{i,j+\frac{1}{2}}^{d}]$ 
+  $c_{i-1,j}^{n+1} [-\beta_{i-\frac{1}{2},j}^{d}]$ 
+  $p_{i,j}^{n+1} [-K_{ij}^{p}]$ 
=  $c_{ij}^{n}$ 

$$p_{i,j-1}^{n+1} \left[ - \alpha_{i,j-\frac{1}{2}}^{p} \right]$$

$$+ p_{i,j}^{n+1} \left[ 1 + \alpha_{i,j+\frac{1}{2}}^{p} + \alpha_{i,j-\frac{1}{2}}^{p} + \beta_{i+\frac{1}{2},j}^{p} + \gamma_{i,j-\frac{1}{2}}^{p} + \kappa_{ij}^{p} \right]$$

$$+ p_{i,j+1}^{n+1} \left[ - \beta_{i-\frac{1}{2},j}^{p} \right]$$

$$+ c_{i,j}^{n+1} \left[ - \kappa_{ij}^{d} \right]$$

$$= p_{ij}^{n}$$

where:

$$\alpha_{i,j+l_{2}}^{d} = \frac{\Delta t \ \varepsilon_{i,j+l_{2}}^{d} A_{i,j+l_{2}}}{\Delta z_{i,j+l_{2}} V_{ij}}$$
$$\beta_{i+l_{2},j}^{d} = \frac{\Delta t \ u_{i+l_{2},j} A_{i+l_{2},j}}{V_{ij}}$$

- 96 -





- 98 -
















# SECTION 6

## APPLICATION TO KEPONE DISTRIBUTION IN JAMES RIVER

#### DESCRIPTION OF THE STUDY AREA

The James River is a tributary of Chesapeake Bay. From its fall line at Richmond, the river is characterized by a narrow channel, oftentimes dredged, bordered by shallow zones, some of which are productive shell fish areas. The channel cross section increases in the downstream direction and broadens perceptively at locations known as Bailey, Tar, Cobham and Burwell Bay.

This section of the river, downstream of Richmond, as shown in Figure 6-1, is a coastal plain estuary. The circulation - produced by tidal action, freshwater flow and horizontal and vertical salinity gradients, is typical of estuarine systems. The average annual runoff is 5,000 cfs, with extreme high and low water flows in the order of 25,000 and 1,000 cfs, respectively. These freshwater flows carry varying loads of suspended solids into the

estuarine system. Estimates of the solids load are in the order of 10<sup>6</sup> metric tons per year, with the principle contributions occurring in short pulses during spring snow melt and major storm events in the region. The composition of these river-borne solids is primarily clay and silt material consisting of approximately four to ten percent organic matter. Another source of solids - containing somewhere in the order of fifty percent sand particles by weight, is associated with the alternating tidal currents at the typical estuarine circulation, produce spatial distributions of suspended solids frequently characterized by a maximum concentration in the vicinity of the saline intrusion, commonly referred to as the "turbidity maximum".

## KEPONE HISTORY

Kepone, which is the tradename of a chlorinated ketone, was developed by the Allied Chemical Company in the early 1950's as a means of controlling specific insect pests. Production of the pesticide in the Hopewell area, which began with the intermittent manufacture of the chemical in 1966, was finally halted in the summer of 1975 (Table 6-1). Throughout this time and continuing into the present, various amounts of discharged Kepone have reached the James River via the municipal sewer system, leaching of contaminated soil and runoff in the area. Only sketchy information on the actual quantity of the pesticide to enter the river is available; however, field investigations have shown that the region of resulting contamination extends upstream of Hopewell down the river approximately 120 km. to the mouth of the James and possibly out into Chesapeake Bay. A major portion of this contaminated region has subsequently been closed to the commercial fisheries, notably crabs and

- 107 -

# AVAILABLE DATA

Data from numerous sources (references 1-6) were collected in connection with the various phases of the mitigation studies of the Kepone-contaminated areas of the James River. The source data pertinent to the analyses reported herein are presented in Table 6-2 and their position with respect to the daily hydrograph is shown in Figure 6-2.

At the request of the Virginia State Health Department, the Health Effects Research Laboratory of the Environmental Protection Agency conducted a survey to determine the environmental distribution of the pesticide. Among the various phases of the survey, one was directed to the sampling of the aquatic environment. Water samples were collected from a number of locations including both the water and wastewater treatment plants and various domestic and industrial users. Both water and sediment were analyzed in samples taken from the James River, Appomatox River and Bailey's Creek. The concentration of Kepone was in the range of tenths to a few micrograms per liter. Sediment from Bailey's Creek area was contaminated with Kepone to levels as great as 10 micrograms per gram. In addition, soil near the manufacturing site and sludge from the various disposal sites had significant concentrations.

Sampling of the region continued throughout 1976-77 by the Commonwealth of Virginia, State Water Control Board. In assessing possible threats to public health, water samples and sediment cores were collected at more than 50 stations to measure total Kepone content. Of particular value are the results of the sediment sampling which established the general pattern of Kepone residuals in the James River.

The Virginia Institute of Marine Science, supported by the Gulf Breeze Research Laboratory of the Environmental Protection Agency, initiated a field and laboratory program in 1976, the various phases of which are presented in the table. Previous work on the sediments of the James River system provided an excellent basis for the analyses of the Kepone concentration. During the period of 1976-1977, four surveys of the bed were conducted in which both surficial samples and core samples (to 100 cm in depth) were analyzed. Locations of sampling stations extended from upstream of the Kepone source at Hopewell to Chesapeake Bay, covering zones of sediment deposition, natural and dredged channels, natural shoals and banks of dredged material. For each bed surface sample the following characteristics in addition to the Kepone concentrations were measured: composition (% clay, silt, sand and organic content), density and water content, and particle size (mean, median and standard). The bulk Kepone concentration and that on the fraction less than 63 µM were recorded. On the core samples, Kepone concentrations at between 5 and 10 cm increments were measured. In December, 1978, extensive coring of bed samples was conducted and kepone, % moisture and % organics were measured at a number of intervals in the 60 cm sample.

Some difficulty in obtaining a representative sample in the heterogenous environment of the sediments existed. Variations, which held for the sedi-

- 108 -

ment properties as well as the kepone content, have been exhibited over a 200 meter distance (3). Also, coring around the Coggins Point region (approximately km 90-100) was not plausible due to the compact nature of the sediments. According to Nichols (personal communication), since this area is believed to be a scoured zone, minimal Kepone accumulation in the sediments of this region was assumed.

VIMS also conducted extensive water sampling programs in August '77 and April-May '78. During the former survey, four transects were monitored for hourly measurements over the complete tidal cycle at Hog Island (46 km), Chickahominy River (73 km), Kennan Marsh (88 km) and Coggins Point (111 km). Each transect consisted of a deep channel station - sampled with depth at approximately two meter intervals, and two off channel stations - sampled at two depths. Parameters of interest were salinity, temperature, dissolved oxygen, current velocity, suspended solids and particulate kepone. Measurements of dissolved Kepone in the water were all below the detection limit of  $0.10 \ \mu g/l$ . The information gathered during this survey period represents a steady state depiction of the water column since a low flow condition of approximately 1,000 cfs persisted for 6-8 weeks prior to sampling.

A subsequent survey of the water column was conducted in April-May '78 to reflect the effects of freshwater flow and the change in Kepone concentrations since 1977. In addition to an extensive intratidal sampling in early May at transects at Pagan Creek (29 km), Burwell Bay (30 km), Hog Island (47 km), Jamestown Island (66 km) and the Chickahominy River (73 km), fifteen slack water stations were sampled during the prior month. This information permitted some assessment of the effects of a fluctuating freshwater discharge between 11,000 and 18,000 cfs during the intratidal sampling. Although dissolved Kepone concentrations again were below the detection limit of 0.10  $\mu g/\ell$ , subsequent sampling by VIMS using an improved analytical technique showed the dissolved Kepone to be on the order of 0.01 to 0.1  $\mu g/\ell$ . However, no field surveys were conducted in which this improved technique was used.

Concurrent with some of the VIMS sampling effort, Battelle undertook a data collection program in June 1977 as part of the EPA Kepone Mitigation Feasibility Study. Water column information was collected at eight transects including the James River Bridge (19 km), Rocklanding Shoal (31 km), Hog Island (55 km), West Swann Point (70 km), Windmill Point (104 km), Jordan Point (116 km), Bailey Bay (118 km) and City Point (121 km). Three stations were located on each transect and one to three depths were sampled per station for each of three current conditions (flood, slack and ebb). Velocity, temperature, conductivity, pH, dissolved oxygen, suspended solids, particulate and dissolved Kepone were measured. Discrepancies in the conductivity measurements, in some respects limited the application of this data. Battelle also performed an extensive sediment sampling program concentrating mainly on the Bailey Bay and Hopewell vicinity. Twenty seven cores were collected in Bailey Bay with seven of these being analyzed for vertical distributions of Kepone. A comprehensive sampling plan for Bailey Creek, Gravelly Run, the terrestrial areas of the town of Hopewell, the primary sewage treatment plant area, and the municipal landfill was also established to quantify inflows of Kepone to Bailey Bay and the James River system.

- 109 -

Numerous laboratory studies were also conducted to determine the physical, chemical, biological and toxicological effects of Kepone. Information on the effects of biodegradation, volatility and the adsorption-desorption behavior of Kepone has been compiled by Garnas et al. (5) at the EPA Gulf Breeze Environmental Research Laboratory. Studies on the effects of Kepone to the marine biota were conducted at the Gulf Breeze Laboratory with some additional analysis performed by VIMS.

# GEOPHYSICAL FACTORS AND SYSTEM SEGMENTATION

#### Geomorphology

The James River is a typical coastal plain estuary draining into Chesapeake Bay (Figure 6-3). A deepwater channel is maintained at a depth of approximately 30 feet and depths vary considerably from the shallow embayments to the deepwater channel. The River generally becomes more broad as it flows downstream but there are several locations where natural constrictions occur. Cross sectional areas vary widely in shape from the broad shallow shape at the mouth to the narrower deeper profile more upstream. Several embayments, such as Baileys Bay, Tar Bay, Cobham Bay and Burwell Bay, are present with characteristic shallows at the shore and a deeper main channel section. Selected cross sectional areas along the length of the River are shown in Figure 6-4 where the kilometer points of the cross sections refer to distances upstream of the Chesapeake Bridge-Tunnel. Note that the vertical scale is distorted in order that the variation of depth across the River might be visible.

The variation of the cross sectional area, river width and river depth from above Hopewell downstream to Norfolk is shown in Figure 6-5. The abscises represents the distance from the mouth of the River to the point in question, in kilometers. Note the general increase of all parameters in the direction of flow, with an exponential increase in cross sectional area typical of coastal estuaries. Values of all parameters are averaged longitudinally over some distance upstream and downstream, and/or averaged laterally, in order to diminish highly localized geomorphology.

## Hydrology and Tidal Factors

Freshwater flow in the James River is the result primarily of the runoff contributed by the more than 6750 square miles of drainage area upstream of the City of Richmond, Virginia. Annual average flow in the James is approximately 7000 cfs. This is supplemented, at Hopewell, by the runoff from the 1340 square miles draining to the Appomattox River and further downstream by the Chickahominy River near Providence Forge, Virginia. Other sources of runoff are negligible in comparison to these three rivers. Thus, in Figure 6-6, the spatial variation of freshwater flow in the study area is shown for several different flow conditions by three horizontal lines. In the figure the James River runoff is the most upstream horizontal line, the next line downstream represents the sum of the James and Appomattox River flows, and the last line is the cumulative flow of the James, Appomattox and

- 110 -

#### Chickahominy Rivers.

During the period when kepone was manufactured (1966-1975) flows in the River varied substantially, as is typical in any ten year record. To illustrate this, monthly averaged flow is plotted in Figure 6-7 from 1966 to 1977. In most cases, typical higher spring runoff values are followed by lower summer-early fall flows, although the durations and magnitudes vary from year to year. The drought condition of 1976-1977 is clearly reflected in the figure.

The tidal current is an important factor in the transport of the solids and constituents in both the water and bed. The longitudinal distribution of the current amplitude is shown in Figure 6-8.

#### System Segmentation

In order to formulate a model to predict toxicant concentrations in the water column and sediment of a river-estuary system, the actual geomorphology, hydrology and total phenomena must be adequately reflected. To accomplish this, the water body is divided into a number of segments, each of which represents localized parameters of the system. In this way, variations of any parameter along the length of the river can be taken into account. Segment lengths must be short enough so that expected gradients in water and sediment concentrations can be accurately calculated.

With the above criteria in mind, a James River model was constructed of 126 completely mixed segments. The main channel of the river consists of 108 segments and the four side bays and two tributaries of the river are represented by a total of 18 segments. Four layers of segments are used for the main channel, two in the water column and two in the sediment. In the more shallow side bays and tributaries, three vertical layers of segments are used, one for the water and two for the river bed.

A schematic of an elevation view of the segments in the main channel is shown in the upper portion of Figure 6-9. Note that segments 1 through 54 define the two layers of the water column, segments 61 through 87 are in the first sediment layer and segments 94 through 120 constitute the second sediment layer.

The first sediment layer, subjected to movement by the lower water layer velocities, is referred to as the "moving sediment" layer or the "moving bed" and the second sediment layer is the "stationary bed". As shown in the lower portion of the figure, segments 55 through 60 are the water segments, sequentially numbered, in the Appomattox River, Baileys Bay, Tar Bay, Chickahominy River, Cobham Bay and Burwell Bay. For the same locations, segments 88 through 93 and 121 through 126 represent the moving and stationary bed segments, respectively.

In the main channel, segment lengths are all approximately 5 kilometers long. With 27 segments end-to-end, the model represents 135 kilometers of river from its mouth to above Hopewell. This length was deemed adequate to

- 111 -

properly characterize the natural system as well as give adequate definition to water and sediment concentration profiles. Water column depths, which vary along the river, dictate the depth of the water column segments, that is the depth of layer 1 plus layer 2. The location of the plane of no net motion - described previously - defines the individual depths of the top and bottom water column layers. Except for the upstream tail of the salinity gradient, the plane of no net motion is located near the mid-depth and, thus top and bottom water segments are generally of equal depth. Based on available sediment data, depths of 10 and 30 centimeters were selected for the moving and stationary beds, respectively.

In all cases, the horizontal interfacial area between water column segments at a location is set equal to that between the lower water layer moving bed interface and that between the moving bed-stationary bed interface. Vertical interfacial areas, that is, cross sectional areas, are selected to adequately represent that parameter at a location in the river.

#### CIRCULATION AND MASS TRANSPORT

#### General

With the geometry of the model selected, the next step in the analysis is to produce a water circulation field which incorporates the significant features of the estuarine tidal movement. For this study, a two layer flow averaged over the tidal cycle is adopted as the appropriate flow field. Thus, density driven net landward flows will occur in the lower water column layer and net flows will be seaward in the surface layer. These flows are calculated by averaging the vertically varying longitudinal net velocities over the depth of each layer. Adequacy of the calculation is tested by comparing the net longitudinal velocities with measurements. Typical measurements, made in the field or in a hydraulic model of the River, include instantaneous observations of velocity at fixed time intervals across the tidal cycle. Observations are generally available at several depths at a given station and data are usually gathered at several locations in the estuary. For purposes of comparison to net velocities calculated in the hydrodynamic analysis described previously in this report, the instantaneous intratidal velocities at a given depth at one station are integrated over the ebb and flood phases of the tidal cycle. Resulting net velocities are, thus, much less than the magnitude of the tidal velocities since the averaging is done on an algebraic basis.

Salinity data are used in the above analysis to calculate the net velocities and they are also used to select vertical mixing coefficients between the upper and lower water layers. Since the model framework is on a steady state, tidally averaged basis - with mean water depths constant in time, longitudinal salinity profiles for the upper and water layers should represent mean tide conditions. In this study, grab samples of salinity were translated to mean the positions using estimated tidal excursions. When continuous salinity data were obtained, data were averaged over the tidal cycle for those locations where this procedure was considered to produce

- 112 -

# reasonable mean tide salinity concentrations.

#### Vertical Distribution of Longitudinal Velocities

Vertical profiles of net velocity were calculated for a range of James River flows including 1000, 3200, 4380, 6000, 7044, 11500 and 18500 cfs. In each case, several inputs were required for the steady state hydrogynamic equations of momentum and continuity. For each location the analysis is being performed, these inputs include the cross sectional geometry, freshwater flow, longitudinal surface salinity gradient, vertical salinity gradient and the vertical eddy viscosity. For the geometry, a representative depth of the cross section must be stipulated as well as a depth-averaged width. In this study the width was averaged both upstream and downstream of the cross section to diminish highly localized effects. The freshwater flow used for all locations was the flow in the James River above Hopewell. Although this flow is supplemented by the Appomattox and Chickahominy River drainage, the predominant upstream flow was considered to be the representative river flow for all locations. These tributary inflows were later included in the flow balance of each water segment by routing them downstream in the surface layer.

For each flow condition, available salinity data was assembled and longitudinal salinity profiles estimated for the mean water position as discussed above. For locations where the hydrodynamic analysis was to be performed, the slope of the surface salinity curve was graphically determined. By averaging all available salinity data in the surface layer and in the bottom layer, the vertical salinity gradient at a location was calculated as the difference between the bottom and surface layer average concentrations divided by the vertical distance between the centers of the layers.

Finally, the vertical eddy viscosity (N) is input. This value is the only variable remaining and it is selected so that, at a given cross section, the calculated vertical profile of net longitudinal velocities agrees with net velocities determined from tidal velocity measurements. As the eddy viscosity is increased, net velocities decrease and vice-versa. For the James River, values of the vertical eddy viscosity appear to increase in the seaward direction as well as increase with increasing freshwater flow. Thus, for flow conditions where tidal velocity measurements were not available, estimates of the values of N were made using these observations as a guide.

As illustrations of the method, comparisons between calculated and observed vertical velocity profiles are shown in Figures 6-10 and 6-11, together with longitudinal and vertical salinity data. Note the translation of the salinity profile downstream and the sharper vertical salinity gradient with increasing flow. Comparisons between observed net velocities and the calculated vertical net velocity profile, shown as a solid line, are reasonable. For orders of magnitude, note that the surface net velocity is approximately 0.6 ft/sec at the most downstream station for the 6000 cfs flow whereas the comparable value for the 1000 cfs flow is approximately 0.2 ft/sec.

- 113 -

# Horizontal and Vertical Flows

The depth at which the longitudinal velocity profile indicates a zero velocity, that is where velocities change direction from seaward to landward, defines one point on the plane of no net motion. By integrating the velocities above this point, an average seaward velocity for the upper layer is obtained. The product of this average velocity and the cross sectional area above the plane of no net motion defines the horizontal flow in the upper water layer of the model at a particular location. Similarly, the lower water layer flow is derived from the average velocity below the point of no net motion. Thus, for every vertical interface in the model, horizontal flows are derived either directly from the hydrodynamic analysis or interpolated from bounding cross sections where the hydrodynamic analysis was performed.

Given, then, that the upstream and downstream vertical interfacial flows are known, continuity is applied to each model segment to establish the vertical flow. For an upper water layer segment located in the saline region of the estuary, the downstream flow is greater than the upstream flow. Thus, the difference will represent a net loss of water from the segment which will be balanced by the vertical flow of water from the lower water layer into the upper layer segment. The vertical velocity is then computed as the quotient of the vertical flow and the horizontal interfacial area between the upper and lower water segments.

The order of magnitude of the horizontal flows is quite large, in the order of one-half to one order of magnitude greater than the freshwater flow. The horizontal and vertical flows for the 1000 cfs flow condition are depicted in Figure 6-12, as an example. Note that the magnitudes of the upper and lower water layer flows increase seaward from freshwater values of approximately 500 cfs to 40000 cfs at the mouth of the James River. Also note that the tributary inflows are routed downstream in the surface layer of the model. A summary of the freshwater flows in the James, Appomatox and Chickahoming River is given in Table 6-3 for the six flow conditions used in this study, together with the net tidal flows at the mouth of the James. In this table, it may be noted that the sum of the freshwater flows equals the difference between the top and bottom layer downstream net tidal flows. Thus, the 4300 cfs condition has freshwater inputs of 5300 cfs (4380 + 657 + 253) and a net outflow at the mouth of 5300 cfs (73300 - 68000), ensuring an overall water balance.

# Vertical Dispersion and Salinity Distribution

With the advective flow field determined, the dispersive component of mass transport is evaluated next. The turbulent mixing between the upper and lower water layers is dependent on the bulk dispersion coefficient, the value of which depends on the dispersion coefficient as well as the geometry of the segments. Since the vertical eddy viscosity (N) represents the transfer-or "mixing"- of momentum between water layers, empirical relations between the dispersion coefficient and the vertical eddy viscosity have developed. In this study, the first estimate of the mass dispersion coefficient

- 114 -

 $\varepsilon = N(1+Ri)^{-1}$ 

where Ri is the local Richardson number defined as:

$$Ri = \frac{g \frac{d\rho}{dz}}{\rho \frac{d\rho}{dz}} 2$$

Since  $\rho$ , the density of the water, is a function of salinity, the numerator of the Richardson number is defined by the vertical salinity gradient used in the hydrodynamic analysis above. The denominator involves the slope of the horizontal velocity profile, evaluated at the plane of no net motion, a quantity easily derived from the horizontal velocity profile previously discussed. Since this first estimate of the vertical dispersion coefficient is empirical, it is not a quantity derived from first principles and a number of trials may be required to establish final dispersion coefficients for the model.

The conservative parameter, salinity, is most useful in the selection of these coefficients. Thus, with the horizontal and vertical flows for a particular flow condition, observed mean tide salinity boundary conditions are input to the model. Vertical dispersion coefficients, first estimated from the Richardson number, are input and subsequently adjusted until the calculated longitudinal salinity profiles in both the upper and lower water layers agree with observed values. Increasing the dispersion coefficient will cause the two profiles to increase as well as diminish the difference between them and vice versa.

## Longitudinal Variations of Circulation Parameters and Salinity

A graphical summary of the advective and dispersive transport coefficients, as well as the resulting salinity profiles, is shown in Figure 6-13 for the 1000 cfs flow condition. From right to left, the various panels in the figure show the variation in the particular parameter from the mouth of the James River, at kilometer point 0, to its freshwater region near Hopewell, approximately 120 kilometers upstream of the mouth. The uppermost panel indicates the depth of the river and the depth to the plane of no net motion, the latter occurring at approximately mid-depth for the majority of the river. The circles represent locations at which the hydrodynamic analysis was performed, twelve stations in all.

Layer averaged horizontal velocities, in feet per second, for the upper and lower water layers appear next. Note that surface layer velocities are plotted as positive, or downstream, values and velocities in the lower water layer are negative, or in the landward direction. Again, the circles and triangle represent the twelve locations where the hydrodynamic analysis was applied. At the upstream end, at km 120, the velocities in both layers

- 115 -

are of the same magnitude and direction, indicating that it is in the freshwater region above the null zone. The null zone, where the lower water layer velocity is zero, is located approximately 10 kilometers downstream, at km 110. Net velocities are seen to range from 0.05 to 0.3 ft/sec in the surface layer and from 0.05 to - 0.13 ft/sec in the bottom layer.

Calculated values of the vertical velocities are indicated by the squares in the third panel of Figure 6-13, with units of feet per day. Except at the null zone where the vertical velocity somewhat increases, the upstream vertical velocities are relatively constant, between 0.5 and 1 ft/day. These velocities increase to a maximum of approximately 4.5 ft/day at the downstream end of the model.

The next to last panel of the figure summarize the eddy viscosities used in the hydrodynamic analysis at the twelve locations in the river - and the vertical dispersion coefficients. The former are represented by the triangles and the latter by both the diamonds and the solid curve, all in units of square centimeters per second. The diamond symbol represents the initial estimate of the vertical dispersion coefficient from the eddy viscosity and Richardson number. The solid curve indicates the final values of the vertical dispersion coefficient used to ensure agreement between the calculated and observed salinity profiles.

In the lowest panel of Figure 6-13, the calculated concentrations of salinity, in parts per thousand, are shown as the solid curves for the upper and lower water layers, with the higher curve for the lower water layer. Observed data are shown as circles and triangles for the bottom and top water layers, respectively. The good agreement between observed and calculated values is apparent.

Repeating the above procedure for five other flow conditions, agreement between calculated and observed salinity profiles also is obtained, as is evident in Figure 6-14. The downstream migration of the salinity profiles may be noted with increasing flow as well as the increasing gradient in the vertical direction inferred from the greater spread between the upper and lower layer salinity profiles.

A summary of pertinent circulation parameters is contained in Table 6-4 for six flow conditions ranging from 1000 cfs to 18500 cfs.

# SUSPENDED AND BED SOLIDS

# Suspended Solids in the Water Column

The advective and dispersive transport coefficients in the two layers of the water column were determined in the preceding section. The analysis procedure continues with the evaluation of two coefficients required to produce suspended solids concentrations in the upper and lower water column layers, the settling velocity and the resuspension flux. As discussed in Chapter 3, the settling velocity of the suspended solids found in the James River can vary from approximately 4 to 6 feet per day. A value of 4 feet

- 116 -

per day was selected as the representative settling velocity. This parameter was kept constant throughout the entire length of the River and was used for all freshwater flow conditions which ranged from 1000 cfs to 18500 cfs.

Scouring of the surficial bed sediments due to tidal velocities is the mechanism by which bed solids are introduced back into the water column. Thus, a net flux of solids occurs between the water-bed interface. In the James River model, this entrainment rate, or resuspension flux, was computed as the product of a resuspension velocity ( $w_u$ ) and the concentration of solids in the active bed layer.

The transport components which enter into the suspended solids balance in the water column are graphically illustrated in Figure 6-15 for the 1000 cfs flow condition. Horizontal velocities, in the uppermost panel, translate suspended solids in the longitudinal direction in the upper and lower layers. Transport across the upper and lower water layers is affected by the upward vertical water velocities, shown in the second panel of the figure, the downward suspended solids settling velocity and by the vertical dispersion of solids, the coefficients of which are shown in the third panel. It may be noted that the dispersive flux of solids is generally in the upward direction, since the suspended solids concentrations are generally higher in the lower water layer, as seen in the last panel of Figure 6-15.

For any selected flow condition, the two layer model is run for suspended solids in a steady state mode. Sediment loads from the tributaries are input in the appropriate segments, a downstream boundary condition is selected at the mouth of the River, the settling velocity is input and a resuspension flux estimated. This latter value is spatially varying, with peak values slightly downstream of the null zone. It is adjusted until calculated and observed suspended solids concentrations in the upper and lower water layers are in reasonable agreement.

Examples of the suspended solids concentrations, both observed and calculated, are shown in Figures 6-16, 6-17 and 6-18 for the 1000, 7044 and 18500 cfs flow conditions, respectively, together with the resulting resuspension fluxes (entrainment rates). In Figure 6-16, for example, salinity profiles are shown for the 1000 cfs flow condition in the top panel. The upstream tail of the salinity profile, which corresponds to the null zone, is located at KP 110. Suspended solids concentrations appear in the middle panel of the figure, with the calculated lower water layer concentrations shown as a solid curve. Agreement between calculated and observed data is reasonable. Peak solids concentrations of approximately 60 mg/ $\ell$  in the lower layer occur slightly downstream of the null zone.

The entrainment rate, in the lower panel of Figure 6-16, is relatively constant upstream of the null zone, has a maximum value of approximately

75 gm/m<sup>2</sup>-day approximately 5 kilometers downstream of the null zone and decreases in the seaward direction thereafter. Similar longitudinal profiles for the higher flows of 7044 and 18500 cfs may be seen in Figures 6-17 and 6-18, respectively. With increasing flow, the salinity profiles, as well as

- 117 -

the null zone, are displaced downstream. Peak solids concentrations increase with flow with values of approximately 60, 110 and 125 mg/ $\ell$  for the 1000, 7044 and 18500 cfs flows, respectively. The entrainment rates also increase with the higher, more turbulent flow with maximum rates of approximately 75,

170 and 225  $\text{gm/m}^2$ -day for the 1000, 7044 and 18500 cfs flows, respectively. These values are consistent with the range of 50 to 100  $\text{gm/m}^2$ -day reported by Partheniades who used estuarine clays - similar to those in the James River - in a set of controlled laboratory experiments.

# Bed Solids

As discussed previously, the sediment is an integral part of the James River model. It is divided into two layers, the active bed and the stationary bed. The active bed has a longitudinal transport component due to motion imparted to it through shearing stresses caused by tidal velocities in the lower waters. In the James River model, the longitudinal velocity was set equal to one one-hundredth of the net horizontal velocity in the lower water layer. Thus, if the lower water layer had a net velocity of 0.3 ft/sec in the landward direction, the active bed layer would have a velocity of 0.003 ft/sec, also in the landward direction. Since the lower water layer velodities will decrease landward, be equal to zero at the null zone and will be in the seaward direction upstream of the null zone, the latter direction predominating for the highest flow conditions.

With constant volume segments in the James River model and with a temporally and spatially constant sediment solids concentration of 50000 mg/k, the mass of solids in each active bed segment remains constant in time. Thus, mass into the each segment must be balanced by mass out. Downstream of the null zone, for example, the mass rate of solids entering the active bed segment will consist of solids settling from the water column and a net transport of active bed solids due to the induced horizontal velocities of the active bed. Solids will leave the active bed segment due to resuspension into the water phase and by deposition into the stationary bed. In a mass balance about the segment, then, the deposition mass rate is the only unknown, and, there is the unknown quantity that is calculated in this step. Note that the deposition flux may be a "scouring" flux, depending on the relative magnitudes of the other three mass rates.

A segment in the stationary bed of the James River model has only two mass rates of solids to balance. The flux between the active bed and stationary bed, as determined in the mass balance about the active bed segment, is one component and the flux out of, or into, the stationary bed is the second component. Since there are only two components and the volume and stationary bed solids concentration of 500,000 mg/& are constant in time, the two fluxes are equal and the mass rate leaving the active layer equals the mass rate leaving the stationary bed. If the flux between the active bed and stationary bed is downward, or into the stationary bed, the solids flux out of the lower horizontal interface of the bed will be downward indicating that solids are depositing at that location in the estuary. Scour zones are indicated when the flux between the active and stationary bed is upward. The

- 118 -

resulting deposition or scour rates of the stationary bed  $(w_d)$  can be com-

pared with independent estimates of the estuarine sedimentation or scour rates to ensure compatibility of the model and prototype. It may be noted that the locations of deposition and scour zones, as well as the rates of sedimentation or scouring, vary with each flow condition, and a deposition zone under a low flow condition, for example, may be a scour zone under a higher flow condition. This must be considered when long term sedimentation rates obtained by field measurements, such as dredging records, are compared to calculated values for one constant flow condition. In any case, using typical low and high flow conditions gives a bound on the order of magnitude of the prototype rates which can be compared with the independent estimates.

The magnitude and spatial variation of the main channel sedimentation or scour rates are shown in Figures 6-19, 6-20 and 6-21 for the 1000, 7044 and 18,500 cfs flow conditions, respectively. In Figure 6-19, for example, the suspended solids longitudinal profiles are in the top panel for the upper and lower water layers. The resuspension, or entrainment rate, appears in the center panel, as presented previously in Figure 6-16. In the last panel, the sedimentation rate, in centimeters per year, is shown for the main chan-nel of the estuary, for the 1000 cfs flow. Note the alternating deposition and scour zones, and the maximum deposition rate of approximately 0.8 cm/yr from km 95 to km 80. The maximum deposition rate for the higher flows are translated downstream with peak values of approximately 1.1 cm/yr for the 7044 cfs flow (Figure 6-20) and 2.3 cm/yr for the 18,500 cfs flow (Figure 6-21), both located at km 25. In the latter two figures, scouring seems to predominate in the main channel and typical reported values of from 1 to 2 cm/yr sedimentation are higher than the calculated sedimentation values. Τn the side embayments of the model, however, sedimentation rates are much higher, with values increasing with increasing flow. In Figure 6-22, embayment sedimentation rates are seen to vary between 1 and 3 cm/yr, with the highest values occurring for the 18,500 cfs flow.

In all, six flow conditions were analyzed in this study. Values of characteristic solids coefficients and boundary conditions are summarized in Table 6-5.

#### KEPONE DISTRIBUTIONS

#### Kepone in the Water Column

With best estimates of the coefficients governing solids transport available-following the procedure in the preceding section, the parameters affecting Kepone distributions in the water and sediment phases can be addressed. The first step is to evaluate the significant kinetic coefficients in the water column, that is, the adsorption-desorption rates. Since the time scale of the problem being addressed is in the order of years and decades, it is presumed that instantaneous equilibrium exists and, thus, a partition coefficient must be obtained. The two layer steady state model was used to estimate the partition coefficient in the water column of the James River as follows.

- 119 -

The active production of Kepone having ceased in 1975, the dominant source of Kepone to the water column is the mass of Kepone in the bed sediments. From survey data, the concentration profile of Kepone in the sediments is known. Since Kepone in the bed is predominantly in the particulate phase, a flux of particulate Kepone occurs across the water bed interface. This flux is equal to the product of the resuspension flux of solids and the mass of Kepone per unit mass of solids. Note that the flux of dissolved Kepone from the bed to the water is assumed negligible, an assumption examined in the next chapter of this report.

For a relatively constant flow period, when survey data are available in the water column, the advective and dispersive transport coefficients in the water column - corresponding to the particular freshwater flow - are input to the two layer model. Suspended solids concentrations in the water column have been calculated previously and all fluxes of solids between the two water column layers and the water-bed interface are known. Kepone boundary conditions are set for the upstream and downstream boundaries and the flux of resuspended Kepone from the bed input to the lower water layer. A solids-dependent partition coefficient formula, based on laboratory Kepone equilibrium experiments, is used to calculate the partition coefficient for each segment in the model, values of which range from approximately 4100 to 1800 for suspended solids concentrations of 20 and 60 mg/L, respectively. The final partition coefficient expression selected which gives reasonable agreement between calculated and observed Kepone concentrations in the water column - and which is consistent with laboratory data using solids similar in composition to those in the James River - is:

$$\P = 500 + \frac{63700}{0.96}$$

where  $\P,$  the partition coefficient, is in  $\mu g/kg$  per  $\mu g/\ell$  and m is the concentration of solids in  $mg/\ell.$ 

As an example of the input and results of their analysis step, for the 1000 cfs flow condition of August 1977, calculated longitudinal profiles of Kepone are compared with all available data in Figure 6-23. Suspended solids in the water column in mg/l, are shown in the top panel to emphasize the dependence of the Kepone concentrations on the suspended solids mechanisms. Calculated values of total Kepone, expressed in micrograms per liter, are generally within the range of the observed data, as seen in the second panel of the figure. The higher values shown for the measurement near the mouth of the James River are considered unreliable and a downstream boundary condition of 0.00  $\mu g/\ell$  was used. The dissolved and particulate fractions of the Kepone, both in  $\mu g/l$ , appear in the next panel of Figure 6-23, and, as may be seen, the majority of the Kepone in the water column is in the dissolved form. Note that the sum of the dissolved and particulate concentrations at any one location equals the total Kepone concentration plotted above. In the fourth panel of the figure, particulate Kepone, in  $\mu g/g,\ com$ pares well with data from four stations in the estuary. The final panel portrays the Kepone concentrations in the bed, in micrograms of Kepone per gram of solids, which were used to calculate the flux from the bed to the

- 120 -

#### water column.

Similar examples of calculated Kepone concentrations are shown in Figures 6-24 and 6-25 for the 4380 and 18500 cfs flow conditions, respectively. The latter figure also contains data obtained during that flow condition in May 1978 which indicates reasonable agreement between calculated and measured values in the water column. In all figures, the bed Kepone flux into the water column was equal to the product of the resuspension flux of solids corresponding to the particular flow condition - and the mass of Kepone per unit of mass of solids which was kept the same for all analyses.

## Kepone in the Bed - Constant Flow

The analysis procedure described in Section 5 is continued with the calculation of the Kepone in the sediment. The four layer time variable input model is used for various constant freshwater flow conditions. In addition to all transport, settling and kinetic coefficients previously used in the two layer model for the water column, bed coefficients are added. These include the resuspension rate, the advective coefficients for the transport sediment layer and the sedimentation rate in the stationary bed, all described previously in the section. Kepone coefficients include the bed partition coefficient, which was calculated from the solids-dependent expression used in the water column. This was equal to approximately 500 µg/kg per µg/ $\lambda$  in both the active and stationary beds due to the high solids concentrations of 50,000 and 500,000 mg/ $\lambda$ , respectively. Vertical dispersion coefficients for the dissolved Kepone fraction were stipulated between the active and stationary beds at a molecular diffusivity level of 5 x 10<sup>-4</sup>

 $^2$ /sec, whereas the diffusion of dissolved Kepone from the interstitial waters of the active bed to the lower water layer was set equal to zero. Sensitivity to this latter assumption is examined subsequently.

For the four layer run, time zero corresponds to the year 1965, just prior to the manufacture of Kepone in the Hopewell area. Thus, both water column and bed are free of Kepone and the initial conditions for Kepone are zero for all segments of the model. The estuary is then subjected to discharge of Kepone for the next ten years, until 1975 when production ceased. Lacking any historic data on this loading, it was assumed that one percent of the mass of Kepone produced was introduced into the river when it was being manufactured. As seen in Figure 6-26, production averaged less than 100,000 lb/day in 1966 and peaked in 1974 with approximately 1,000,000 lb/day of Kepone manufactured that year. A total of approximately 3,650,000 lb of Kepone was produced in the ten year period.

Kepone loading, thus, consists of a total of 36,500 pounds discharged over the ten year period, with uniform annual rates proportional to the production. As an estimate of subsequent discharge of Kepone, the loading in the last year of 1975 is assumed to decrease exponentially to zero over the subsequent five year period.

The four layer model is then run with all transport and kinetic coefficients discussed above, subjected to the time varying Kepone loading, under

- 121 -

a constant flow condition. It was decided to perform this anaysis for a range of constant flows so that results could be examined under the less complex constant transport conditions and comparisons with subsequent time varying flow runs might be made to assess the reliability of the more complex simulation.

Sample results of this computation are shown in Figure 6-27 for the 1000 cfs flow condition, ten years after the beginning of the simulation. This corresponds to the approximate time when production ceased. The spatial distributions of suspended solids and total Kepone in the water column are shown in the upper two panels. The particulate Kepone concentrations in the lower water column and bed appear in the next two panels. Comparison between the calculated profile and observations was effected by plotting the data collected during 1976, 77 and 78. The agreement between the calculation and the data is generally good, with the obvious exception in the vicinity of km 80-100, which is the region of the null-zone for the l000 cfs flow. This is a consequence of this flow being much lower than median flow in the River, thus having higher sedimentation rates than exist in the estuary on a longer term basis.

Comparisons of the particulate Kepone concentrations in the bed with observed data are shown in Figure 6-28 for the 1000, 4380 and 18,500 cfs flow conditions for bed partition coefficients of 500 and 1000. As the 1000 cfs condition overestimated the bed concentration, the higher flow of 18,500 cfs underestimates them, with the flow of 4380 cfs, close to the median flow, reproducing the bed Kepone concentrations best. It is concluded that the constant flow runs produce bed Kepone concentrations which bound the observed data in the stationary bed. The Kepone concentration in the transport layer is about an order of magnitude greater for the low flows.

#### Kepone in the Bed - Variable Flow

In this final step of the Kepone bed analysis, the actual hydrology of the James River is input to the model. The monthly average flow hydrograph of the James River above Richmond, Figure 6-29, was used to describe a sequence of constant flow conditions which would adequately represent the historical hydrology during the years that Kepone was being manufactured. Six constant flow conditions of 1000, 3200, 4380, 7044, 11500 and 18500 cfs were arranged in the sequence as shown by the solid lines in Figure 6-29. These flows were selected on the basis of available data on salinity intrusion.

As discussed previously for the constant flow condition, the computation begins with initial Kepone concentrations of zero throughout the system and the load is introduced at levels following the production. The flow condition of 1000 cfs is used for the first 30 days of the computation. During that period, all transport coefficients which correspond to the 1000 cfs flow are operating in the model together with appropriate resuspension and sedimentation rates and suspended solids boundary conditions. At the end of thirty days, the 7044 cfs flow is introduced for the next 60 days, together with its attendant transport and solids parameters. The simulation proceeds in this fashion, using one of the six flow conditions at a time for a specified duration until the run is completed. In this way, the best estimate of longer

122

term solids behavior, that is deposition or scour zones, is obtained and thus, the best estimate of the bed Kepone concentration profile results.

A comparison with the observed bed concentrations is found in Figure 6-30. The simulation was performed with two estimates of the partition coefficient - 500 and 1000. It may be noted that the stationary bed concentrations are not radically affected by this change in the partition coefficient. The profiles of Kepone concentrations in Figure 6-30 are for ten and fifteen years after production of Kepone began. Total Kepone concentrations in the water column, in  $\mu g/\ell$ , in the top panel are followed by the particulate Kepone ( $\mu g/g$ ) in the water column. The last panel of the figure contains the calculated bed Kepone concentrations together with the data obtained in the middle to later 1970's. The agreement is satisfactory, with the calculated concentration peaks located in zones where maximum concentrations were observed and the order of magnitudes of both calculated and observed values in reasonable agreement in the bed layer.

Having established a basis of computing Kepone concentrations in the water column and bed, the model may be used in a projection mode to simulate depuration periods and to estimate the residual Kepone mass in the water column and bed. For the mid 1970's, however, the mass of Kepone in the active and stationary beds amounts to between 4000 and 25000 pounds as estimated for the range of constant flow conditions from 1000 cfs to 18,500 cfs, as summarized in Table 6-6. These estimates are in the same order as other reported estimates of Kepone resident in the estuary.

#### PROJECTIONS AND SENSITIVITY ANALYSES

#### Projections

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This section describes the application of the time-variable model to projected conditions and the utility of the model in a sensitivity analysis: With respect to the former, the mass input of Kepone during production and after cessation of its manufacture has been assumed. This loading pattern is input to the time variable model for a fifteen year period - 10 years of production, followed by an exponentially decreasing input for the subsequent 5 years. The freshwater flow from the James River is also input data. The historically recorded flow data were used for the period of Kepone production and the period since its ban to the present. The flow pattern assumed from the present through the future period essentially reproduces the previous period.

The model output for the total period is shown in Figures 6-31 to 6-34, which presents the concentration of relevant Kepone variables in the water and in the bed at four locations in the estuary - in the vicinity of and downstream from the input, in the approximate location of the null zone for the median flow, in mid point of the salinity intrusion and in the vicinity of the mouth near Chesapeake Bay. The temporal pattern is similar in each case, increasing in concentration during the period of production, after which a relatively rapid decrease occurs in the bed transport layers over the subsequent year. In the deeper stationary bed, the concentration increases

- 123 -

for the first five years after the ban due to the transfer of higher concentration solids in the upper bed layers. As the concentration in layers approaches each other, the transfer into the deep bed levels off, after which a relatively slow decline sets in. ŝ.

While the order of magnitude of the concentrations in the bed is similar to measurements made in the late 1970's, the difference between the bed transport layer and the stationary layer in some cases is greater than that presently observed. Notwithstanding, the order of magnitude is correct for the entire estuary. At some locations the agreement between the model calculations and field observations is very good. Sensitivity analyses are presently being conducted, to address this point.

Any conclusions following from such projections, reported above, are dependent in varying degrees on the assigned coefficients of transport and transfer, as well as input and boundary conditions. The most critical assumption relates to the input mass of Kepone at Hopewell. The rationale for its assignment was discussed in a previous section. The Kepone concentration responds in a linear manner to any change in input load. Therefore, if subsequent investigations yield more reliable data on input, the concentrations may be directly computed by ratio.

#### Sensitivity

The mechanisms and parameters about which some uncertainty exists include the diffusion of the dissolved Kepone within the bed and between the bed and water, the concentration of solids in the transport layer of the bed, the thickness of the bed transport layer and the magnitude of the velocity of the bed transport layer. To evaluate the effects of these relevant model parameters, a series of sensitivity analyses were performed. In all analyses, the transport and kinetic coefficients of a 1000 cfs constant flow run were used, except as modified for a specific sensitivity. The bed partition coefficient was approximately 1000 for all runs and the Kepone was discharged to the River uniformly over a ten-year period. Values of specific parameters which were used in each of the seven runs, together with the selected values used throughout this report are shown in Table 6-7.

The first set is shown in Figure 6-31. In run 1, the dissolved exchange between the bed transport layer and the stationary bed was increased by an order. Changes in the bed transport layer and stationary bed are noted, due to the increased mixing between the layers, transferring more dissolved material into the upper bed layer which then partitions onto the solids. The remaining sensitivity analyses, 2 and 3, produced no significant changes. These consist of increasing the exchange of dissolved Kepone between the bed and the water column. Marked increases in this exchange, equal to or greater than the particulate exchange, produced essentially the same concentration of Kepone in the bed.

The next set of sensitivity analyses, 4, 5 and 6, in which the bed concentration was analyzed, are shown in Fig. 6-32. The concentrations of the bed solids were measured in the field survey conducted in December, 1978. These data, although not finalized at this time to the writer's knowledge,

- 124 -

indicate concentrations in the order of hundreds of thousands in the bed layer and less than this in the upper few centimeters. The assumption of 250,000 mg/& in the stationary bed appears most reasonable. The assignment of 50,000 mg/& to the moving bed layer is much more uncertain. The sensitivity analyses therefore varied the concentrations in each layer, as well as the bed thickness. In each case, only one value was changed and the remaining kept constant in order to assess most realistically the sensitivity. The 250,000 concentration produced results more in accord with the measurements. The less the bed concentration, the more quickly the system responds and the less the Kepone concentration in the transport layer.

The thickness of the bed transport layer, the most tenuous assumption of the analysis, was next investigated. The results are shown in Figure 6-33, which indicate significant changes in the transport layer and moderate changes in the stationary bed. The response time at the cessation of the input is particularly pronounced for the shallower bed transport.

Although there appears to be little doubt about the upstream movement of solids in the water or bed, it was informative to investigate the effect of changing this motion. The final sensitivity analysis is directed to this change. Bed motion was deleted so that both sediment layers were stationary, but mixing and sedimentation between the two layers was maintained. The result is shown in Figure 6-34. This surprisingly produced little difference in the transport layer, a result to be more thoroughly checked.

- 125 -

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- 126 -

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1	ABLE	6-	1. PRODUCT	ION LEV	ELS	OF KEP	ONE	FROM	ALLIED	SEMI-WORKS	PLANT
		2							Prod	uction	
			Year					kį	3	1b	
			1966					35.9	935	78,125	
			1967					47,9	990	1.05,800	
			1968					36,5	535	80,550	
			1969					46,9	990	103,600	
			1970					41,4	460	91,400	
			1971					204,8	300	451,515	
			1972					176,9	970	390,150	
			1973					100,4	435	221,425	
			1974					72,2	260	159,300	
			TOTAL					763,3	375	1,681,865	
			PRODUCTION	LEVELS	OF .	KEPONE	FRO	M LIF	E SCIE	NCE PLANT	
		•							Prod	uction	
			Year					kį	3	15	
			1974					385	,370	849,600	
			1975					384	,020	846,625	

TOTAL

- 127 -

769,390 1,696,225

NO.	DATE	NOTES	REFERENCE
1	August, 1975	Water & Bed	Dec. '75 USEPA Re- search Team
2	1976-77	Water Grab Samples & Sedi- ment Cores	Commonwealth of Vir- ginia, State Water Control Board
3	Dec. 1976 Mar. 1977 July 1977 Nov. 1977	Bed Surface & some cores	VIMS - Nichols
4	June 1977	Water & Bed	Batelle
5	Aug. 1977	Water & Bed Intratidal	VIMS - Huggett
6	April-May 1978	Water & Bed Intratidal	VIMS - Huggett
7	Dec. 1978	Bed-Cores Total Water & Bed	VIMS - Nichols State Water Advis- ory Board

TABLE 6-2. SURVEY DATA

- 128 -

	FLOW (CFS)						
Flow	James	Appomattox	Chickahominy	Downstream Circu	Downstream Net Tidal Circulation		
Pattern	River	River	River	Top*	Bottom		
1	1.000	152	56	41600	40400		
2	3200	495	182	43380	39500		
3	4380	657	263	73300	68000		
4	7044	1334	407	74790	66000		
5	11500	1770	651	89920	76000		
6	18500	2775	1110	126400	104000		

TABLE 6-3. SUMMARY CHARACTERISTICS OF SELECTED FLOWS

<sup>1</sup> Top Layer flows into Chesapeake Bay

 $^2$  Bottom Layer is in the landward direction

# - 129 -

Flow (cfs)	Location (KP)	Horizontal Y	Jelocity <sup>(1)</sup> (cfs) Bottom	Vertical Velocity (ft/day)	Eddy Viscosity (cm <sup>2</sup> /sec)	Vertical Dispersion Coefficient (cm <sup>2</sup> /sec)
1000	100	0.07	-0.05	0.9	6.5	2.2
	70	0.08	-0.06	0.5	7.5	2.3
	40	0.05	-0.11	0.4	8.8	3.0
	10	0.18	-0.12	3.5	10	5.8
3200	100	0.05	0.05	-	_	2.2
	70	0.08	-0.02	0.9	20	2.3
	40	0.07	-0.12	1.1	12	3.0
	10	0.20	-0.12	3.1	26	5.8
4380	100	0.07	0.07	-	-	2.2
	70	0.04	0.04			2.3
	40	0.09	-0.16	2.8		3.0
	10	0.31	-0.19	5,4	-	5.8
7044	100	0.12	0.12	-	-	2.2
	70	0.06	0.06	-	-	2.3
	40	0.11	-0.15	2.4	_	3.0
	10	0.34	-0.19	6.2	-	5.8
11500	100	0.19	0.19		-	2.2
	70	0.10	0.10			2.3
	40	0.13	-0.12	2.1	9	3.0
	10	0.38	-0.19	6.9	22	5.8
18500	100	0.30	0.30		-	4.0
	70	0.16	0.16	-		4.0
	40	0.09	0.09	2.8	6	4.0
	10	0.50	-0.24	8.2	29	6.0

TABLE 6-4. SUMMARY OF CIRCULATION PARAMETERS FOR SELECTED FLOWS

(1) + seaward, - landward

- 130 -

TABLE 6-5. CHARACTERISTIC SOLIDS PARAMETERS

Settling Velocity = 4 ft/day, all water column segments, all flows 1.

- Active Bed Layer 2.
  - A. Depth = 10 cm
  - в.
  - Solids Concentration = 50,000 mg/ &Horizontal Velocity = 0.01 x lower water layer net velocity с.
- 3. Stationary Bed Layer

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- Α.
- Depth = 30 cm Solids Concentration = 500,000 mg/l в.
- Suspended Solids Concentrations at the Boundaries and in Tributaries 4.

Flow (cfs)	Upstrea (1	am Boundary ng/l)	Downstream Boundary (mg/l)	Tributaries (mg/l)
	top	bottom		
100D	20	20	20	20
3200	20	20	22	22
4380	20	25	26	26
7044	20	30	30	30
11500	35	40	40	40
18500	50	50	50	50

- 131 -

	TABLE 6-6.	ESTIMATED KEPONE MASS	IN JAMES RIVER BED	
Flow (cfs)		Pounds of Kepone Pre $f = 500 + \frac{63700}{m.96}$	esently in James River Bed $\P = 1000 + \frac{127400}{0.96}$	
1000		17000	25000	
4380		9000	12000	
7044		5600	7200	
18500		4300	6300	
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- 132 -

Analysis Number	Bed Diffusion <sup>(1)</sup> cm <sup>2</sup> /sec	Bed-Water Diffusion D 2,3	Transport Bed Solids Conc (mg/l)	Transport Bed Thickness (cm)	Transport Bed Velocity	Fig. No.
1	$5 \times 10^{-3}$	0	50,000	10	0.01 U <sub>2</sub> <sup>(3</sup>	) <sub>6-31</sub>
2	$5 \times 10^{-4}$	wu <sup>(2)</sup>	50,000	10	0.01 U <sub>2</sub>	6-31
3	$5 \times 10^{-4}$	10 w_u	50,000	10	0.01 U <sub>2</sub>	6-31
4	$5 \times 10^{-4}$	0	250,000	10	0.01 U <sub>2</sub>	6-32
5	$5 \times 10^{-4}$	0	10,000	10	0.01 U <sub>2</sub>	6-32
6	$5 \times 10^{-4}$	0	50,000	1	0.01 U <sub>2</sub>	6-33
7	$5 \times 10^{-4}$	0	50,000	10	0	6-34
ORIGINAL	$-5 \times 10^{-4}$	0	50,000	10	0.01 U <sub>2</sub>	

TABLE 6-7. MODEL PARAMETERS FOR SENSITIVITY ANALYSES

(1) diffusion of dissolved Kepone

(2) same as particulate resuspension

(3)  $U_2 = 1$  ower water layer net velocity

# - 133 -



- 134 -




JAMES RIVER STUDY AREA

FIGURE 6-3

- 136 -





- 138





- 140 -



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## SECTION 7

## CONCLUSIONS AND RECOMMENDATIONS

The distribution of an organic chemical in an estuary is defined by a model, which includes the water column and bed of both the saline and nonsaline regions. The transport regime is based on the tidally averaged twodimensional hydrodynamic analysis which describes the characteristic estuarine circulation of landward flow in the bottom layer and seaward flow in the upper. Mixing between the main channel and lateral embayments is incorporated. The bed is composed of a transport layer which interacts with a deeper stationary zone and the overlying water. The salinity intrusion is used for calibrating and validating the fluid transport, consisting of horizontal and vertical velocities and vertical dispersion. The distribution of suspended solids is defined by adding the settling velocity to the above transport regime with the appropriate flux condition at the water-bed interface, which may be either negative (settling) or positive (scour). A mass balance of the bed solids allowing for transport, settling, entrainment, and compaction is the basis of the bed model. The net sedimentation velocity is the calibrating variable for the solids.

Having established the fluid and bed transport regimes and the distributions of the suspended and bed solids, the adsorption-desorption kinetics are assigned to define the dissolved and particulate components of the organic chemical. The "instantaneous" equilibrium condition which appears to be a valid assumption for many cases, simplifies the analysis and computations. Although not included in the Kepone analysis of the James River, the relevant reaction and transfer terms may be added to the present model structure for general application to other chemicals and estuaries. Given the coefficients which describe the above Processes, the model computes the spatial and temporal distributions of both the dissolved and particulate components of an organic chemical in the water and the bed. Either steady-state or time variable modes under tidally averaged conditions may be addressed, each having particular functions and applications.

A procedure of analysis to address the problem of organic chemicals in estuaries has been structured and applied to the Kepone distribution in the James River. The procedure involves a series of analytical and computational steps, relating to the fluid transport, the solids distribution and the concentrations of the organic chemical in the water and the bed. Each step involves the determination or assignment of the appropriate transport transfer and/or reaction coefficients to analyze a particular constituent of the system. Equally important, each step provides the input for the computation of the next element, for which an additional coefficient is required. The analysis proceeds in a sequence of increasing complexity, each element yielding a calibration or validation of an essential constituent. The final

- 168 -

output is the temporal or spatial distribution of the organic chemical, which provides the necessary information for waste load allocation procedures. Alternately, the output establishes the ambient levels for a food-chain model. It is emphasized that, in the opinion of the authors, the contributions of this project lie not only in the structure of the model but also in the recommended procedure of analysis.

The model has been structured to account for all the relevant factors which affect the concentration of an organic chemical in an estuarine environment. It is capable of reproducing prototype observations in varying degrees as demonstrated in its application to the James River. Based on this work, it may be concluded that the present model is a realistic portrayal of the significant phenomena relating to the transport, salinity, solids and chemical. With respect to Kepone in the James River, one conclusion may tentatively be drawn: the deeper bed sediment will require an extensive period, in the order of decades, to diminish in Kepone concentration. By contrast, the upper transport bed layer decreases relatively rapidly in less than a decade. This finding, furthermore, indicates that the bed sediment should be more finely segmented over various depths to minimize the vertical gradients which appeared in these projections. This step will also yield greater accuracy of the numerical computation, particularly with respect to sedimentation and interstitial diffusion.

The most pressing need for model validation of the Kepone distribution in the James is field data on the dissolved component of the chemical. The ambient concentrations are presently less than the capability of available analytical techniques. To date, no reliable information on this component exists. However, there has recently been developed an analytical procedure which permits accurate measurements of concentrations in the range of estimated present levels. Detailed data on both components and the various forms of solids in the water and the bed should be collected at one or two stations over the tidal cycle. Such data will provide the necessary information for a total mass balance and for model validation.

The model contains the coefficients quantifying the flux of the various constituents and as such, there are degrees of freedom, increasing in number as the analysis increases in complexity - i.e., more coefficients than state variables. With respect to the salinity and the suspended solids, there are essentially no degrees of freedom, assuming the vertical dispersion and the settling velocities are known, at least within limited ranges. With respect to the bed solids and the organic chemical, the additional parameters and coefficients to be assigned exceed the state variables - which can be measured or which can be calculated a priori, given the present state of knowledge. As indicated above, data on the dissolved component of the Kepone in the James is the most significant need at the present time. This information would eliminate one degree of freedom and reduce the range of the assignable coefficients. It would also provide closure for the mass balance computations and a necessary element for model validation. Notwithstanding, it can be stated that these parameters may be assigned at least within an order of magnitude. Therefore, sensitivity analyses may be conducted to determine the significance of the boundary and initial conditions, as well as the flux, about which there are varying degrees of uncertainty.

- 169 -
In summary, the following are conclusions based on the work done in this project:

- 1. A model of the distribution of an organic chemical in the water column and bed of an estuarine system has been developed which includes both the saline and non-saline regions.
- 2. A procedure of analysis is presented which is an integral part of the calibration-validation process. It consists of a series of analytical and computational steps relating sequentially to the fluid transport, solids distributions and concentration of organic chemicals.
- 3. In its present state of development, the model is characterized by a few degrees of freedom in the bed segments, due to limited knowledge of the phenomena and minimum field and laboratory data.
- 4. In spite of this limitation, the model may be used, with appropriate sensitivity analyses, to assess existing contamination, to estimate removal times, to provide a basis for waste load allocations and to provide input for a food chain analysis.

It is strongly recommended that additional data on Kepone in the James Estuary and, more important, organic chemicals in other estuaries be gathered for further model calibration and validation. Historically, water quality models have required varying degrees of validation, depending on the significance of the problem and the complexity of the analysis. In view of the fact that the question of organic chemicals in natural water systems is highly significant and that the analysis is particularly complex in estuaries, this recommendation has the greatest priority and should be implemented throughout the country in applied research and development-application projects.

Specifically the following elements should be studied in further detail. They are subdivided in the three general categories of inputs, bed characteristics and kinetics of organic chemicals.

#### 1. Inputs

Specific attention must be directed to a better assessment of input load determination from both point and non-point sources. This comment applies to both suspended solids (clays, silts, sands) and the dissolved and particulate components of the organic chemical. It is undoubtedly the area of greatest uncertainty in the James River analysis, a situation which is not uncommon in other estuarine systems. Downstream boundary conditions in the lower estuarine layer, indicative of input from the ocean or larger bays, are included in this category.

#### 2. Bed Characteristics

Limited experimental and field data are available on scour and entrainment of cohesive sediments in estuarine systems. In addition, the bed characteristics associated with these processes, such as thickness and velocity of transport layers, compaction and compressibility of recent and long-term sediments have been little studied.

- 170 -

The tidally averaged concentration, addressed in the model presented herein, should be studied in greater detail. Specifically, an intratidal model should be developed to calibrate the time variation of solids and organic chemicals over the tidal cycle, from which the average value may be computed and the method of averaging field data established.

## 3. Organic Chemical Reactions

Much work has been done on the kinetic and transfer processes of various organic chemicals and expressed in forms amenable to incorporation in the present model framework: evaporative fluxes, kinetic transformations through oxidation-reduction, hydrolysis and photolysis and microbial degradation. The computational program should be expanded to include these kinetic and transfer routes in conjunction with further field and laboratory studies. Work, presently underway, is addressing some of these questions. Specifically the kinetic and transfer routines are being programmed and further analysis of the evaporative transfer is being conducted.

- 171 -

## APPENDIX

The following papers were prepared under this project:

- The Effect of Concentration of Adsorbing Solids on the Partition Coefficient; O'Connor, D.J. and Connolly, J.P.; Water Research, Vol. 14, pp. 1517-1523, Oct. 1980.
- Suspended Solids Analysis of Estuarine Systems; O'Connor, D.J. and Lung, W.S; Jnl EED, Proceedings ASCE; Jan. 1981.
- Steady-State Analysis of Organic Chemicals and Heavy Metals in Reservoirs and Lakes; O'Connor, D.J. and Schnoor, J.L.; Submitted to Environmental Science and Technology for publication.
- 4. The Effect of Winds on the Gas-Liquid Transfer Coefficient; O'Connor, D.J.

- 172 -

THE EFFECT OF CONCENTRATION OF ADSORBING SOLIDS ON THE PARTITION COEFFICIENT

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## ABSTRACT

The results of a number of laboratory studies are presented to demonstrate an inverse relationship between concentration of adsorbing solids and partition coefficient. Various functional forms which define the relation are developed and correlated with the data. A power-law dependence of partition coefficient on concentration of solids is shown. The significance of this relationship in assessing the fate of hydrophobic pollutants in natural water systems is discussed.

## INTRODUCTION

The distribution of heavy metals and organic chemicals in natural water systems is greatly influenced by the interaction between the dissolved and particulate components. This interaction may be due to a number of physiochemical factors, among which adsorption-desorption is one of the most significant. The nature and concentration of the adsorbing solids determine, in large measure, the rates of these reactions and the resulting equilibrium conditions. The equilibrium condition defines the ratio between the solid-phase and dissolved concentrations, which is referred to as the partition coefficient. This coefficient is a function of various characteristics of the adsorbate and adsorbent. The purpose of this paper is to indicate the effect of the concentration of adsorbing solids on the partition coefficient and to develop various functional forms to define the relationship.

## THEORETICAL CONSIDERATIONS

Solids in natural systems consist of inorganic and organic species: the latter may be categorized by detrital and viable components, whereas the former is usually classified by size and chemical composition, clays, silts and sands. Each type of solid has an adsorptive capacity,  $\underline{q}_c$ , that is the ratio of the mass of adsorbate to the unit mass of adsorbent. The total capacity is there-fore  $\underline{q}_c\underline{m}$ , in which  $\underline{m}$  equals the concentration of adsorbing solid. The rate of adsorption is assumed to be proportional to the dissolved concentration of the constituent and the difference between the capacity,  $\underline{q}_c\underline{m}$ , and the amount adsorbed,  $\underline{q}\underline{m}$ . The rate of desorption is proportional to the concentration of the absorbed mass,  $\underline{q}\underline{m}$ , thus the kinetic equation may be written:

$$\frac{dc}{dt} = -K_0 mc (q_c - q) + K_2 qm$$
(1)

At equilibrium, equation (1) reduces to

$$= \frac{q_c c}{\frac{1}{b} + c}$$
(2)

in which

$$b = \frac{K_0}{K_2}$$

q

The coefficient,  $\underline{b}$ , is related to the energy of adsorption. Equation (2) is the Langmuir isotherm, originally derived for the adsorption of gases by solids.

In natural systems, the adsorptive capacity of the solids,  $\underline{q}_c$ , is invariably an order of magnitude greater than the solid phase concentration,  $\underline{q}$ , and, in many cases, many orders of magnitude greater. Under this condition, equation (2) reduces to

$$q = bq_c c$$

or

$$\frac{q}{c} = bq_c = 1$$

in which I = partition coefficient.

The partition coefficient is the ratio of the solid phase to the dissolved concentration in the linear portion of the Langmuir isotherm. The magnitude of this coefficient depends on the characteristics of the adsorbate and the adsorbing solids. In general, it varies inversely with the solubility of the adsorbate and directly with the organic and clay fractions of the solids.

Experimental data that do not conform to the Langmuir equation may, in many instances, be fitted by the empirical relation,

$$q = Kc^{1/n}$$

where <u>K</u> and <u>n</u> are constants. Equation (4) is the Freundlich isotherm. For  $\underline{n} = 1$ , it is identical to the linear portion of the Langmuir isotherm, the exponent,  $\underline{1/n}$ , usually being  $\leq 1$ .

## REVIEW OF PREVIOUS WORK

Many laboratory studies on adsorption to soils, sediment and suspended solids have focused on equilibrium behavior, in accordance with the various isotherms described above. The linear relationship has been observed in numerous adsorption studies (e.g., Lambert et al., 1965; Haque et al., 1968;

(4)

(3)

Garnas et al., 1978; Karickhoff et al., 1979), and is the most frequently employed isotherm for describing pesticide adsorption in soils and sediments (Hamaker and Thompson, 1972; Pionke and Chesters, 1973). Hamaker and Thompson (1972), who summarized available data for the Freundlich isotherm of chemicals in soil, have shown that the exponent 1/n varies from about 0.7 to 1.0. Lotse et al. (1968), studying adsorption of lindane to lake sediment, found the data to fit a Freundlich isotherm with the exponent ranging from 0.75 to 0.92. Suzuki et al. (1979) found sorption of cadmium to sediment of the Tama River in Japan to follow a Freundlich isotherm with an exponent of about 0.76.

In a series of studies (Reynolds and Gloyna, 1963; Yousef and Gloyna, 1964; Bhagat and Gloyna, 1965), the distributions of radioactive substances in Texas rivers and lakes were investigated. Strontium, cobalt, and ruthenium were among the metals studied. In all cases, the authors noted a decrease in partition coefficient with increasing concentration of sediment, but no corresponding effect as the initial metal concentration was changed. Cox (1970) has reported the partition coefficient for DDT and phytoplankton in a natural environment to be inversely related to phytoplankton density. Using an inverse linear relationship between partition coefficient and concentration of solids, O'Connor and Leahy (1978) modeled the spatial distribution of manganese in Narragansett Bay. The results compared favorably with the observed values of both the dissolved and particulate forms.

The effect of organic matter content and clay content on the extent of adsorption is well-documented (e.g., Lambert et al., 1965; Lambert, 1968; Lotse et al., 1968; Choi and Chen, 1976; Karickhoff et al., 1979). Increased adsorption with increasing clay or organic matter content is due to the high cation exchange capacity and high specific surface area of these materials. Lambert et al. (1965), Lambert (1968), and Karickhoff et al. (1979) have found the partition coefficient to be linearly related to organic matter content. Soluble organics and colloidal particles are also important to sorption equilibrium. Using UV light absorption to distinguish free and sorbed paraquat, Karickhoff and Brown (1979) found that centrifuging at 20,000 rpm for one hour failed to remove all sorbed paraquat from the water column. In fact, most of the paraquat that remained in the water phase was in the sorbed form. Duursma (1970) found that the addition of soluble amino-acids lowered the sorption of Co and Zn to sediment. Thus, because of the importance of soluble organics and colloidal particles, isotherm studies that use standard phase separation techniques may yield erroneous partitioning values. Centrifugation or filtration is normally used to separate the sediment and water. The compound that remains in the water is assumed to be free and the sorbed compound is computed by difference from the total compound added to the system. Hence, compound sorbed to soluble and colloidal substances not removed by normal phase separation techniques would be incorrectly reported as free compound.

## ANALYSIS OF DATA

The primary purpose of this paper is to demonstrate the variation of the partition coefficient with the concentration of suspended solids. It is evident that the nature and characteristics of the adsorbing solids are significant factors in this regard, i.e., the greater capacity of organic matter and the clay fraction to adsorb by contrast to the sands and gravels. It is pertinent to review first the effect of the type of solid as preface to the effect of concentration.

Effect of Various Types of Solids

A typical example is found in data of Garnas et al. (1978), which presents the equilibrium between solid-phase concentration and dissolved concentration of Kepone for various types of solids (Figure 1). The slope of one on the logarithmic coordinates is an indication of the appropriateness of the linear portion of the Langmuir isotherm in the region in which the adsorptive capacity,  $\underline{q_c}$ , is much greater than the solid phase concentration,  $\underline{q}$  (equation 3). The influence of the type of adsorbing solids is apparent: the highest partitioning occurring with sediment from Range Point Salt Marsh off Santa Rosa Sound, Florida, which is primarily clay with a high percentage of organic matter.

As the organic content decreases, the partition coefficient decreases, the lowest values being associated with material that is primarily sand. The effect of the organic fraction is presented in Figure 2. Although each point represents a different sediment, and, therefore, varying fractions and types of clays, the general trend of increasing partitioning with increasing organic content is evident.

Effect of Solids Concentration

For each solids type shown in Figure 1 the concentration of the absorbing solids was held constant for the range of Kepone concentration. For a given type of solids, the effect of varying its concentration on the partition coefficient is shown in Figure 3, which presents the dissolved and solid phase distribution of Kepone for two solid concentrations viz. 100 and 1000 mg/ $\ell$  (Connolly, unpublished data). Again, the linearity indicates the validity of the Langmuir isotherm and their displacement the difference in partition coefficient viz. 5900 and 3400 due to the varying solids concentration. Similar analyses of data on other substances indicated the same general trend of decreasing partition coefficient with increasing concentration of solids. Although comparable data on all the substances reported in this paper were not available, the fact that the dissolved and solid phase concentrations were relatively low supports the assumption of linearity. The dependence of the partition coefficient of various constituents on the concentration of solids is shown in Figure 4. Since the purpose of this figure is simply to indicate the

spectrum of the general relationships, the lines of correlation are sketched by eye. These data, representative of more extensive sets, include heavy metals, radioactive substances and organic chemicals. The range of solids concentration (10 to 10,000 mg/ $\ell$ ) covers values for solids in suspension in rivers and estuaries up to values for solids representative of the lower limit encountered in the beds of natural water systems.

The solids effect is most pronounced for constituents characterized by large partitioning, e.g., DDT & radioactive cobalt. For constituents that are represented by intermediate partitioning, the effect of solids concentration is less pronounced and the coefficient approaches a constant value for substances of low partitioning - e.g., strontium.

Data Correlation

A functional form that correlates the data presented in Figure 3 is:

$$\mathbb{I} = \mathbb{I}_{\infty} + \frac{\beta}{m_{\rm O} + m^{\alpha}} \tag{5}$$

 ${\tt I}_\infty$  = limiting partition coefficient at high concentration of solids  ${\tt m} = {\tt concentration} \ {\tt of} \ {\tt solids}$ 

 $m_{o}, \alpha, \beta$  = empirical coefficients

The coefficient,  $\underline{\beta}$ , reflects the relative influence of the solids effect by contrast to the lower limiting value,  $\mathbb{I}_{\infty}$ . The coefficient,  $\underline{m}_{\Omega}$ , allows for the observational fact that, in a few cases, an upper limiting value of the partitioning is approached as the solids concentration decreases. Where a leveling off at low concentration of solids is not evident, the relationship is more appropriately expressed as

$$I = \P_{\infty} + \frac{\beta}{m^{\alpha}}$$

The linearity of many of the data sets also indicates that the limiting value,  $\mathbb{1}_{\infty}$ , is substantially zero, at least over the range of solids reported.

(6)

 $1 = \frac{\beta}{m^{\alpha}}$ 

As is shown in the following sections, equation (7) fits the majority of the data as well as does equation (6). However, this may be due to the limited range of solids concentrations (10-10,000 mg/ $\ell$ ) for which values of the partition coefficient are available. At high concentrations ( $\sim$  500,000 mg/ $\ell$ , approximately an average value for bed sediments), a limiting value may be more representative. Equation (6), therefore, is considered to be a more valid, albeit empirical, relationship.

The derived coefficients, determined by least squares, are presented in Table 1. Correlations for organic chemicals are presented in Figures 5 and 6; for radioactive substances, Figure 7a; and for heavy metals, Figure 7b. These graphs and the information in Table I show that different compounds adsorbing to the same solids have similar concentration dependences (i.e., similar slopes). This is seen for DDT, heptachlor and dieldrin adsorbing to kaolinite, illite and, with the exception of heptachlor, montmorillonite. Cobalt and ruthenium, adsorbing to Lake Austin sediment have comparable slopes, as do Dimilin and Kepone adsorbing to Range Point sediment and the heavy metals adsorbing to digested sludge. This observation is, in general, not characteristic of single compounds adsorbing to different solids types. For example, the concentration of solids dependence for Kepone adsorbing to James River sediment is much different from that for Kepone adsorbing to Range Point saltmarsh sediment.

It may be inferred from this observation that solids concentration dependent partitioning is a function of the solids, not the compound. A solid-solid interaction may be mediating the adsorption process, resulting in a lowering of

(7)

the partition coefficient with increasing solids concentration. As noted earlier, the general trend is an increasing level of dependence on concentration of solids with increasing degree of adsorption. Although this may reflect a compound-related effect, it appears that for compounds with the same range of adsorption order the effect of solids-type controls.

#### SIGNIFICANCE IN NATURAL WATER SYSTEMS

The relationships, presented above, have numerous implications with respect to the distribution of heavy metals and organic chemicals in natural systems. For constituents that achieve equilibrium rapidly with the suspended and bed solids, the application of the principle is particularly significant.

Consider those problem areas, where such constituents have been discharged for some period of time in the past, e.g., Kepone in the James River and PCB in the Hudson River. How much time is required to flush them from the system? The relationship reported here implies that the period required is greater than that for a constant-partition condition. This assessment is based on the following reasoning. The material is now concentrated in the bed. When scoured, the contaminated solids are transported vertically into the flowing waters, diluting the concentration by at least one and, more likely, two or three orders of magnitude. Assuming equilibrium is achieved rapidly, these solids accumulate more of the metal or chemical, due to the increase in partitioning. Upon subsequent settling, the solids re-establish the previous equilibrium by releasing dissolved material to the interstitial waters. The subsequent diffusion of the dissolved material is a relatively slow process, thus retaining the constituent in the system longer than if it remained in the flowing waters.

The extent to which conversion between the particulate and dissolved state occurs depends on the rates of adsorption and desorption and on the solids concentrations in the bed and in suspension. For many chemicals and metals, the kinetic rates are relatively rapid (in the order of minutes); for others, the kinetic time scales are of the order of hours and, in some cases, days. The net flux is determined by the kinetic rates and the supply of fresh solids in conjunction with the average residence time in the bed and in the flowing suspension.

## CONCLUSION

A functional correlation between the partition coefficient and the concentration of adsorbing solids has been presented as indicating an inverse relationship. Although there is now no fundamental basis for the correlation, a vast amount of experimental data is available to substantiate its validity. In view of the heterogeneity of suspended and bed sediments and variations in experimental conditions, controlled and standardized laboratory evaluation of partition coefficients are recommended. The implications to the distribution and retention of heavy metals and organic chemicals in natural water systems are significant and indicate a tendency to greater retention in these systems than would be the case for a constant partition coefficient. Further work is being directed to a more fundamental understanding of the phenomenon and to the quantitative assessment of this effect in prototype systems.

## ACKNOWLEDGEMENT

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# Table 1. Regression of Partition Coefficients on Concentration of Solids

System		No. of				2
Sorbate	Sorbent	Data Pts	mo	β	α	r *
_				5		
Heptachlor	Illite	7	0	$1.03 \times 10_{5}$	0.75	.961 <sup>a</sup>
Heptachlor	Kaolinite	7	0	$3.98 \times 10^{\circ}_{L}$	0.80	.997 <sup>a</sup>
Heptachlor	Montmorillonite	7	0	7.41x105	0.57	.967a
DDT	Illite	7	0	$1.80 \times 10_{5}$	0.52	.993ª
DDT	Kaolinite	7	0	7.20x105	0.83	.991ª
DDT	Montmorillonite	7	0	$9.41 \times 10$	0.69	.986 <sup>a</sup>
Dieldrin	Illite	7	0	2.63x10	0.67	.980ª
Dieldrin	Kaolinite	7	0	$8.44 \times 10^{-7}$	0.81	.997 <sup>a</sup>
Dieldrin	Montmorillonite	6	0	1.79x103	0.92	.996a
PCB	Woodburn Soil	5	0	5.50x10	0.24	.954 <sup>b</sup>
PCB	Illite	3	0 6	1.30x10	0.19	.997 <sup>b</sup>
Lindane	Lake Sediment	7	2.48x10	1.14x10 <sup>°</sup>	1.25	c
Dimilin	Range Point	4	0 .	7.60x10 .	0.34	•926 <sup>d</sup>
Cobalt	Lake Austin	. 6	0	$3.60 \times 10^{2}$	0.47	.983e
Ruthenium	Lake Austin	6	0 2	$1.80 \times 10^{5}$	0.55	.964f
Strontium	Lake Austin	7	5.82x10	$1.41 \times 10^{2}$	0.812	g
Cadmium	Digested Sludge	3	0	$5.70 \times 10^{3}_{5}$	0.585	.996h
Manganese	Digested Sludge	3	0	9.59x10	0.870	.998h
Nickel	Digested Sludge	3	0	$6.39 \times 10^{4}$	0.546	.991h
Copper	Digested Sludge	3	0	1.25x10	0,546	.918 <sup>h</sup>
Calcium	River Clay	5	0	$5.59 \times 10^{3}$	0.31	.943i
				······		

System		No. oi	•				
Sorbate	Sorbent	Data Pts	¶∞	<u></u> o	β	α	r <sup>2</sup> *
Kepone Kepone	James River Range Point	13 11	1000 300	0 0	$2.59 \times 10^{5}$ $2.69 \times 10^{4}$	1.20 0.34	.877j .911j

\* From regression of linearized equation

Bhagat and Gloyna (1903) <sup>g</sup> Reynolds and Gloyna (1963) <sup>h</sup> Rohatgi and Chen (1975) <sup>i</sup> Garder and Skulberg (1964) <sup>j</sup> Connolly (unpublished) USEPA, Gulf Breeze, FL













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SUSPENDED SOLIDS ANALYSIS OF ESTUARINE SYSTEMS By Donald J. O'Connor<sup>1</sup>, M. ASCE and WuSeng Lung<sup>2</sup>

INTRODUCTION

The concentration of suspended solids influences the quality of natural water systems in various ways. It is not only an important water quality variable in itself, but also because of interaction with other constituents. Suspended solids, affect the transmission of light and, thus, the growth of phytoplankton and other plants. They provide sites for the growth of micro-organisms which impact water quality. They adsorb heavy metals and pesticides and thereby influence the concentration of these substances both in the bed and in suspension. In estuaries, suspended solids are particularly significant because of the characteristic circulation pattern which increases the retention of solids in these systems and produces the phenomenon of turbidity maximum. It is the purpose of this paper to present an analysis of the spatial distribution of suspended solids in estuaries under steady state conditions and to demonstrate applications of the analysis for the Sacramento, James River and Rappahannock Estuaries.

The differential equation defining the longitudinal and vertical transport of suspended solids is first presented. Terms included are the horizontal and vertical fluid velocities, the vertical dispersion

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and the settling velocity of the solids. This is followed by a description of a simplified approach to calculate the net tidally averaged horizontal velocities in the saline zone of the estuary. The estuary is segmented into an upper and lower layer, in accordance with the plane of no net horizontal motion, as determined by the velocity calculations. The circulation pattern is characterized by a landward velocity in the lower layer and a seaward velocity in the upper layer in balance with a vertical motion to maintain hydraulic continuity. These velocities, with the associated vertical dispersion coefficient, are used to calculate the salinity distribution in each layer to confirm the estuarine transport pattern. The settling velocities of the suspended solids determined from field measurements and laboratory tests are then introduced into the transport equation and the spatial distribution of suspended solids in each layer is computed.

Comparisons of the calculated profiles and observations from the Sacramento-San Joaquin Delta, James River and Rappahannock Estuaries provide reasonable validations of the overall approach. The approach described in this paper was originally developed in order to provide a basis for evaluating water quality conditions from various operational plans of the Sacramento-San Joaquin Delta. The results were originally reported in 1975 to the California Department of Water Resources (22), one of the major agencies concerned with the management of water supply

- 2

for that region. The approach was further developed and applied to the distribution of the suspended solids in James River Estuary, an important component in the analysis of Kepone distribution in that system (24).

## REVIEW OF PREVIOUS WORK

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The temporal and spatial distribution of suspended solids has received increased attention by engineers and scientists in many parts of the world over the past few decades (2,3,9,14,15,19,20,21,28,31). Sediment sources both from upstream freshwater flow and from downstream marine origin, in conjunction with the typical estuarine circulation, produce a spatial distribution of suspended solids which is characterized, in the vicinity of the salinity intrusion limit, by a peak concentration higher than that of either the river or ocean. This phenomenon, usually referred to as the "turbidity maximum," decreases with decreasing river flow and is frequently washed out under relatively high flow conditions.

A turbidity maximum has been observed in many estuaries (14,15,19, 20,21, 28,29,31) and also has been analyzed theoretically in varying degrees (12,23,27). One of the early analyses of the suspended solids distribution was presented by Odd and Owen for the Thames (25,27). They formulated a two-layer model with a rectangular section to simulate the tidal flow and transport of mud. Festa and Hansen (12) developed a steady state two-dimensional suspended sediment model which was based on

- 3 -

their earlier circulation analysis (11) to investigate the presence of the turbidity maximum in partially mixed estuaries. Although no attempt was made to model any particular estuary, the results presented qualitatively describe the behavior of the turbidity maximum for a range of estuarine dynamics.

The distribution of suspended solids is highly dependent on the circulation in the estuary. The typical pattern in partially mixed estuaries was first observed and reported by Pritchard (30). Subsequently, a number of hydrodynamic analyses designed to quantify the circulation pattern has been published. Among them are simplified analytical frameworks (13,23,26). The rapid development of computer hardware and numerical solution techniques has enabled use of complex hydrodynamic models (1,4,5,6,7,8,11,16,17,32). The approach taken in this paper follows the work of these investigators and presents a practical engineering method to analyze this type of estuarine circulation and the associated suspended solids distribution.

## FRAMEWORK OF ANALYSIS

The mass transport equation for suspended solids in two-dimensional estuaries on a tidally averaged basis may be written as:

$$\frac{\partial (uS)}{\partial x} + \frac{\partial (v+v_s)S}{\partial y} + \frac{\partial}{\partial x} (u_t S_t) = \frac{\partial}{\partial y} (\xi \frac{\partial S}{\partial y})$$

(1)

in which S = concentration of suspended solids, u and v = horizontal and vertical velocities, respectively;  $v_s$  = settling velocity of suspended particles;  $\xi$  = vertical eddy diffusion coefficient; and  $u_t$  and  $S_t$  = tidal components of horizontal velocity and suspended solids concentration, respectively. The coordinate system is shown in Figure 1, in which the longitudinal x-axis is positive toward the ocean and the vertical y-axis is positive toward the bed of the channel. Longitudinal turbulent diffusion is neglected because its effect is relatively insignificant compared to the terms in Eq. 1.

The saline portion of the estuary is divided into two vertical layers with the interface at the plane of no net motion, the vertical location at which the horizontal velocity is zero. After vertical averaging, Eq. 1 becomes:

 $\frac{\partial}{\partial x}(\bar{u}\bar{S}) + \frac{\partial}{\partial x}(\bar{u}_{t}\bar{S}_{t}) + \frac{\partial}{\partial x}(\bar{u}'\bar{S}') + \frac{\partial}{\partial y}[(v+v_{s})\bar{S}]_{o} - \frac{\partial}{\partial y}(\xi\frac{\partial\bar{S}}{\partial y})_{o} = 0$ 

for each layer. The terms  $\overline{\mathbf{u}}$  and  $\overline{\mathbf{S}}$  are layer averages of the velocity

- 5

(2)

and solids, respectively, such that:

 $u = \overline{u} + u'$ and  $S = \overline{S} + S'$  where u' and S' are deviations from the mean values in each layer. The subscript 'o' in the last two terms of Eq. 2 represents the plane of no net motion.

Each term in Eq. 2 represents a distinct transport mechanism. The first term,  $\overline{uS}$ , defines the contribution to the flux of suspended solids by the advective flow in each layer. The second term,  $\overline{u_tS_t}$ , is referred to as tidal diffusion. The third term,  $\overline{u'S'}$ , arises from the layeraveraging process and represents the shear effect in each layer. In the region of the estuaries investigated in this paper, the net effect of tidal diffusion and shear effect is not significant. They are briefly discussed for completeness and for their potential importance in other applications. The last two terms in Eq. 2 are the vertical advective and dispersive fluxes of suspended solids across the plane of no net motion.

The final equation of suspended solids applicable to each layer of a two-dimensional estuary is:

$$\frac{\partial}{\partial x} (\bar{u}\bar{S}) + \frac{\partial}{\partial y} [(v + v_{s})\bar{S}]_{o} = \frac{\partial}{\partial y} (\xi \frac{\partial \bar{S}}{\partial y})_{o}$$
(3)

The solution is based on a finite difference approximation of Eq. 3. A central difference scheme is used in the numerical calculation. The estuarine system is divided into 2 vertical layers.

- 6 -

The upper flow is net seaward and the lower is net landward.

The longitudinal boundary conditions of salinity are the concentrations associated with the freshwater inflow at the upstream limit and with saline waters in the lower layer at the downstream location. Similar boundary conditions are required for the suspended solids and, in addition, the vertical boundary conditions are established by the bed-water interaction. A net flux from the water to the bed implies that the mean settling is greater than resuspension of particles due to the scour and conversely a net flux from the bed to the water stipulates that scour is greater than settling. In either case, a steady state may be achieved in which the rates are equal and the net flux is zero on a tidally averaged basis. This is the bed condition adopted in the present analysis. The evaluation of each of these coefficients is described in the following sections.

Inspection of Eq. 3 indicates that the suspended solids distribution is dependent on four transport coefficients. The horizontal and vertical velocities are determined by the momentum and continuity equations and the vertical dispersion is calculated from an empirical relation involving the eddy viscosity and the Richardson number. The settling velocity is assigned based on field observations and laboratory experiment. CIRCULATION AND MASS TRANSPORT

## Under steady state tidally averaged conditions, the longitudinal

momentum equation for a laterally homogeneous estuary is:

$$0 = \frac{1}{\rho} \frac{\partial p}{\partial x} - N \frac{\partial^2 u}{\partial y^2}$$
(4)

The vertical component of momentum equation is simply the hydrostatic pressure equation:

$$\frac{1}{\rho} \frac{\partial p}{\partial y} = g$$
 (5)

The equation of state is approximated as:

 $\rho = \rho_{f} (1 + \alpha C)$ (6)

The equation of continuity can be expressed as:

$$\frac{\partial(bu)}{\partial x} + \frac{\partial(bv)}{\partial y} = 0$$
(7)

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In these equations,  $\rho$  = density of the saline water; p = pressure; N = vertical eddy viscosity (assumed constant with depth); u = horizontal velocity; g = gravitational acceleration;  $\rho_f$  = density of freshwater;

- 8 -
$\mathcal{L} = 0.000757$  (parts per thousand<sup>-1</sup>); C = salinity, b = depth-averaged width; and v = vertical velocity.

The justification of these equations and a simplified approach to obtain an analytical solution of the horizontal and vertical velocities has been reported (13,23,26). The salient features of a simplified analysis (23) are presented in this paper. The solution procedure consists of decoupling Eq. 4 from the other equations by assuming that salinity distribution is given or can be assigned. Thus, the pressure gradient term in Eq. 4 may be readily evaluated. Eq. 4 may then be used to solve for the horizontal velocity, u, subject to the following boundary conditions: at the free surface  $(y = -\eta)$ ,  $\partial u/\partial y = 0$ , i.e. no wind effect; and at the bottom (y = h),  $-N(\partial u/\partial y) = C_d |u_h| u_h$  in which  $C_d$  is a dimensionless friction coefficient and  $u_h$  is the velocity at the bed. The absolute value sign in the frictional resistance term assures that the bottom stress always opposes the direction of flow.

The vertical distribution of the horizontal velocity, following two integration steps of Eq. 4 incorporating the above boundary conditions, is:

9

$$u = \frac{gs}{2N} (y^2 - h^2) - \frac{g\alpha}{N} \frac{dC_s}{dx} + \frac{y}{f} + \frac{y$$

in which s is the surface slope = dn/dx;  $C_s$  is the salinity at the surface; and  $\phi(y)$  = vertical variation of salinity such that the salinity distribution can be expressed as  $C(x,y) = C_s(x) \cdot \phi(y)$ . An analytical solution is easily obtained by assuming a linear function for  $\phi$ , such as  $\phi(y) = 1+ay$ . Although this may be an approximation in some cases, it is sufficiently realistic to reproduce measured velocities in the vertical, as shown subsequently.

The vertically-averaged velocity in each layer,  $\bar{u}$ , is obtained from Eq. 8,

- - 10 -

$$\overline{u} = \frac{y_0}{y_0 + \eta} \int u dy$$

in which  $y_0 = depth of zero velocity.$ 

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The vertical velocity may be evaluated by means of Eq. 7:

$$\frac{1}{b} \frac{\partial}{\partial x} (bu) + \frac{\partial v}{\partial y} = 0$$
(10)

Differentiating Eq. 8 with respect to distance, x, substituting into Eq. 10 and integrating with respect to depth, y, yields:

$$v(x,y) = \int_{-\eta}^{y} \frac{\partial v}{\partial y} \, dy = -\frac{1}{b} \int_{-\eta}^{y} \frac{\partial}{\partial x} (bu) \, dy = -\frac{1}{b} \frac{\partial}{\partial x} (b \int_{-\eta}^{y} u \, dy)$$
(11)

Therefore,

$$v(x,y_{o}) = -\frac{1}{b} \frac{\partial}{\partial x} (b \int_{-\pi}^{y_{o}} u dy) = -\frac{1}{b} \frac{\partial}{\partial x} [b(y_{o} + \pi)\overline{u}]$$
(12)

Given the surface salinity, the salinity gradient and the geometry, and by assigning the vertical eddy viscosity, the order of magnitude of which is known, Eqs. 8, 9 and 12 are used to calculate the horizontal and vertical velocities.

An initial estimate of the vertical dispersion coefficient may be obtained from the empirical relationship with the eddy viscosity, N.

- 11 -

$$\xi = \frac{N}{1 + R_{i}}$$

(13)



The salinity profiles in the upper and lower layers are calculated using Eq. 3 with  $v_s = 0$ . Minor adjustments of this coefficient are usually necessary to achieve a suitable fit of the observed salinities.

(14)

# SETTLING VELOCITY OF SUSPENDED SOLIDS

The settling velocity of a particle in water is a function of its size, shape and density. Furthermore, the density of cohesive solids depends on the water content and nature of the particle. Recent work on marine particles from various sources provides a basis to relate particle density to inorganic composition and to particle size. Figure 2 demonstrates the variation in particle density as a function of particle diameter. The solid line represents the correlation originally proposed by McCave (18) based on a 60-40 ratio of inorganic-organic composition. The dashed line represents the correlation based on a particle size study (10) as used for the Sacramento-San Joaquin Delta. A regression analysis of particle count data was used to estimate size distributions by number and by weight for a series of samples. The inorganic-organic composition

- 12 -

of the suspended solids was determined as 85-15. The relationship between particle density and particle size is derived as follows:

$$\delta_s = 2.0 \, d^{-0.15}$$

in which  $\delta_s = \text{density, gm/cm}^3$ 

d = particle diameter, m

The settling velocity is estimated by substituting this expression into Stokes' equation, yielding the distribution of settling velocities for the range of the observed particle sizes, as shown in Figure 2. Since the size distribution did not vary significantly over the region of concern, this distribution of the settling velocity is considered representative of the system. A mean settling velocity in the Sacramento-San Joaquin Delta is taken as 8 ft/day (2.4 m/day).

### PROCEDURE OF CALCULATION

The calculation is, in principle, simple and straightforward, and is briefly summarized in the following steps:

1. The assignment of salinity gradients and the associated freshwater flow, channel characteristics at selected locations throughout the saline zone is first made. The surface salinity,  $\dot{C}_{c}$  and

- 13 -

(15)

the longitudinal salinity gradient,  $dC_s/dx$  are calculated from tidally-averaged salinity data.

- 2. The above parameters and a first estimate of eddy viscosity, N, are substituted into Eq. 8 to obtain the vertical profile of horizontal velocity at each station. Within the range of reported values for estuaries, the eddy viscosity is adjusted such that the calculated vertical profile of horizontal velocity agrees with the data at a particular station.
- 3. The point of no net motion is known from the above calculation at each station where a velocity calculation is made. The plane of no net motion is defined for the entire saline zone by interpolation forming a two-layer system.
- 4. The average horizontal velocity in each layer is then determined from the velocity profiles calculated in Step 2. The estuary is further segmented horizontally and the horizontal flow in the surface and bottom layers at each vertical cross section is calculated.
- 5. The difference in horizontal flow between two adjacent vertical planes gives the vertical flow between the surface and bottom layer. The average vertical velocity is obtained by dividing the vertical flow by the average horizontal interfacial area of the segment. The procedure is a solution of the hydraulic continuity, Eq. 12.

- 14 -

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- The empirical relationship in Eq. 13 is used to provide an initial estimate of vertical dispersion at each station.
- 7. The advective transport derived in Steps 4 and 5 is incorporated with the vertical dispersion in Eq. 3 with  $v_s = 0$ . The average salinity in both layers is calculated for comparison with the data. The above procedure, including velocity and salinity calculations, may be iterated in order to reproduce the observed salinity distribution and thus, to obtain the appropriate transport pattern.
- 8. The transport pattern derived in Step 7 and the settling velocity of suspended particles provide the necessary coefficients. for the two-layered suspended solids analysis, Eq. 3.
- Comparison between the observed and calculated values of velocity, salinity and suspended solids provides the basis for calibration and validation of the models.

# SACRAMENTO-SAN JOAQUIN DELTA

A map of the Sacramento-San Joaquin Delta is shown in Figure 3. The Sacramento and San Joaquin Rivers junction in the vicinity of Chipps Island. Grizzly and Honker Bays are relatively shallow water bodies, adjoining the main channel between Port Chicago and Chipps Island. Downstream of Benicia, Carquinez Strait, a deep channel leads to San Pablo Bay. Under the drought flow conditions of 1976, 4,400 cfs, (126  $m^3/sec$ ) the salinity intrusion extended to Emmaton while under moderate summer freshwater flow 10,000 cfs, (285  $m^3/sec$ ), the limit of salinity is approximately at Chipps Island.

Annual distributions of suspended solids have been reported for various locations in the system (28). High sediment loads typically occur during winter-early spring flood periods and result in high spring time concentrations of suspended solids. Lower values are observed in late summer and early fall. Resuspension of particles by wind action over the adjacent shallow bays may influence the concentration in the main channel during the summer months.

Variation of the concentration over the tidal cycle is shown in Figure 4 for stations at Chipps Island, Collinsville and Emmaton. The concentration of suspended solids varies with current speed, being highest near the bed. Concentrations near the surface are slightly higher at the end of ebb than at the end of flood. Concentrations near the bed are greater during flood especially near maximum current.

Electrical conductivity and suspended solids were measured at both low and high slack waters for various freshwater flow conditions. Electrical conductivity was converted to salinity which was then tidally translated to represent the tidally averaged values. Suspended solids

- 16 -

was also represented by the tidally translated values with ranges for variation between slack waters. Tidal velocity measurements with depth at a limited number of stations were also taken. These values were averaged over a tidal cycle to determine the net velocity.

Observed data and the results of the analysis applied to those data are presented in Figures 5 and 6. Figure 5 data were taken July 8, 9, 1976, and Figure 6 data were measured August 18, 19, 1974, when the flows were 4400 cfs ( $126 \text{ m}^3/\text{sec}$ ) and 10,000 cfs ( $285 \text{ m}^3/\text{sec}$ ), respectively. The observed salinity distributions are shown first. The vertical distribution of horizontal velocity as calculated by Eq. 8 is shown next. Available velocity data are also shown on Figure 5. Calculated layer-averaged horizontal velocities and vertical velocities are shown next. These are the results of Eqs. 9 and 12, respectively. These transport parameters together with the dispersion coefficients shown in Figures 5 and 6 were used to obtain the calculated salinity profiles. The calculated salinity reproduces the observed distribution in twolayer fashion for both flow conditions.

The results of the analysis applied to suspended solids is shown on Figure 7. A settling velocity of 8 ft/day (2.4 m/day) gives reasonably good agreement between calculated and observed distributions. Note that the turbidity maximum is located immediately downstream of the limit of salinity intrusion.

- 17 -

The longitudinal and vertical distribution of the suspended solids is sensitive to the magnitude of the settling velocity. Figure 8 presents the distributions for a range of settling velocity from 6 to 10 feet per day (1.8-3.1 m/day) for the 4400 cfs (126 m<sup>3</sup>/sec) flow case. The results indicate the importance of this coefficient and the need for its accurate assessment. It appears that the value derived from particle size analysis provides a reasonable estimate of the settling velocity.

The relative importance of the upstream and downstream inputs of suspended sediments is shown in Figure 9 for the 10,000 cfs (285  $m^3$ /sec) flow case. The freshwater source from Sacramento River is primarily responsible for the turbidity maximum while the input from downstream significantly influences the suspended solids distribution in the lower estuary.

## JAMES AND RAPPAHANNOCK ESTUARIES

The analysis was also applied to the James River and Rappahannock Estuaries which are both tributary to Chesapeake Bay. This area is shown on Figure 10. The calculated profiles and prototype observations for the James are shown in Figure 11. The data were collected in a 1965 survey at which time the freshwater flow was 8,800 cfs,  $(251 \text{ m}^3/\text{sec})$  (20). The average settling velocity of the suspended solids, which was assumed constant over the salinity intrusion, was obtained from a particle size distribution, following the procedure described above.

- 18 -

The procedure of calculation was identical to that employed in the Sacramento-San Joaquin Estuary. The calculated tidally averaged velocity profiles together with the vertical velocity and vertical dispersion, provided the basis for the two layer transport. Knowledge of the settling velocity permitted calculation of the suspended solids distribution. Comparisons of the calculated profiles and observed values, as shown in Figure 11, indicate that the approach is valid and provides a realistic first approximation of the various phenomena. This analysis was conducted as part of a research project on the Kepone distribution in the James River Estuary (24).

The Rappahannock Estuary is relatively straight and the bottom geometry is simple. The turbidity maximum has been regularly observed in this area and a net intertidal two layer transport pattern has been documented (21). The calculation procedure described above was used to model the Rappahannock. Salinity and total suspended sediment data shown in Figure 12 were measured in April 1965 when the freshwater flow was 1285 cfs (37 m<sup>3</sup>/sec). The calculated profiles are presented in Figure 12. A settling velocity of 6 ft/day (1.8 m/day) and the vertical dispersion coefficient between 0.5 to 1 cm<sup>2</sup>/sec were used. Again the model reasonably reproduces the salinity and suspended solids data.

- 19 -

#### SUMMARY AND CONCLUSIONS

One of the better understood aspects of estuarine hydrodynamics is that of the longitudinal circulation and mixing characteristics for partially mixed estuaries as averaged over a tidal cycle. These features are also the key to the formation of turbidity maxima in estuaries. Based on the understanding of this circulation pattern, a two-layer salinity and suspended solids model is presented, which includes a seaward advective flow in the surface layer, landward in the bottom layer, vertical advective flow, vertical dispersion across the layer interface, and the settling of suspended solids.

A simple hydrodynamic analysis is used to evaluate the horizontal and vertical transport coefficients. An empirical relationship with the Richardson number provides a preliminary estimate of the eddy dispersion coefficient from the eddy viscosity, determined in the velocity calculation. Methods of estimating the particle settling velocity are also presented.

Applications of the analysis to Sacramento-San Joaquin Delta and James River Estuary and Rappahannock demonstrate the overall validity of the approach. The distributions of salinity and suspended solids in all systems are reasonably reproduced.

Further work, both theoretical and experimental, should be directed to better understanding and measurement of the eddy viscosity and dispersion coefficients, the settling velocities of cohesive particles and the exchange with and motion of the bed.

- 20 -

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#### APPENDIX I

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# APPENDIX II

# NOTATION

The following symbols are used in this paper:

а	-	coefficient defining the vertical distribution of salinity;
Ъ	=	depth-averaged width of estuary channel;
c <sub>d</sub> '	=	bottom friction coefficient;
с	=	tidally averaged salinity
C <sub>s</sub>	=	tidally averaged salinity at water surface;
d	12	particle diameter;
g	.=	acceleration of gravity;
h		depth;
N		tidally averaged vertical eddy viscosity;
Р	=	pressure;
Pa	H	atmospheric pressure;
Q	×	freshwater flow;
R <sub>i</sub>	=	Richardson number;
s		surface slope;
S	=	concentration of suspended solids;
St	=	tidal component of suspended solids concentration;
ŝ	=	layer-averaged suspended solids concentration;
s'	=	s-5:

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t	=	time;
u	=	tidally averaged horizontal velocity,
u <sub>t</sub>		tidal component of horizontal velocity;
ū	a .	layer-averaged horizontal velocity;
u'	=	u-ū;
V	5	tidally averaged vertical velocity;
vs	=	settling velocity of suspended solids,
x	=	longitudinal axis toward ocean;
у		vertical axis toward the bed of estuary channel;
У <sub>О</sub>	u.	depth of zero horizontal velocity;
φ	· =	vertical variation of salinity;
α	ш.	0.000757 (parts per thousand $^{-1}$ );
ρ	=	density of saline water;
ρf	=	density of freshwater;
٥	25	particle density;
η	=	surface elevation;
Ę,		vertical eddy diffusion coefficient.



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VELOCITY, SALINITY AND SUSPENDED SOLIDS DI "RIBUTIONS- JAMES R



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# STEADY-STATE ANALYSIS OF ORGANIC CHEMICALS & HEAVY METALS IN RESERVOIRS & LAKES

Ъу

Donald J. O'Connor Professor Environmental Engineering & Science Manhattan College Bronx, New York 10471

Jerald L. Schnoor Professor Environmental Engineering-Energy Engineering Division University of Iowa Iowa City, Iowa 52242

#### ABSTRACT

Equations are developed to estimate the steady-state concentration of suspended solids, organic chemicals and heavy metals in reservoirs, based on the assumption of complete mixing. The equations, which define the trap efficiency of impoundments, contain three dimensionless numbers, involving the hydraulic detention time, mean depth, settling velocity of the particles, the partition coefficient and first-order reaction coefficients. The analysis was applied to heavy metal and pesticide data from three reservoirs, with a range of partitioning, transfer and degradation parameters. The model correlated the heavy metal data, with the exception of copper and zinc. Estimating evaporation and decay, the organic chemical data were in reasonable agreement with the values calculated by the model.

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#### INTRODUCTION

The spatial and temporal distribution of organic chemicals and heavy metals in natural water systems depends on the hydrodynamic transport through the system and the kinetic interactions within it. One of the most important factors is the nature and concentration of those constituents which either adsorb or assimilate and thus establish the partitioning between the dissolved and particulate components of the organic chemical or heavy metal. Inorganic and organic solids provide surfaces for the adsorption and the various levels of the food chain both adsorb and assimilate. The transport, in both the water column and in the bed, plays a major role and, in addition, transfer and transformation may be important routes which determine the distribution of these substances. The former category includes evaporation and settling and the latter biochemical decay, photolysis and hydrolysis, among others. The relative influence of these pathways for a specific chemical or metal is in large measure determined by the distribution between the dissolved and particulate components.

- l -

It is the specific purpose of this paper to present the development of equations, including these factors, which define the distribution of organic chemicals and heavy metals in completely mixed systems and to apply the analysis to steady-state conditions in lakes and reservoirs. While point sources may provide a reasonably constant input of mass to these, as well as other natural systems, a major fraction of the input is due to episodic events, generally associated with the heavy rainfall-runoff periods. It is thus recognized that the steady-state analysis is an approximation which is only valid if the inputs and responses are properly flow weighted so as to be appropriate for the time scale of the relevant phenomena. This averaging interval, in turn, establishes the time scale of the analysis, which, in this case, is annual. The model is therefore suitable to determine an order of magnitude of the problem and, as such, may be used for environment impact and chemical exposure assessments. It also provides a basis for more detailed modelling framework in time or space and for data collection programs.

In view of the importance of the partitioning of heavy metal or organic chemical into its dissolved and particulate phases, this aspect of the analysis is first addressed. It is followed by a development of the equation defining the suspended solids levels in reservoirs, which in turn, provides a necessary element for the equivalent analysis of the chemical or metal. Field data are presented for comparison with model output. The concluding section consists of applications of the analysis and suggestions for future field and analytical work.

EQUILIBRIUM CONDITIONS

Consider the most simplified conditions of a batch reactor in which the mixing is of sufficient magnitude to maintain a uniform concentration

- 2 -

throughout the volume of fluid. Assume the concentration of absorbing solids, m, is constant. Let c and p be the concentrations  $(M/L^3)$  of the dissolved and particulate components. If there is neither transfer nor decay of the chemical, the total concentration,  $c_T$ , remains constant in time and is equal to the sum of the dissolved and particulate:

$$c_{\eta} = c + p \qquad (1)$$

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(2)

(3)

The latter is related to the concentration of suspended solids, m:

in which

r = mass of chemical/unit mass of solids (M/M)

## m = concentration of solids $(M/L^3)$

The equilibrium between the dissolved concentration in the water and the mass concentration of the solids is usually expressed in terms of a partition coefficient:

$$1 = \frac{r}{c} = \frac{p}{mc}$$
$$1_m = \frac{p}{mc}$$

or

Equation (3) is the linear portion of the Langmuir isotherm. Although not always representative of actual conditions, it is a resaonable approximation when the solid phase concentration, r, is much less than the ultimate absorbing capacity of the solids. Combining equations (1) and (3), the total concentration may be expressed as:

$$c_{T} = c + \lim_{m \to \infty} c_{T} = \frac{p}{\lim_{m \to \infty} p} + p \qquad (4)$$

The product, m, is a convenient dimensionless parameter, characteristic of a particular system under equilibrium condition. For a specified value of m, the equilibrium distribution between the dissolved and particulate concentrations is established by equation (4).

- 3 -
The distribution between the dissolved concentration and the particulate concentration in the various levels of the food chain may be expressed in an identical fashion. Accounting for the distribution for various types of adsorbing solids and various levels of the food chain, each with its character-istic partition coefficient, equation (4) may be more generally expressed:

(5)

 $\mathbf{c}_{\mathrm{T}} = \mathbf{c} \left[ \mathbf{l} + \Sigma \mathbf{\eta}_{\mathrm{T}} \mathbf{m}_{\mathrm{T}} \right]$ 

The distribution may thus be categorized in accordance with the adsorbing solids (organics, clays, silts and sands) or the accumulating biomass (phytoplankton, zooplankton, fish and macrophytes). Since the total mass of the latter category is usually an order of magnitude less than that of the non-viable solids, it is not included in the following analysis. Under those conditions in which it may be significant, it may be readily incorporated as shown in the above equation.

SUSPENDED SOLIDS DISTRIBUTION

The concentration of suspended solids in a reservoir or lake depends on the physical characteristics of the incoming sediment and the hydraulic features of the reservoirs and inflow. The important characteristics of the sediment are the grain size and settling velocity distributions and the behavior of the finer fractions with respect to aggregration and coagulation. The detention time and the depth of the water body are the significant hydraulic and geomorphological features. The following analysis assumes steady-state conditions in a completely mixed system, in which the concentration of solids is spatially uniform.

These assumptions are obviously crude, but of sufficient practicality to admit at least an order of magnitude analysis of the problem. They are precisely the assumption, implicit in the analysis of the "Trap Efficiency" of reservoirs in which the efficiency of removal of solids has been cor-

- 4 -

related to the ratio of the reservoir capacity to the tributary drainage area (1).

Consider a body of water whose concentration is spatially uniform throughout its volume, V, receiving an inflow, Q. Under steady state conditions, hydraulic inflow and outflow are equal. The mass balance of the solids takes into account the mass inputted by the inflow, that discharged in the outflow and that removed by settling. The mass rate of change of solids in the reservoirs is the net of these fluxes:

$$v \frac{dm}{dt} = Qm_{i} - Qm - V_{s}A_{s}m$$
(6)

in which

 $m_i$  = concentration of solids in inflow

m = concentration of solids in reservoirs

 $V_{c}$  = settling velocity of the solids

 $A_s$  = horizontal area thru which settling occurs

The flux  $Qm_i$ , equals the rate of mass input, W. Dividing through by the volume V, equation (6) becomes

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}\mathbf{t}} = \frac{W}{V} - \mathbf{m}[\frac{1}{t_{o}} + K_{s}]$$
(7)

in which

 $t_o = detention time = \frac{V}{Q} (T)$   $K_s = settling coefficient \frac{s}{H} (\frac{L}{T})$  $H = mean depth = \frac{V}{A_s} (L)$ 

Under the steady state condition, equation (7) may be expressed as.

$$= \frac{W/Q}{1 + K_s t_o}$$
(8)

(9)

Division by W/Q = m, yields

m

m m.

$$= \frac{1}{1 + K_{s} t_{o}}$$

- 5 -

which is the fraction of the incoming solids remaining in suspension and, with the assumption of complete mixing, is also the concentration in the outflow. The fraction removed is simply

$$1 - \frac{m}{m_{i}} = 1 - \frac{1}{1 + K_{s} t_{o}}$$
(10)

The dimensionless parameter,  $K_{st_{o}}$ , represents the combined effects of the settling characteristics of the solids and the average detention time of the system. The coefficient,  $K_{s}$ , may be replaced by its equivalent,  $V_{s}/_{H}$  and the dimensionless parameter is  $V_{s}/V_{o}$ , in which  $V_{o} = \frac{H}{t_{o}} = \frac{Q}{A}$ , the over-flow rate of the system.

A plot of equation (10) is presented in Figure 1 for a range of settling coefficients, K<sub>s</sub>. Common values of the settling velocity of solids in reservoirs are in the range of a few feet per day and average depths are 10-100 feet, yielding values of  ${\rm K}_{\mathop{\rm S}}$  in the order of 0.1 per day with approximate limits of 0.025 to 0.5 as shown. The majority of the data is abstracted from reference (1) and supplemented by more recent measurements (2)(3)(4)(5)(14)from reservoirs for which concentrations of heavy metals\_and organic chemicals are also available. Data from the earlier reference are characterized by  $K_s \ge 0.1$  per day. The latter data with  $K_s \le 0.1$  per day are representative of settling velocities between 0.25 and 2.5 feet per day, as shown in Figure 2. This figure presents the correlation in a more fundamental manner. It is evident from equation (10) that replacement of K  $_{\rm S}$  with V  $_{\rm S}/_{\rm H}$  yields the correlating term,  $t_o/_H$ , with V as a parameter as shown in Figure 2. Settling velocities, in the order of 0.5 to 5.0 feet per day, which is representative of clays and fine silts, encompass the majority of the data. These types of solids are most relevant to the problem, since they have the

- 6 -

greatest capacity to absorb organic chemicals and heavy metals than sands. ORGANIC CHEMICALS/HEAVY METALS DISTRIBUTION

The distribution of organic chemicals and heavy metals in reservoirs is established by application of the principle of continuity or mass balance, in a manner similar to that employed in the case of the suspended solids. Each phase, the dissolved and particulate, is analyzed separately, taking into account the adsorptive-desorptive interaction with the other. For the dissolved component, the mass balance includes decay and transfer terms  $^{(6)(7)}$ in addition to the inflow and outflow. The basic differential equation

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}\mathbf{t}} = \frac{\mathbf{W}_{\mathbf{c}}}{\mathbf{V}} - \frac{\mathbf{c}}{\mathbf{t}_{\mathbf{o}}} - \frac{\mathbf{L}}{\mathbf{t}_{\mathbf{o}}} \mathbf{K}_{\mathbf{i}} \mathbf{c} - \frac{\mathbf{n}}{\sum_{j=1}^{n} \mathbf{K}_{\mathbf{o}j} \mathbf{m}_{j} \mathbf{c}} + \frac{\mathbf{n}}{\sum_{j=1}^{n} \mathbf{K}_{2j} \mathbf{P}_{j}} \mathbf{K}_{2j} \mathbf{P}_{j}$$
(11)

in which

V = reservoir volume (L<sup>3</sup>)

 $W_c$  = rate of mass input of the dissolved component (M/T)

c = dissolved concentration  $(M/_{13})$ 

4  $\Sigma$  K = sum of the first order rate coefficients including the following i=1

 $K_{b} = K_{b}$  [Bacteria] = biological degradation coefficient  $(T^{-1})$ 

 $K_{h} = K_{h} [OH^{-}] = base catalyzed, hydrolysis coefficient (T^{-1})$  $K_{D} = K_{D} (quantum yield) = direct photolysis coefficient (T^{-1})$ 

 $K_{u} = volatilization coefficient (T<sup>-1</sup>)$ 

 $\begin{array}{l} & n \\ \Sigma & K \\ j= \end{array} \\ \begin{array}{l} \text{sum of the adsorption coefficients for the } j^{\text{th}} \text{ size fraction,} \\ j=1 \\ \end{array} \\ \begin{array}{l} \text{of n total fractions } (L^3/M_{-}T) \end{array}$ 

- 7 -

 $m_{,i}$  = suspended solids concentration in the j<sup>th</sup> size fraction.(M/L<sup>3</sup>)

 $\sum_{j=1}^{n} K_{2j} = sum of the desorption coefficients for the j<sup>th</sup> size fraction, n total fraction <math>(T^{-1})$ 

 $p_j = particulate$  chemical concentration due to the j<sup>th</sup> size fraction, (M/L<sup>3</sup>)

For the particulate concentration in the  $j^{th}$  size fraction:

$$\frac{dp_{j}}{dt} = \frac{W_{pj}}{V} - \frac{P_{j}}{t_{o}} - K_{sj}p_{j} - K_{2j}p_{j} + K_{oj}m_{j}c$$
(12)

in which

 $W_{pj}$  = rate of mass input of the particulate adsorbed chemical of size fraction j( M/T)

 $K_{sj}$  = settling coefficient of the j<sup>th</sup> size fraction (T<sup>-1</sup>)

Summing the total over j size fractions or considering only one size fraction equations (11) and (12) reduce to:

$$\frac{dc}{dt} = \frac{W_c}{V} - \frac{c}{t_o} - K_c c - K_o m c + K_2 p$$
(13)

$$\frac{dp}{dt} = \frac{w_p}{V} - \frac{p}{t} - K_s p - K_2 p + K_o mc$$
(14)

in which

 $K_c$  = overall decay coefficient,(T<sup>-1</sup>)  $K_s$  = overall settling coefficient (T<sup>-1</sup>)  $K_2$  = overall desorption coefficient (T<sup>-1</sup>)  $K_o$  = overall adsorption coefficient (L<sup>3</sup>/M-T)

Adding equations (13) and (14) cancels the adsorption and desorption terms and yields the rate of change of the total concentration  $c_T$  in terms of the dissolved and particulate:

- 8 -

$$\frac{dc_{T}}{dt} = \frac{W}{V} - \frac{c_{T}}{t_{o}} - K_{c}c - K_{s}p$$
(15)

The sorption coefficients,  $K_0$  and  $K_2$  are usually orders of magnitude greater than the decay and transfer coefficients of the dissolved and particulate. The rate at which equilibrium is achieved between the two phases is very rapid by contrast to the rates of transfer and decay. Thus liquidsolid phase equilibrium is assumed to occur instantaneously. The dissolved and particulate concentrations, c and p, may therefore be expressed in terms of  $c_{\rm T}$  by equation 4, substitution of which in equation (15) yields:

$$\frac{\mathrm{d}\mathbf{c}_{\mathrm{T}}}{\mathrm{d}\mathbf{t}} = \frac{W}{V} - \frac{\mathbf{c}_{\mathrm{T}}}{\mathbf{t}_{\mathrm{O}}} - \frac{K_{\mathrm{C}}}{1 + \pi} \mathbf{c}_{\mathrm{T}} - \frac{K_{\mathrm{S}}^{\mathrm{S}}\mathbf{m}}{1 + \pi} \mathbf{\delta}_{\mathrm{T}}$$

Under steady-state conditions. the above may be expressed, after multiplying through by t

$$e_{\rm T} = \frac{W/Q}{1 + \frac{t_{\rm o}}{1 + \Pi_{\rm m}} [K_{\rm c} + \Pi_{\rm m} K_{\rm s}]}$$
(16)

The fraction removed is therefore

$$f = 1 - \frac{c_{T}}{W/Q} = \frac{1}{1 + \frac{c_{T}}{1 + \lim_{k \to \infty} [K_{c} + \lim_{k \to \infty} K_{s}]}}$$
(17)

For those substances, whose dissolved components are not susceptible to transfer/decay, such as heavy metals, equation (17) reduces to

$$f = 1 - \frac{1}{1 + K_{s} t_{o} \left[\frac{\eta_{m}}{1 + \eta_{m}}\right]}$$
(18)

Note that equation (18) is identical to equation (10) with the exception that the dimensionless settling parameter  $K_{s\,o}$  is multiplied by the fraction  $\frac{\eta_m}{1+\eta_m}$ . The latter term expresses the fraction of the total concentration which is in

- 9 -

the particulate form. For values of m >> 1, it is apparent that equation (18) is identical to (10).

Inspection of equation (10) indicates that the removal efficiency of suspended solids is dependent on the detention time and settling coefficient, which is the ratio of the settling velocity of the solids and the average depth of the reservoir or lake. For heavy metals and conservative chemicals, the additional parameter required is the partition coefficient (equation 18). In the case of organic chemicals, which are susceptible to biodegradation, evaporative transfer, hydrolytic or photochemical reaction, knowledge of the relevant reaction coefficients is necessary to calculate the removal efficiency (equation 17).

The detention time and average depth, which are readily determined, are based on the average annual conditions, given the time and space scales of the analysis. The settling velocity and settling coefficient may be measured directly or implied from inflow-outflow concentrations in accordance with equations (9) and (10). The partition coefficient may also be evaluated directly, which, with the solids concentration, yields the dimensionless parameter ¶m. Alternately given measurements of the total and dissolved concentrations of the heavy metal/organic chemical, the term ¶m may be calculated by means of equation (4). With such information, the removal efficiency is readily computed for those metals and chemicals which are non-reactive.

As indicated above, certain chemicals may be subjected to additional transfer or transformation. The fundamental properties of the constituent are indicative of the potential magnitude of these routes - e.g. the vapor pressure and solubility are properties which permit assessment of the evap-

- 10 -

orative transfer (8)(9). Laboratory experiments may be necessary to determine the chemical and biological routes - e.g. the biodegradability of the substance (6)(10-14). In any particular case, an assessment, either analytical or experimental, should be made to establish the degree to which transformation or transfer may be significant. The above procedure was followed in the analysis of the data from the reservoirs described in the following section.

## SITE DESCRIPTIONS

Coralville Reservoir, located in eastern Iowa, Serves as a mainstream impoundment of the Iowa River. It is a variable-level, flood control and recreational reservoir which has undergone considerable sedimentation since its construction in 1958. The original capacity of more than 53,000 acre-feet has been reduced to 38,000 with an average depth of approximately eight feet, and a mean annual detention time of 14 days. Draining more than 3000 acres of prime Iowa farmland, Coralville Reservoir receives extensive agricultural runoff with 90% of its drainage basin in intensive agriculture.

Lake Livingstone, a multi-purpose reservoir for flood-control, recreation and low-flow augmentation is located on the main stem of the Trinity River in central Texas. It has a capacity of  $7.8 \times 10^{10} \text{Ft}^3$ , which provides a detention time of 110 days. The average depth is approximately 26 Ft. The drainage area is primarily agricultural with undeveloped pastures, and includes the large metropolitan areas of Dallas-Fort Worth.

Rathbun Reservoir is located in south central Iowa, impounding the Chariton River, and was constructed by the Corps of Engineers in 1969 to provide flood control, recreation, and low flow augmentation. At normal pool elevation, the reservoir covers 11,000 acres, extends 11 miles upstream from the dam, and contains approximately 200,000 acre-ft. The drainage basin area is 342,000 acres of which 52% is used for row crop or other agriculture, 24%

- 11 -

pasture, 12% forest, and 12% other uses.

ANALYSIS OF DATA

A water quality survey of heavy metals and organic chemicals was conducted during the latter part of 1976 and the first few months of 1977 on the Trinity River through Lake Livingstone. At a number of stations, measurements of the total and dissolved concentrations in the water columns and in the bed were made. Pesticides were measured in grab samples for Coralville Reservoir at inflow, outflow and in-lake stations during 1969 and 1976, while bi-weekly suspended solids measurements have been made since 1965 (3,4). Data utilized in this report for Lake Rathburn was collected bi-weekly from May through August, 1978, when the reservoir contained 350,000 acre-ft. with a mean detention time of 162 days and a mean depth of 29 feet (5).

From these data, a value of the removal efficiency of each reservoir was determined and presented in Figure 3. The range of suspended solids removal in accordance with equation (10) is shown for comparison. The purpose of this figure is simply to demonstrate the relative removal of the various constituents. For many of the heavy metals, it is to be noted that the removal is equivalent to that of the suspended solids, implying that the particulate fraction is predominant. For some of the organic chemicals the removal fraction is much less, indicative of a larger fraction in the dissolved state. Constituents which have removal fractions greater than that of the suspended solids may be subject to additional mechanisms, such as biodegradation, evaporation, chemical hydrolysis and oxidation, and direct or sensitized photolysis.

Since both the dissolved and total concentrations were measured in the Livingston survey, it is possible to calculate the m values for each sub-

- 12 -

stance by means of equation (4). Using these data a more fundamental relationship is presented in Figure 4 for Lake Livingston in which the particulate fraction, as determined by the observations, is correlated to the fraction removed. The removal fraction is calculated in accordance with equation (18) for a range of values, representative of conditions in this reservoir. The sequence for pesticides shown in Figures 3 and 4 - Lindane, dieldrin, heptachlor and endrin - is in accord with increasing tendency to the particulate state. The data on metals indicate greater variation and are not as consistent, particularly with respect to copper and cadmium.

Removal fractions for non-conservative substances (i.e. those which are removed by mechanisms in addition to settling) should exceed the expected removals caused by sedimentation of sorbed material. Heptachlor may be susceptible to evaporation and endrin to biological decay. Evaporation and biodegration may also affect dieldrin but to a lesser extent.

Mean removal fractions for Lasso, atrazine, and dieldrin in Rathbun Reservoir, are presented in Figure 5. The representation of equation (17) in Figure 5 is similar to that of Figure 4 except that  $K_{sto}$  is equal to 4.0 and isopleths of  $K_{cto}$  are reported for these reactive substances. It is estimated that the highly soluble herbicicides Lasso and atrazine undergo rather rapid biodegradation in natural waters with  $K_{cto} = 10$  and 4 respectively, and overall first order rate constants ( $K_c$ ) of 0.06 and 0.02 per day. Grab samples and partition coefficients from other rivers and reservoirs in Lowa indicate that a small fraction of Lasso and atrazine are in the particulate phase. Dieldrin removal rates were quite variable, but it appears that the removal is due primarily to sedimentation of sorbed material, and the estimated first order reaction rate constant ( $K_c$ ) was nearly zero.

- 13 -

Equation (17) represents the most generalized correlation and is shown in Figure 6. The dimensionless parameter is the product of the particulate fraction (m/1 + m) the reaction factor  $(1 + K_2/K_s m)$  and the settling term  $(K_{sto})$ . The vertical lines in the figure indicate the values of the latter term for the three reservoirs and are representative of purely particulate substances  $(\frac{m}{1+m} = 1)$  and conservative substances  $(K_c = 0)$ . Data falling to the right of the respective verticals suggest that in addition to settling, transfer and/or decay may be operative. The most marked deviations are for copper and zinc with lower removals than calculated, which may be due to release from the bed. On the other hand, the fact that dieldrin is in reasonable agreement for the three reservoirs is encouraging. The remaining values are in general accord assuming Endrin and Lasso are non-conservative ( $K_c = 0.05/day$ ). Atrazine and heptachlor are being removed by sedimentation of adsorbed chemical as well as by gas transfer and/or decay reactions.

## CONCLUSIONS

Recognizing the simplicity of the analysis and appreciating the limited number of observations, it is apparent that comparisons such as presented in Figures 3-5 are not necessarily validations of the model. It is encouraging to note that the observations are not inconsistent with the theoretical analysis and in order of magnitude indicate reasonable agreement, as shown in Figure 6.

Given the nature of the assumptions on which the model was formulated, it may be used to estimate long-term concentrations for average values of flow and loadings. Furthermore, the time to reach equilibrium or steady-state conditions may also be approximated. Additional field

- 14 -

data are required to test and validate the model. Such field programs should be conducted in conjunction with laboratory measurements of sediment-water partitioning, volatilization and degradation reactions, the results of which may be incorporated directly in the model.

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- 15 -

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- 16 -











