

MANHATTAN COLLEGE
ENVIRONMENTAL ENGINEERING & SCIENCE PROGRAM
WASTELOAD ALLOCATION SEMINAR
US EPA REGION I

LEXINGTON, MASSACHUSSETS

JULY 14-16, 1981

TOXIC SUBSTANCES

	<u>Page</u>
Introduction and Basic Concepts	1
Adsorption-Desorption	13
Modeling Framework	29
Lakes and Reservoirs	45
Saginaw Bay-Solids and PCB Model	61
Stream and River Models	90
Application to PCB's in the Hudson River	99

INTRODUCTION AND BASIC CONCEPTS*

The presence of toxic substances, such as organic chemicals and heavy metals, has become a major environmental problem in recent years. The 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 nonviable 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. The approaches developed herein are, therefore, directed to two broad areas: an evaluation of the present extent and distribution of these substances, with particular regard to their diminution and removal and secondly, a methodology to assess the potential impact of proposed chemicals, which may be introduced into the environment.

*D. J. O'CONNOR

Field surveys undoubtedly provide much insight into the nature of the first question, but this approach is evidently limited and not applicable to the analysis of the second, and potentially more important, question. 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 following sections is therefore directed to a review of the basic knowledge of the various phenomena and of the application of laboratory data to the analysis of the problem. This approach, which is less costly and time-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.

In the following sections of these notes, 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. The purpose of this course and these notes is to describe the various pheno-

mena which affect the fate and to develop the equations, incorporating these phenomena, which define the spatial and temporal distribution of toxic substances. The notes are accordingly divided into two general sections: the first which describes the various kinetic and transfer phenomena which affect organic chemicals and heavy metals and the second which presents various mathematical models of natural water systems, incorporating these kinetic terms with the transport characteristic of each type of natural system: streams, estuaries, lakes and the coastal zone.

In order to achieve some perspective of the overall approach, it is first appropriate to indicate the basic concepts which are employed in the development of the various analyses: the principle of mass balance, the dynamic equilibrium between the dissolved and particulate concentrations, and the kinetic interaction between these components.

A. BASIC PRINCIPLE - 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, which are shown diagrammatically in Figure A-1, relate to the transport, reactions and transfer of the substance. The approach taken is identical, in principle, to that used to define the distribution of water quality constituents, which are naturally part of biochemical and ecological cycles. 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. The general expression for the mass balance equation about a specified volume, V , is:

$$V \frac{dc_i}{dt} = J_i + \Sigma R_i + \Sigma T_i + \Sigma W \quad (1)$$

in which

c_i = concentration of the chemical in compartment, i .

J = transport through the system

R = reactions within the system

T = transfer from one phase to another

W = inputs

Equation (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 effect 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.

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:

$$p_i = r_i m_i \quad (2)$$

p = particulate concentration in i compartment (M/L^3)

r_i = mass of chemical/unit of interacting mass (M/M)

m_i = concentration of the interacting species (M/L^3)

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

$$\frac{dp_i}{dt} = r_i \frac{dm_i}{dt} + m_i \frac{dr_i}{dt} = J + \sum R + \sum T + \sum W \quad (3)$$

It is apparent from equation (3) that an equivalent expression must be written for the concentration of the interacting compartment, 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 (2) is more generally expressed as a summation of the individual components of the interacting substances:

$$p_i = \sum_1^n r_i m_i \quad (4)$$

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.

B. 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 volume of fluid. Assume the concentration of absorbing solids, m (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 equal to the sum of the dissolved and particulate:

$$c_T = c + p \quad (5)$$

The latter is related to the concentration of suspended solids, m , as shown by equation (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 coefficient:

$$\eta = \frac{r}{c} = \frac{p}{mc} \quad (6)$$

$$\text{or} \quad \eta_m = \frac{p}{c}$$

Equation (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 (5) and (6), the total concentration may be expressed as:

$$c_T = c + \eta mc = \frac{p}{\eta_m} + p \quad (7)$$

The product, η_m , is a convenient dimensionless parameter, characteristic of a particular system under equilibrium conditions. For a specified value of η_m , the equilibrium distribution between the dissolved and particulate concentrations is established by equation (7), as shown in Figure A-2.

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 (7) may be more generally expressed:

$$c_T = c[1 + \sum m_i] \quad (8)$$

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.

C. KINETIC INTERACTION

The equilibrium, described above, is a result of the kinetic interaction between the dissolved and particulate. This property which distinguishes the analysis from that of purely dissolved substances, leads to equations of a more complex form. In order to gain an insight into the nature of these interactions and an understanding of a practical simplification, consider the kinetics in a batch reactor, as described above, in which interaction is taking place between the dissolved and particulate components and the former is being transferred by volatilization or transformed by chemical or biological degradation:



The reversible reaction ($K_1 \rightleftharpoons K_2$) may represent the adsorption-desorption between the dissolved component and the particulate in inorganic phase (suspended or bed solids) or the assimilation-depuration in the organic phase (aquatic organisms). These kinetic coefficients may be functions of the solids concentrations, as discussed subsequently. In any case, their ratio is a measure of the distribution or partition coefficient. The non-reversible reaction (K_3) describes the decay or volatilization. The kinetic equations are:

$$\frac{dc}{dt} = - (K_2 + K_3)c + K_1p \quad (10)$$

$$\frac{dp}{dt} = - K_1p + K_2c \quad (11)$$

By differentiating (10) and substituting (10) and (11) into the second-order differential equation, there results:

$$\frac{d^2c}{dt^2} + [K_1 + K_2 + K_3] \frac{dc}{dt} + K_1K_3c = 0 \quad (12)$$

An identical expression results for p. Assuming the initial concentration, c_0 , is totally in the dissolved form, the initial condition is

$$c = c_0 \text{ at } t = 0$$

Applying the second condition:

$$\frac{dc}{dt} = - K_2c_0 \text{ at } t = 0$$

the solution of the differential equation (8) subject to these initial conditions is:

$$c = c_0 [\beta e^{gt} + (1-\beta)e^{ht}] \quad (13)$$

in which g,h are the positive and negative roots of the quadratic

$$g,h = - \frac{K}{2} [1 \pm m]$$

in which $K = K_1 + K_2 + K_3$

$$m = \sqrt{1 - \frac{4K_1K_3}{K^2}}$$

It may be readily shown that g and h are always real and negative.

In the case of adsorption-desorption, the assumption of instantaneous equilibrium is frequently made - i.e. the coefficients K_1 and K_2 are of sufficiently large magnitude so that the exchange between particulate and

dissolved occurs very rapidly. Furthermore, for organic chemicals, the decay coefficient is usually of a much smaller magnitude than the adsorption-desorption. Thus equation (12) simplifies to

$$[K_1 + K_2] \frac{dc}{dt} + K_1 K_3 c = 0$$

or

$$\frac{dc}{dt} = \frac{-K_3}{1 + K_2/K_1} c \quad (14)$$

in which

$$\frac{K_2}{K_1} = \text{distribution or equilibrium coefficient}$$

An additional insight is gained by developing equation (14) in an alternate manner by adding equations (10) and (11) which yields

$$\frac{dc_T}{dt} = -K_3 c \quad (15)$$

Assume the interaction between c and p is an adsorption-desorption process. The dissolved concentration, c , may therefore be expressed in terms of the total, c_T , by equation (7) substitution of which in (15) yields

$$\frac{dc_T}{dt} = - \frac{K_3}{1 + \eta_m} c_T \quad (16)$$

The total concentration decays in accordance with the dissolved coefficient modified by the parameter η_m . As a physically realizable example, consider the transfer represents a volatilization process, in which K_3 is the gas transfer coefficient. The total concentration c_T decreases at a slower rate than would be the case if there were no partitioning to the particulate-form, with the total in dissolved form ($\eta_m = 0$). In defining the rate of change of the total, the decay or transfer coefficient is simply modified as shown by equation (16). Conversely, if the decay is associated

with the particulate component, the coefficient would be reduced by the fraction $\eta_m/[1 + \eta_m]$, in accordance with equation (7).

If both the particulate and dissolved components are subject to decay, by more than one mechanism, equation (16) becomes

$$\frac{dc_T}{dt} = - \left[\frac{\sum K_{ci}}{1 + \eta_m} + \frac{\eta_m \sum K_{pi}}{1 + \eta_m} \right] c_T \quad (17)$$

in which the subscripts, c and p, refer respectively to the dissolved and particulate decay coefficients.

The assumption of "instantaneous" equilibrium as expressed by equation (14) through (17) is a valid representation, or model, of kinetic reactions provided the time to equilibrium, determined by K_1 and K_2 is rapid relative to the other phenomena which affect the substance K_c & K_p . This condition is generally applicable to the adsorption-desorption process, since its equilibrium time is usually much shorter (min-hours) than that of other kinetic effects, which may be in the order of days, months or years.

In summary, the models for the analyses of organic chemicals and heavy metals are similar to those developed for constituents which are natural components of ecological cycles. The terms relating to the particulate form and its interaction with the dissolved component are the additional components to be incorporated. These, with the other transform and reactive terms, cover the various pathways of distribution. Accordingly, each of these routes and the associated mechanisms are described in the subsequent sections which comprise the first half of these notes.

The second half is devoted to the development of models, which incorporate these reaction mechanisms with transport and inputs, to define the temporal and spatial distribution of toxic substances in natural systems. By virtue of their interactions with the solids in these systems, it is also necessary to analyze the distribution of the various types of solids. Furthermore, the exchange between the suspended and the bed constituents is taken into account. The models, which are developed in the second part of the notes describe both the physical-chemical effects in the inorganic realm, in conjunction with the solids, as well as accumulation and transfer through the various elements of the aquatic food chain. Application of these models to various natural systems are also presented.

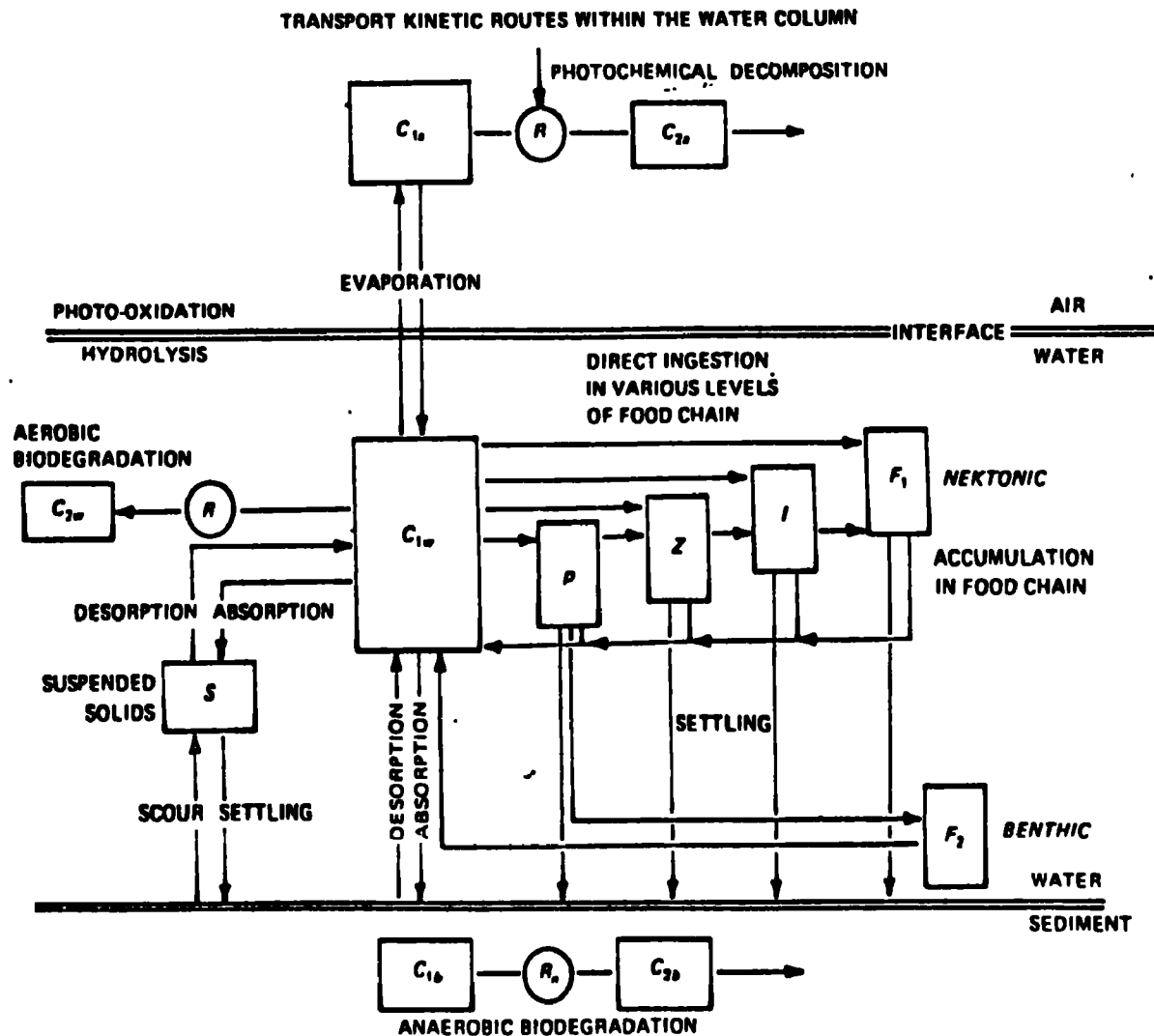


FIGURE A1
TRANSPORT - KINETIC ROUTES WITHIN THE WATER COLUMN

Note: Figure is for constant value of Φ

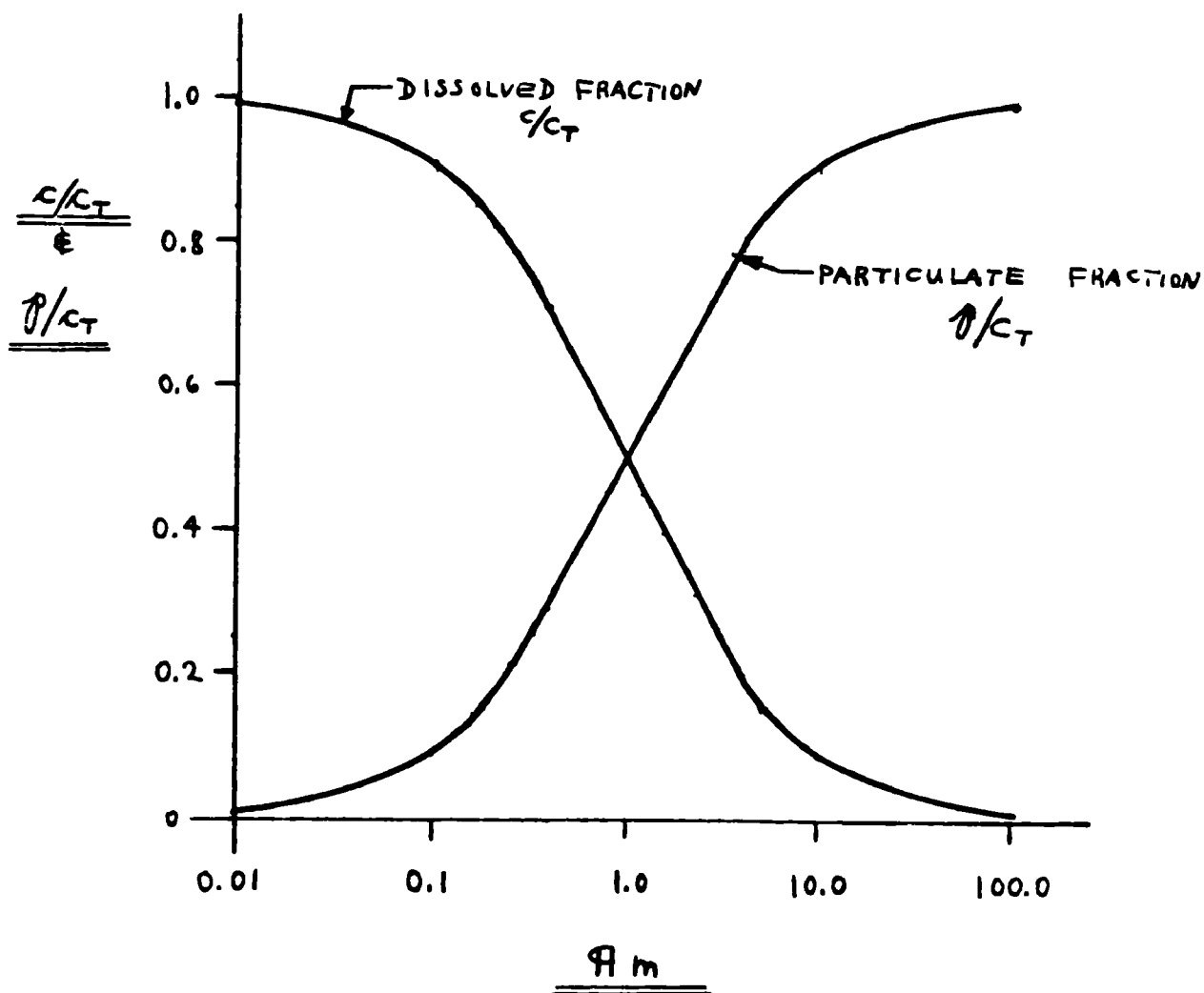


FIGURE A2 Equilibrium Concentrations of Dissolved and Particulate Toxicant as a Function of K_d

ADSORPTION-DESORPTION*

Adsorption is an important transfer mechanism within natural water systems, because of the significance of the substances which are usually involved in this process. The majority of radionuclides, heavy metal and organic chemicals are readily 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 complexed 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 complex 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 complexed species frequently is in the bed of the reservoir or estuary. Furthermore, the physiochemical characteristics of the estuary tend to promote desorption and the 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 sections describe the various factors which affect the adsorption-desorption processes and, based on these,

*Donald J. O'Connor
Kevin Farley

present the development of the relevant equilibrium relations and transfer equations.

1. 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 degree of solubility of the constituent and the affinity of the constituent to the surface of 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.

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.

The affinity of the solute for the solid may be due to an attraction or interaction of an ionic, physical (van der Waals forces) or chemical nature. Most adsorption phenomena consist of combinations of the 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 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:

$$\frac{dc}{dt} = K_1 c [c_{pc} - c_p] - K_2 c_p \quad (14)$$

in which

c = dissolved concentration of solute (M/L)

c_p = particulate concentration (M/L)

c_{pc} = capacity of the adsorbent solids (M/L)

K_1 = adsorption coefficient ($\frac{1}{TM/L}$)

K_2 = desorption coefficient ($\frac{1}{T}$)

The overall reaction is second order with respect to adsorption and first-order 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 (14) may be expressed

$$\frac{dc}{dt} = K_1 c m [r_c - r] - K_2 r m \quad (15)$$

At equilibrium, the rate of change of concentration is zero and equation (15) becomes after rearranging:

$$r = \frac{cr_c}{\frac{1}{b} + c} \quad (16)$$

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

Equation (16) is known as the Langmuir isotherm in which the parameter, b , is related to the energy of adsorption. At $r = r_c/2$, the concentration equals $1/b$. Lacking direct experimental data on r_c , its value and that of $1/b$ may be evaluated graphically by a linear plot of $\frac{1}{c}$ versus $\frac{1}{r}$. The intercept equals $1/r_c$ and the slope $1/br_c$.

The capacity r_c depends on the nature, size and characteristics of the adsorbing solids, as shown in Figure 6. 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 absorption 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, as depicted in Figure B-5, 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 con-

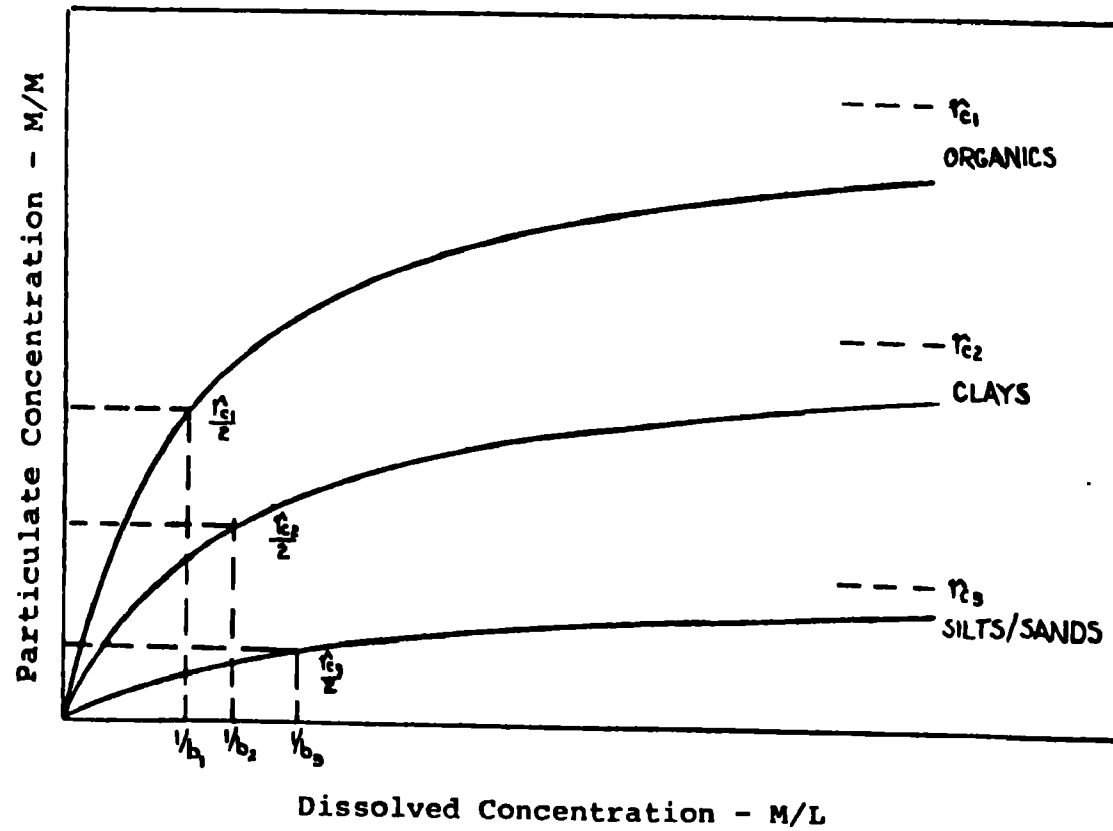


Figure B-5
Langmuir Adsorption Isotherms

centrations 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

$$r = Kc^{1/n} \quad (17)$$

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.

It is generally accepted that the rates of adsorption and desorption occur very rapidly. Consequently equilibrium between the dissolved and particulate species, expressed by equations 16 or 17 is assumed to be established instantaneously.

The above isotherms appear to be particularly appropriate for the analysis of a singular adsorbate or those cases where one is predominant, such as PCB in the Hudson and 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.

2. Partition Coefficient

The partition coefficient is the ratio of the mass of substance adsorbed per unit mass of absorbent solids and the dissolved concentration of solute in the linear range of the Langmuir and Fruendlich isotherms. For very low concentrations of solute, $c \ll 1/b$, the Langmuir isotherm is linear:

$$r = \pi c \quad (18)$$

$$\text{in which } \pi = \frac{K_1 r_c}{K_2}$$

The parameter, π , is a partition coefficient. At high concentrations of solute $c \gg 1/b$, the adsorbent is saturated at its capacity r_c . These characteristics are more dramatically borne out when logarithmic coordinates are used for various values of the partition coefficient.

The constant K in the Freundlich 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_c . Therefore, the same factors which influence its magnitude has a comparable effect on the partition coefficient. Large values are characteristic of organic material and clays, by contrast to silts and sands. Examples are shown in Figure B-6.

3. Dissolved - Particulate Distribution

Under equilibrium conditions, the distribution between the dissolved and particulate fraction is established not only by the partition coefficient as described above, but also by 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,

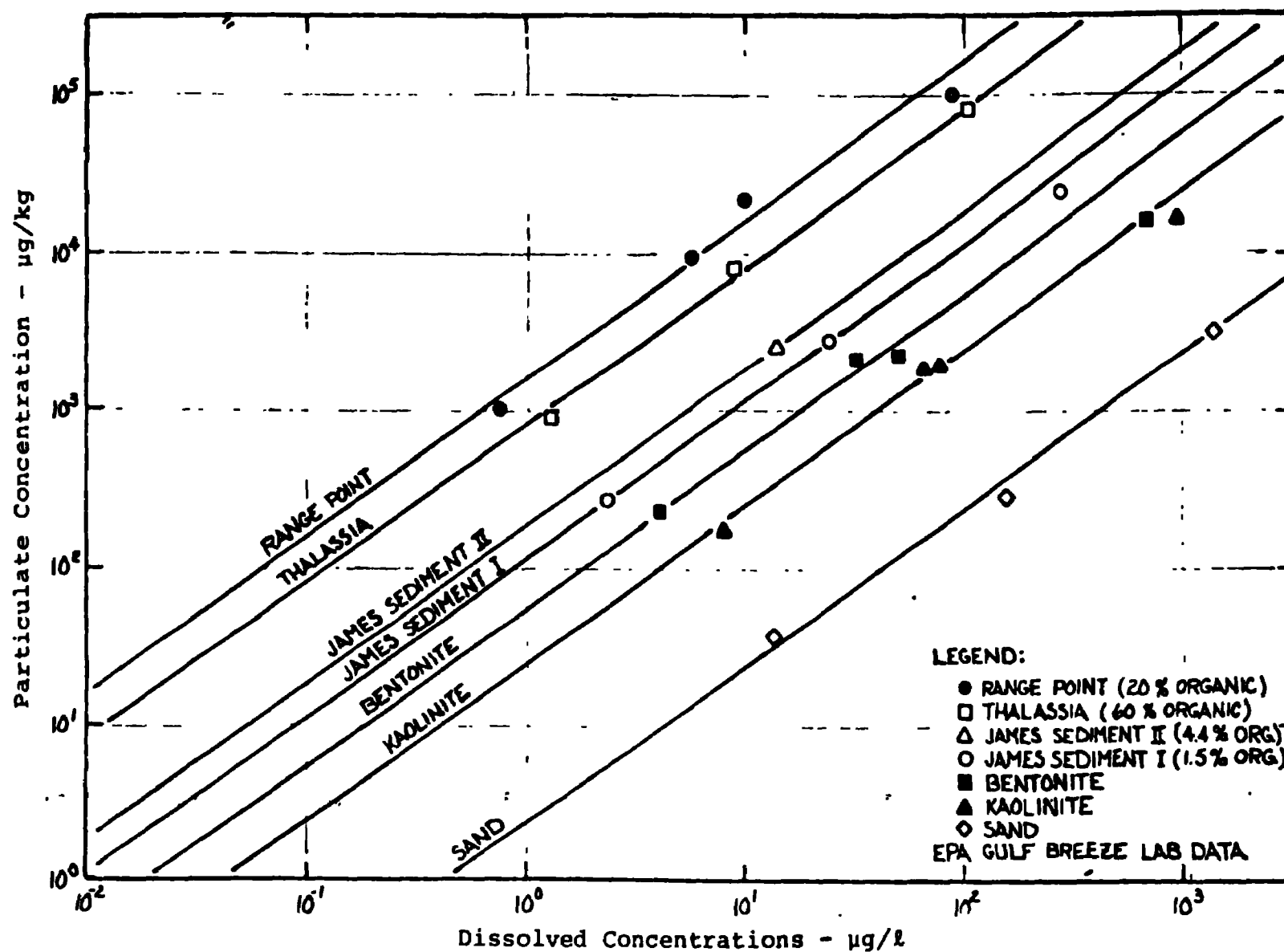


Figure B-6

Equilibrium Concentrations of Kepone

c_T , is the sum of the dissolved and particulate:

$$c_T = c + c_p \quad (19)$$

The dissolved component may be expressed in terms of the particulate fraction, r , and the partition coefficient, while the particulate concentration as a product of the concentration of adsorbing solids, m , and the particulate fraction:

$$c_T = \frac{r}{\pi} + rm \quad (20)$$

The particulate fraction as a function of solids concentration for various values of the partition coefficient is shown in Figure B-7.

Given a chemical or metal, with a large partition coefficient, whose major source is the bed solids, which is of uniform and constant concentration, this equation provides an approximate means of correlation. A linear plot of total concentration of chemical versus suspended solids concentration yields a straight line whose slope is r and intercept is r/π . An example is shown in Figure B-8 for mercury in the Mississippi and Mobile Rivers.

4. Transfer Rates

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; the second is the diffusion of the adsorbate within the pores 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 rate-limiting step. If

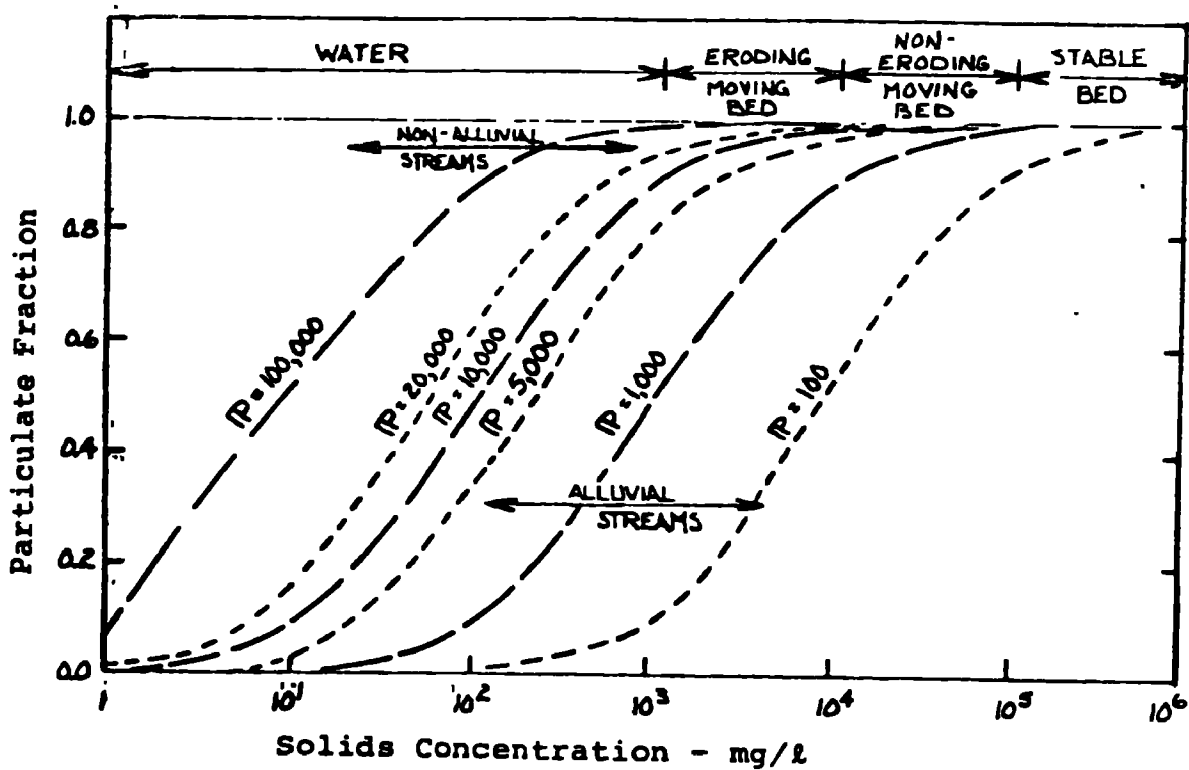


Figure B-7
Relationship - Particulate Fraction - Solids Concentration

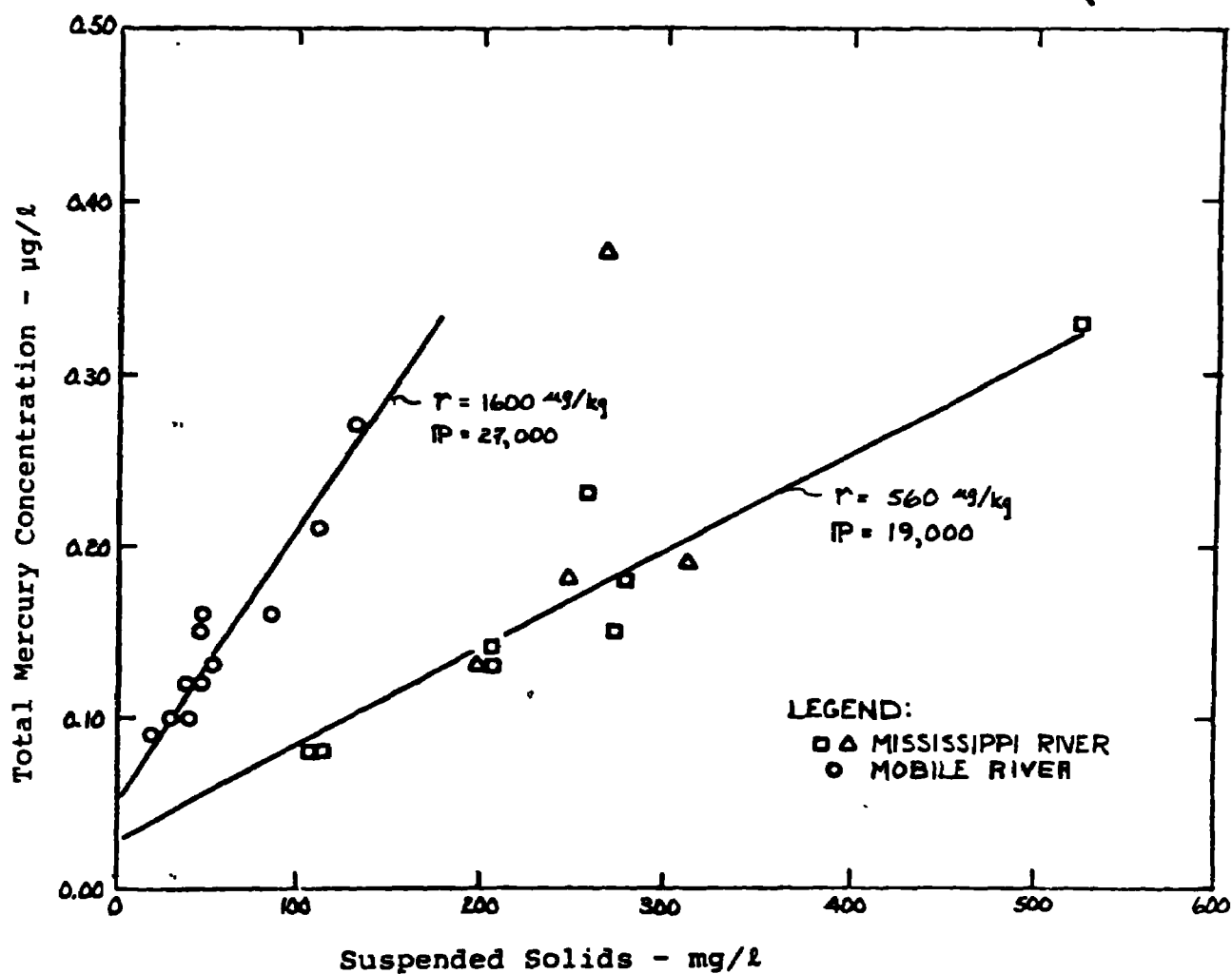


Figure B-8
Total Mercury - Suspended Solids Correlation

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.

In very dilute solution of both species, the frequency with which the solute comes in contact with the absorbent 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.

Given the steps described above, the reaction sequence may proceed in accordance with steps 1-2-3 or steps 1-3-2 depending on the nature of diffusion within the solid. In the latter case the diffusion is referred to as solid-phase internal diffusion. In the former sequence, it is fluid-phase pool diffusion. Various models have been constructed, incorporating these concepts and additional refinements. Most approaches include the three mechanisms: film transfer, diffusion in the particle and an interfacial equilibrium between liquid and solid phase concentrations.

The equilibrium coefficient, as previously discussed, may be readily determined in the laboratory for the various types of solids which may be encountered in natural systems.

The fluid phase film transfer coefficient appears to conform to general mass transfer correlations developed in the field of chemical engineering. In a simplified form the transfer coefficient is approximately:

$$K_L = \left[\frac{D_L U}{d} \right]^{1/2} \quad (21)$$

in which D_L = diffusivity in liquid

U = flow velocity

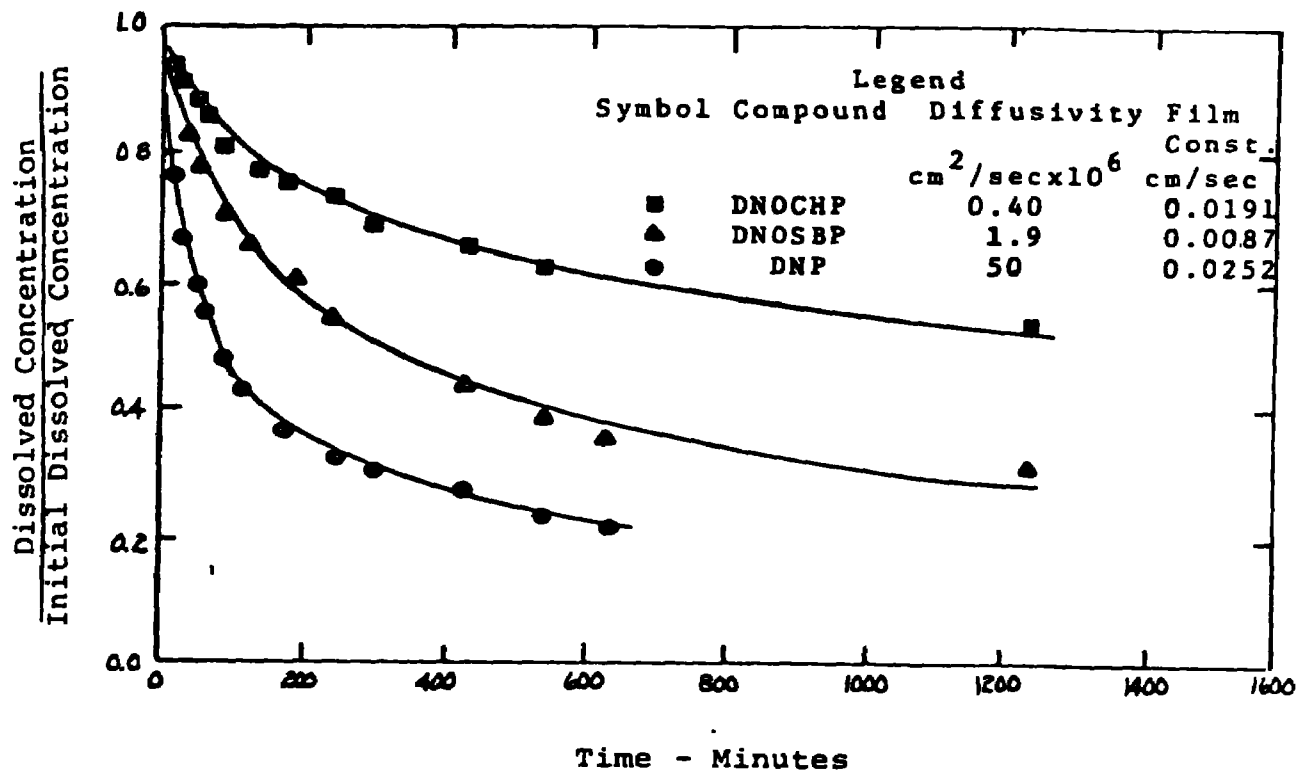
d = effective particle diameter

The diffusivity in the above expression is that in liquid. The diffusivity within the pores is reduced by virtue of the size, porosity and tortuosity of the pore structure. A common correlation is of the form

$$D_p = \frac{D_L \epsilon}{2} \quad (22)$$

in which ϵ = internal porosity of the solid particle

The model is structured with transfer in two phases: liquid and pore. A flux balance is applied at the interface and the concentration equilibrium applied at the appropriate interface. A typical analysis is shown in Figure B-9.



DNOCHP 2,4 - DINITRO - o - CYCLOHEXYLPHENOL
 DNOSBP 2,4 - DINITRO - o - SEC - BUTYLPHENOL
 DNP 2,4 - DINITROPHENOL

Figure B-9
 Example - Adsorption Kinetics

ADSORPTION-DESORPTION REFERENCES

- DiGiano, F.A. and W.J. Weber, Jr. December, 1972. "Sorption Kinetics in Finite-Bath Systems." Journal of The Sanitary Engineering Division, ASCE, Vol. 98, No. SA6, Proc. Paper 9430, pp. 1021-1036.
- Keinath, T.M. et al. April, 1976. "Mathematical Modeling of Heterogeneous Sorption in Continuous Contactors for Wastewater Decontamination." Final Report, U.S. Army Medical Res. Command.
- Keinath, T.M. 1975. "Modeling and Simulation of the Performance of Adsorption Contactors," in Mathematical Modeling for Water Pollution Control Processes, ed. Thomas M. Keinath and Martin P. Wanielista, Ann Arbor, Mich. Ann Arbor Science Publ.
- Matthews, A.P. and W.J. Weber, Jr. November 1975. "Effects of External Mass Transfer and Intraparticle Diffusion on Adsorption Rates in Slurry Reactors." Presented at the 68th Annual Meeting, American Institute of Chemical Engineering, Los Angeles, Calif.
- Mattson, J.A. et al. July 1974. "Surface Chemistry of Active Carbon: Specific Adsorption of Phenols." Journal of Colloid and Interface Science, Vol. 48, No. 1.
- Vermeulen, T. 1958. "Separation by Adsorption Methods," in Advances in Chemical Engineering. T.B. Dren and J.W. Hoopes, Jr., ed., Vol. 2, p. 147, Academic Press, New York.
- Weber, T.W. and R.K. Chakravorty. March 1974. "Pore and Solid Diffusion Models for Fixed-Bed Adsorbers." AIChE Jour., Vol. 20, No. 2.
- Weber, W.J. Jr. 1972. Physiochemical Processes for Water Quality Control. Wiley-Interscience, New York.
- Weber, W.J. Jr. and J.C. Morris. April 1964. "Adsorption in Heterogeneous Aqueous Systems." Journal Amer. Water Works Assoc., Vol. 56, No. 4, pp. 447-456.
- Weber, W.J. Jr. and R.R. Rumer Jr. Third Quarter 1965. "Intraparticle Transport of Sulfonated Alkylbenzenes in a Porous Solid: Diffusion With Nonlinear Adsorption." Water Resources Research, Vol. 1, No. 3.
- Proceedings of The Kepone Seminar II. U.S. EPA Region III, Philadelphia, Pa., Sept. 1977.

SUMMARY OF REACTION RATE COEFFICIENTS

	pH, Temp	Chemical Hydrolysis day ⁻¹	Direct Photolysis day ⁻¹	Biolysis day ⁻¹
Carbaryl	5	4.6×10^{-4}	0.11	2.3×10^{-5}
	6	5.3×10^{-3}		
	7	0.046	0.11	
	8	0.53		
	9	4.6		
Propham	7	6.9×10^{-5}	2.7×10^{-3}	0.22
Chloroprotham	7	6.9×10^{-5}	5.7×10^{-3}	0.24
Malathion	6	slow		
	8, 0°C	0.058		
	8, 27°	0.46	slow	6.1
	8, 40°	17.3		
Parathion	7, 20°	2.8×10^{-3}	0.017	
Diazinon	7, 20°	0.023	0.022	
2,4-D Butoxy ethyl ester	6, 28°	0.63	0.049	
	9, 28°	27.7		
Captan	8, 28	1.39	slow	
Methocychlor	7, 27°	1.9×10^{-3}	0.053	
			0.1-0.3*	
Toxaphene	7	slow	slow	
DDT	7, 27	2.4×10^{-4}	1.3×10^{-4}	
Atrazine	3	0.011	0.017	
	11	8.6×10^{-3}		

* sensitized photolysis in natural waters

MODELING FRAMEWORK*

This section of the notes presents the development and application of various mathematical models which define the spatial and temporal distribution of toxic substances in natural water systems. The previous sections discussed the various transfer and kinetic factors which affect the concentration of such substances. These factors are now combined with the transport regimes characteristic of the different types of natural water systems, both freshwater and marine. The former include reservoirs/lakes and streams/tidal rivers, and the latter estuaries/embayments and the coastal zone.

The purposes of the modeling framework are twofold: the first relates to the general hazard assessment of proposed or existing chemicals which, in turn, may lead to waste-load allocation procedures. Such analyses may usually be accomplished by means of the spatial steady-state 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.

As discussed in the previous sections, 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 at least three simultaneous equations, describing the concentration of the various 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.

* Donald J. O'Connor

In order to provide a perspective of the overall approach, the basic concepts which are employed in the analysis are first presented, followed by the development of the equations defining the dissolved, particulate and solids components. Certain sections which are contained in the first part of the notes are therefore repeated in the following in order to provide continuity of development.

A. BASIC PRINCIPLES

1. 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, which are shown diagrammatically in Figure 1, relate to the transport, reactions and transfer of the substance. The approach taken is identical, in principle, to that used to define the distribution of water quality constituents, which are naturally part of biochemical and ecological cycles. 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. The general expression for the mass balance equation about a specified volume, V , is:

$$V \frac{dc_i}{dt} = J_i + \sum R_i + \sum T_i + \sum W \quad (1)$$

in which

c_i = concentration of the chemical in compartment, i .

J = transport through the system

R = reactions within the system

T = transfer from one phase to another

W = inputs

Equation (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 effect 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.

2. 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:

$$p_i = r_i m_i \quad (2)$$

p = particulate concentration in i compartment M/L^3

r_i = mass of chemical/unit of interacting mass M/M

m_i = concentration of the interacting species M/L^3

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

$$\frac{dp_i}{dt} = r_i \frac{dm_i}{dt} + m_i \frac{dr_i}{dt} = J + \sum R + \sum T + \sum W \quad (3)$$

It is apparent from equation (3) that an equivalent expression must be written for the concentration of the interacting compartment, 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 (2) is more generally expressed as a summation of the individual components of the interacting substances:

$$p_i = \sum_{i=1}^n r_i m_i \quad (4)$$

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.

3. 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 volume of fluid. Assume the concentration of absorbing solids, m (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 equal to the sum of the dissolved and particulate:

$$c_T = c + p \quad (5)$$

The latter is related to the concentration of suspended solids, m , as shown by equation (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 coefficient:

$$\eta = \frac{r}{c} = \frac{p}{mc} \quad (6)$$

$$\text{or} \quad \eta_m = \frac{p}{c}$$

Equation (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 (5) and (6), the total concentration may be expressed as:

$$c_T = c + \eta mc = \frac{p}{\eta_m} + p \quad (7)$$

The product, η_m , is a convenient dimensionless parameter, characteristic of a particular system under equilibrium conditions. For a specified value of η_m , the equilibrium distribution between the dissolved and particulate concentrations is established by equation (7), as shown in Figure A-2, Chap. I.

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 (7) may be more generally expressed:

$$c_T = c[1 + \sum_i m_i] \quad (8)$$

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.

4. Kinetic Interaction

The equilibrium, described above, is a result of the kinetic interaction between the dissolved and particulate. This property which distinguishes the analysis from that of purely dissolved substances, leads to equations of a more complex form. In order to gain an insight into the nature of these interactions and an understanding of a practical simplification, consider the kinetics in a batch reactor, as described above, in which interaction is taking place between the dissolved and particulate components and the former is being transferred by volatilization or transformed by chemical or biological degradation:



The reversible reaction ($K_1 \rightleftharpoons K_2$) may represent the adsorption-desorption between the dissolved component and the particulate in inorganic phase (suspended or bed solids) or the assimilation-depuration in the organic phase (aquatic organisms). These kinetic coefficients may be functions of the solids concentrations, as discussed subsequently. In any case, their ratio is a measure of the distribution or partition coefficient. The non-reversible reaction (K_3) describes the decay or volatilization. The kinetic equations are:

$$\frac{dc}{dt} = - (K_2 + K_3)c + K_1 p \quad (10)$$

$$\frac{dp}{dt} = -K_1 p + K_2 c \quad (11)$$

Addition of equations 10 and 11 yield

$$\frac{dc_T}{dt} = -K_3 c \quad (12)$$

If equilibrium is rapidly achieved by contrast to the other time constants, specifically identified as K_s in this example, the dissolved component, c , may be expressed in terms of the total concentration, c_T , by equation (7), substitution of which in (12) yields

$$c = c_0 [\beta e^{gt} + (1-\beta)e^{ht}] \quad (13)$$

in which g, h are the positive and negative roots of the quadratic

$$g, h = -\frac{K}{2} [1 \pm m]$$

in which $K = K_1 + K_2 + K_3$

$$m = \sqrt{1 - \frac{4K_1 K_3}{K^2}}$$

It may be readily shown that g and h are always real and negative.

In the case of adsorption-desorption, the assumption of instantaneous equilibrium is frequently made - i.e. the coefficients K_1 and K_2 are of sufficiently large magnitude so that the exchange between particulate and dissolved occurs very rapidly. Furthermore, for organic chemicals, the decay coefficient is usually of a much smaller magnitude than the adsorption-desorption. Thus

$$[K_1 + K_2] \frac{dc}{dt} + K_1 K_3 c = 0$$

or

$$\frac{dc}{dt} = \frac{-K_3}{1 + K_2/K_1} c \quad (14)$$

in which

$$\frac{K_2}{K_1} = \text{distribution or equilibrium coefficient}$$

An additional insight is gained by developing equation (14) in an alternate manner by adding equations (10) and (11) which yields

$$\frac{dc_T}{dt} = -K_3 c \quad (15)$$

Assume the interaction between c and p is an adsorption-desorption process. The dissolved concentration, c , may therefore be expressed in terms of the total, c_T , by equation (7) substitution of which in (15) yields

$$\frac{dc_T}{dt} = - \frac{K_3}{1 + \eta_m} c_T \quad (16)$$

The total concentration decays in accordance with the dissolved coefficient modified by the parameter η_m . As a physically realizable example, consider the transfer represents a volatilization process, in which K_3 is the gas transfer coefficient. The total concentration c_T decreases at a slower rate than would be the case if there were no partitioning to the particulate form, with the total in dissolved form ($\eta_m = 0$). In defining the rate of change of the total, the decay or transfer coefficient is simply modified as shown by equation (16). Conversely, if the decay is associated with the particulate component, the coefficient would be reduced by the fraction $\eta_m/[1 + \eta_m]$, in accordance with equation (7).

If both the particulate and dissolved components are subject to decay, by more than one mechanism, equation (16) becomes

$$\frac{dc_T}{dt} = - \left[\frac{\sum K_{ci}}{1 + \eta_m} + \frac{\eta_m \sum K_{pi}}{1 + \eta_m} \right] c_T \quad (17)$$

in which the subscripts, c and p , refer respectively to the dissolved and particulate decay coefficients.

The assumption of "instantaneous" equilibrium as expressed by equation (14) through (17) is a valid representation, or model, of kinetic reactions provided the time to equilibrium, determined by K_1 and K_2 is rapid relative to the other phenomena which affect the substance, K_c & K_p . This condition is generally applicable to the adsorption-desorption process, since its equilibrium time is usually much shorter (min-hours) than that of other kinetic effects, which may be in the order of days, months or years.

In summary, the models for the analyses of organic chemicals and heavy metals are similar to those developed for constituents which are natural components of ecological cycles. The terms relating to the particulate form and its interaction with the dissolved component are the additional components to be incorporated. These, with the other transfer and reactive terms, cover the various pathways of distribution. Accordingly, each of these routes and the associated mechanisms are described in the subsequent sections which comprise the first half of these notes.

The second half is devoted to the development of models, which incorporate these reaction mechanisms with transport and inputs, to define the temporal and spatial distribution of toxic substances in natural systems. By virtue of their interactions with the solids in these systems, it is also necessary to analyze the distribution of the various types of solids. Furthermore, the exchange between the suspended and the bed constituents is taken into account. The models, which are developed in the second part of the notes describe both the physical-chemical effects in the inorganic realm, in conjunction with the solids, as well as accumulation and transfer through the various elements of the aquatic food chain. Application of these models to various natural systems are also presented.

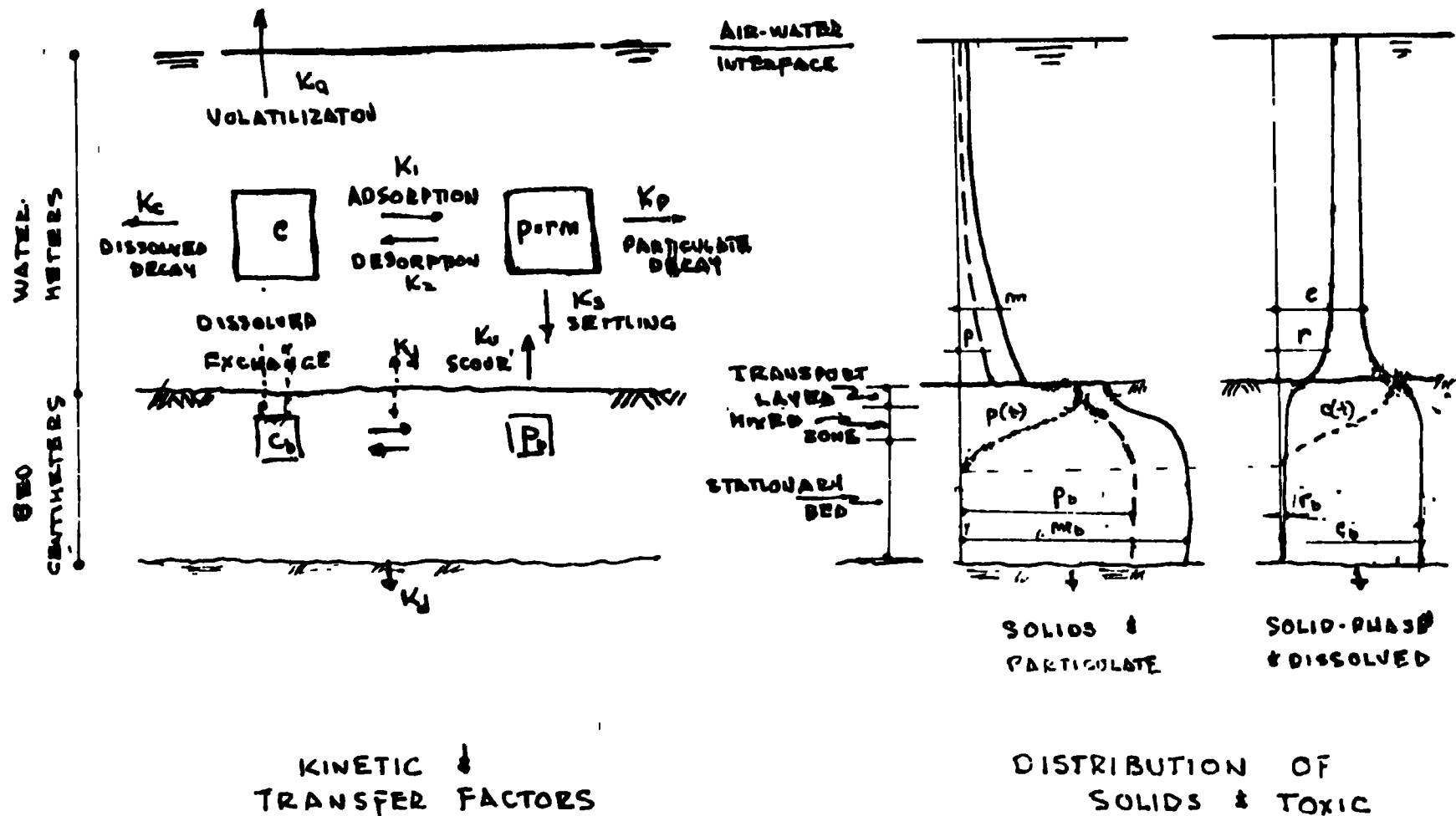


FIGURE 1

B. CLASSIFICATION OF ANALYSIS AND MODELS*

Equation (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 previously, 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, discussed in the subsequent sections of the notes, 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 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. 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 predomi-

* Donald J. O'Connor

nating component, in one of more dimensions. The transport in streams may be frequently approximated by a one-dimensional longitudinal analysis (A), in lakes by one or two dimensions (B), in which the vertical is the major component and in estuaries by a two-dimensional scheme (C) (longitudinal and vertical, as shown in Figure 2A. A spatially uniform condition (completely mixed) is type D whose transport coefficient is the detention time, t_o .

3. Bed Conditions

The bed conditions, which are relevant to the analysis are shown in Figure 2B. 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 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 in these notes, is essentially based on the types of bed conditions shown in Figure 2B, in conjunction with one of the three types of fluid transport shown in Figure 2A. 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.

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 shown in Figure 2A.

The essential characteristic of this type of system is 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 settle. The accumulation of this material in the bed causes an increase in the thickness of the benthic 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 movement of benthic 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.

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 in accordance with velocity vector of the fluid in contact with the bed surface. In fresh water 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 2B.

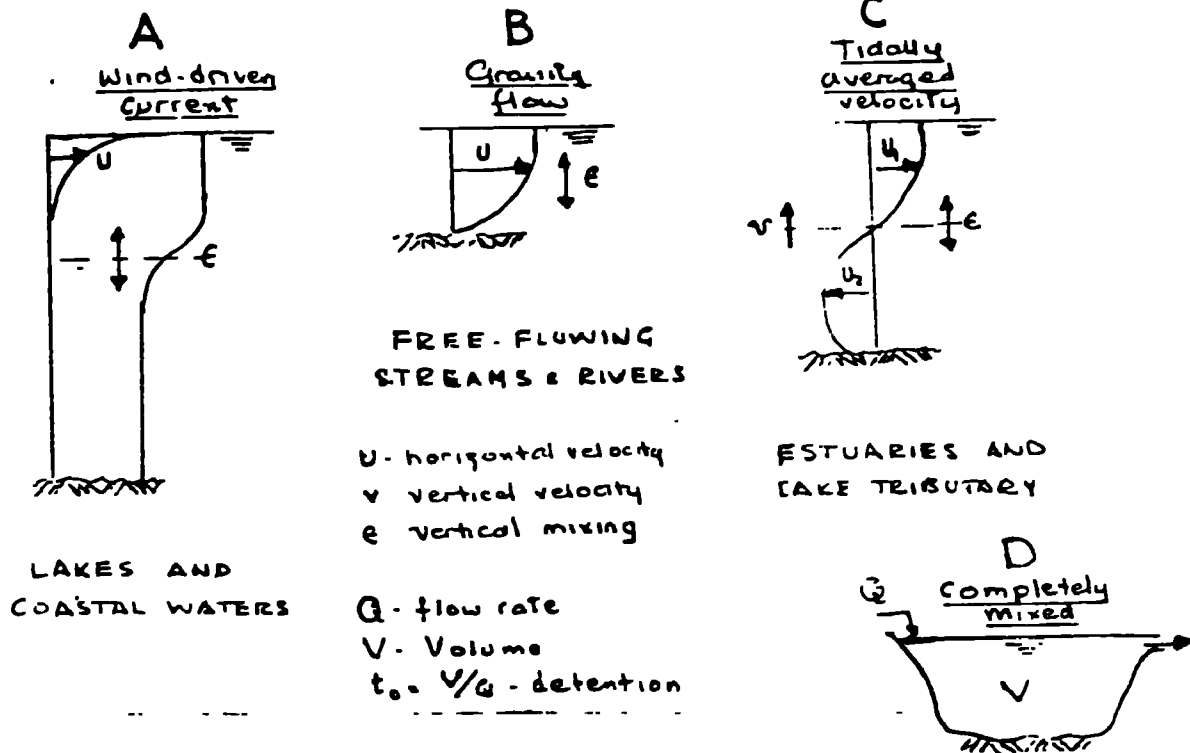


FIGURE 2A - TRANSPORT REGIMES

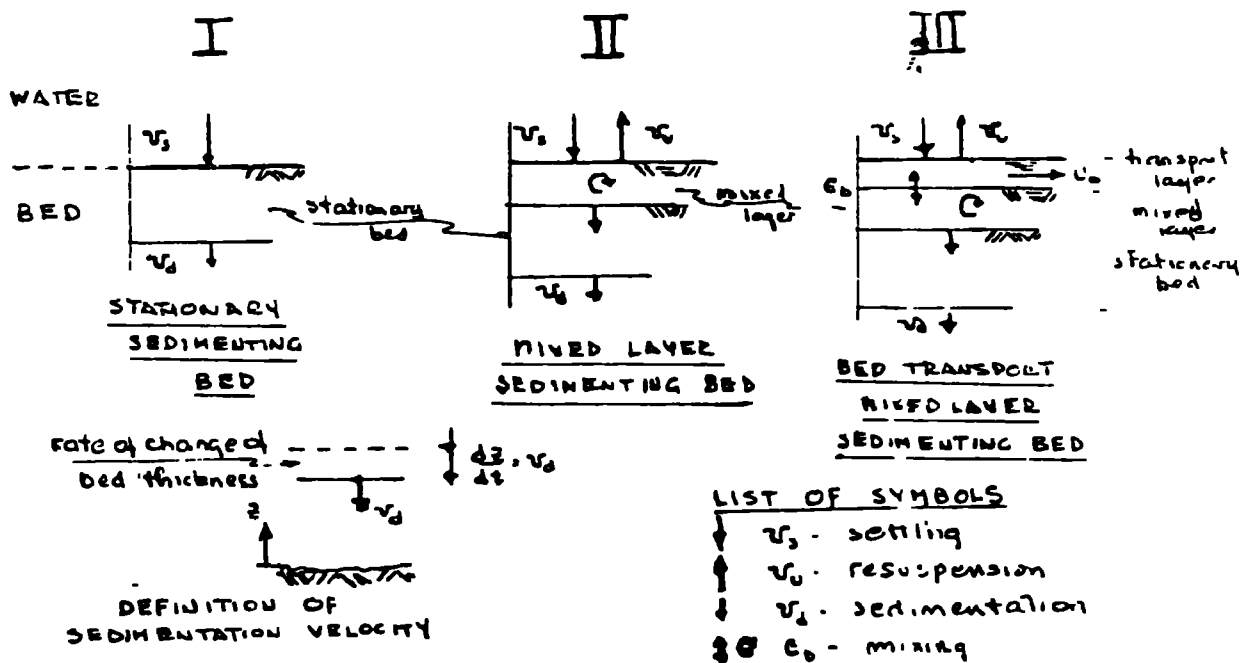


FIGURE 2B - BED CONDITIONS

TABLE 1

		B E D C O N D I T I O N		
		I STATIONARY BED	II MIXED LAYER WITH BED	III SEDIMENT TRANSPORT WITH LAYER & BED
		0	0	>0
		U_b	0	>0
		ϵ_b	>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 TO ALL TYPES, PARTICULARLY TO LAKES RESERVOIRS & EMBAYMENTS		

LAKES AND RESERVOIRS

A. INTRODUCTION*

The analyses of water quality in lakes and reservoirs are considered in this section. Because of certain similarities which exist between lakes and oceans, many of the models described in this chapter are appropriate for problems in the coastal and off-shore regions of the oceans. The spectrum of time-space scales which characterize the analysis in these water bodies is much broader than that encountered in streams and estuaries. This difference is attributable not only to the geomorphology and dimensionality of the respective systems but also to the driving forces and components of the transport terms. Thus, many water quality analyses in rivers, tidal and non-tidal, are one-dimensional within the relatively defined boundary of channel cross section. Furthermore, this uni-dimensionality, which applies both to flow and quality frequently exists under steady-state conditions.

By contrast to the one-dimensional steady-state analysis, many water quality problems in lakes and oceans are time variable in two or three dimensions. The deep, relatively slow moving, hydraulic regime, over wide horizontal scales, is an important factor in this regard. Because of the greater depths, thermal differences and density structures are seasonally encountered. The vertical distribution of many constituents associated with these regimes is a significant water quality problem, which has a counterpart in the toxic problem.

A large scale analysis may frequently be used on the assumption of a spatially uniformity of concentration over the time unit of analysis. Since large scale problems (10-100 miles) are usually associated with equivalently long time scales, the incremental time step of the analysis may be of sufficient duration to justify the assumption of spatially uniformity. For example, if the concern is the long term build-up of conservative toxic substances which may occur over years or decades, an appropriate time step of such an analysis is the year. Over this period many lakes and reservoirs, with their characteristic spring and fall overturn

* Donald J. O'Connor

and mixing due to winds and seiches, reflect a spatially uniform condition. More specifically, the variations which occur over the year are small by contrast to the increase in concentration anticipated in future years. At this relatively large time-space scale, the typical time variable problem is the long term build-up of a toxic constituent. The steady-state relates to the equilibrium concentration, resulting from a constant input, and the time required to establish equilibrium, if indeed one is possible.

The following sections of this chapter describe the toxic distributions in completely mixed systems of lakes and reservoirs and secondly, address the analysis of the vertical distribution of toxic substances in these water bodies. The completely mixed analysis is coupled with Type I and II bed conditions with various applications. It is unlikely that a Type II condition would be encountered in lakes under this scale assumption. The vertical analysis is presented with a Type I bed condition with a specific example of quarry with lindane and DDE inputs. A final application is discussed with respect to Toxic Substances in the Great Lakes. In each case, the distribution of suspended solids is first developed, followed by the analysis of toxic substances, which receives input from the solids analysis.

B. ANALYSIS OF COMPLETELY MIXED SYSTEMS*

1. Type I Analysis - Stationary Bed - No Resuspension - Sedimentation a) Suspended Solids

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 system and inflow. The important characteristics of the solids are the grain size and settling velocity distributions and the behavior of the finer fractions with respect to aggregation 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 correlated 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 , as shown in Figure B-1. 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:

$$V \frac{dm_1}{dt} = Qm_i - Qm_1 - v_s A_s m_1 \quad (1)$$

in which

m_i = concentration of solids in inflow

m_1 = concentration of solids in water body

v_s = settling velocity of the solids

A_s = horizontal area thru which settling occurs

The flux $\dot{Q}m_i$, equals the rate of mass input, W . Dividing through by the volume, V , the above equation becomes

$$\frac{dm_1}{dt} = \frac{W}{V} - m_1 \left[\frac{1}{t_0} + K_s \right] \quad (2)$$

* Donald J. O'Connor

in which

$$t_o = \text{detention time} = \frac{V}{Q} (T)$$

$$K_s = \text{settling coefficient} \frac{v_s}{H} \left(\frac{L}{T} \right)$$

$$H = \text{mean depth} = \frac{V}{A_s} (L)$$

Under the steady state condition, equation (2) may be expressed as,

$$m_1 = \frac{W/Q}{1 + K_s t_o} \quad (3a)$$

Division by W/Q yields

$$\frac{m_1}{W/Q} = \frac{1}{1 + K_s t_o} \quad (3b)$$

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

$$f = 1 - \frac{1}{1 + K_s t_o} \quad (4)$$

The dimensionless parameter, $K_s t_o$, 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 overflow rate of the system.

It is apparent from the above development that conditions in the bed have no effect on the concentration in the water body, because there is no resuspension of the bed material. The benthal concentration, on the other hand, is due directly to the influx of the settling solids. The rate of change of mass of solids in the bed is therefore

$$\frac{dM_2}{dt} = + A_1 v_s m_1$$

The mass, M_2 , equals the product of the bed volume V_2 , and bed concentration, m_2 . Thus

$$\frac{dM_2}{dt} = \frac{d(V_2 m_2)}{dt} = m_2 \frac{dV_2}{dt} + V_2 \frac{dm_2}{dt} = + A_s v_s m_1 \quad (5a)$$

Dividing through the A_s , and expressing the resulting $\frac{dz_2}{dt}$ as V_d , the final result is

$$\frac{dm_2}{dt} = \frac{v_s}{z} m_1 - \frac{v_d}{z} m_2 \quad (5b)$$

at steady-state - i.e. when the mass settling rate equals the accumulation rate:

$$m_2 = m_1 \frac{v_s}{v_u} \quad (5c)$$

b) Toxic Substances

The distribution of toxic substances, such as organic chemicals and heavy metals in reservoirs and lakes 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⁽²⁾⁽³⁾ in addition to the inflow and outflow. The basic differential equation

$$\frac{dc_1}{dt} = \frac{W_c}{V} - \frac{c_1}{t_o} - K_c c_1 - K_o m c_1 + K_2 p_1 \quad (6)$$

in which

- V = reservoir volume (L^3)
- W_c = rate of mass input of the dissolved component (M/T)
- c_1 = dissolved concentration in water body (M/L^3)
- K_c = overall first order rate coefficients (T^{-1}) which may include biological degradation, hydrolysis, direct photolysis & volatilization.
- K_o = the adsorption coefficient ($L^3/M-T$)
- m = suspended solids concentration (M/L^3)
- K_2 = the desorption coefficient (T^{-1})
- p_1 = particulate chemical concentration (M/L^3)

For the particulate concentration:

$$\frac{dp_1}{dt} = \frac{W_p}{V} - \frac{p_1}{t_o} - K_{s_1} p_1 - K_2 p_1 + K_o m c_1 \quad (7)$$

in which

W_p = rate of mass input of the particulate adsorbed chemical (M/T)

K_s = settling coefficient (T^{-1})

Adding equations (6) and (7) 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:

$$\frac{dc_{T1}}{dt} = \frac{W}{V} - \frac{c_{T1}}{t_o} - K_c c_1 - K_{s1} p_1 \quad (8)$$

The sorption coefficients, K_o 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 liquid-solid phase equilibrium is assumed to occur instantaneously. The dissolved and particulate concentrations, c and p , may therefore be expressed in terms of c_T by equation 4, substitution of which in equation (8) yields:

$$\frac{dc_{T1}}{dt} = \frac{W}{V_1} - \frac{c_{T1}}{t_o} - \frac{K_{c1}}{1 + \eta_{m1}} c_{T1} - \frac{K_{s1} \eta_{m1}}{1 + \eta_{m1}} c_{T1}$$

Under steady-state conditions, the above may be expressed, after multiplying through by t_o :

$$c_{T1} = \frac{W/Q}{1 + \frac{t_o}{1 + \eta_{m1}} [K_{c1} + \eta_{m1} K_{s1}]} \quad (9)$$

For those substances, whose dissolved components are not susceptible to transfer/decay, such as heavy metals, equation (9) reduces to

$$c_{T1} = \frac{W/Q}{1 + K_{s1} t_o \left[\frac{\eta_{m1}}{1 + \eta_{m1}} \right]} \quad (10)$$

Note that equation (10) is identical to equation (3a) with the exception that the dimensionless settling parameter $K_s t_o$ is multiplied by the fraction $\frac{\eta_{m1}}{1 + \eta_{m1}}$.

The latter term expresses the fraction of the total concentration which is in the particulate form. For values of $f_n \gg 1$, it is apparent that equation (10) is identical to (3a). With reference to equations (9) and (10), the fraction removed is

$$r = 1 - \frac{C_n}{W/Q} \quad (11)$$

Inspection of equation (4) indicates that the removal efficiency of suspended solids is dependent on the retention 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 10). 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 (equation 5).

The retention time and average depth, which are readily determined, are based on the average seasonal or 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 (3) and (4). The partition coefficient may also be calculated directly, which, with the solid concentration, yields the dimensionless parameter f_n . Alternately given measurements of the total and dissolved concentrations of the heavy metal/organic chemical, the term f_n may be calculated. 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 evaporative transfer (4)(5). Laboratory experiments may be necessary to determine the chemical and biological routes - e.g. the biodegradability of the substance (6)-(9). 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. Solutions of the above are shown in Figure E-2.

The bed concentration may be described by constructing its mass balance. Influx is due to the toxic substance associated with the settling solids and the volumetric accumulation is accounted for by the sedimentation velocity, as in the bed solids analysis (equation 5)

$$\frac{dc_{m_2}}{dt} = f_{p_1} K_{s_2} c_{T_1} - f_{p_2} K_{d_2} c_{T_2} \quad (12)$$

at steady state

$$c_{T_2} = \frac{f_{p_1} v_s}{f_{p_2} v_d} c_{T_1} \quad (13)$$

in which

f_{pn} = the fractions dissolved and particulate

v_s = settling velocity

v_d = sedimentation velocity

Since the bed solids concentration $m_2 \gg m_1$ and f_{m_2} is usually $\gg 1$, as a reasonable approximation

$$f_{p_2} \sim 1 \text{ and } f_{d_2} \sim 0$$

$$c_{T_2} = p_2 = f_{p_1} \frac{v_s}{v_d} c_{T_1} = \frac{v_s}{v_d} p_1 \quad (14)$$

substituting for $p = rm$

$$r_2 m_2 = \frac{v_s}{v_d} r_1 m_1$$

since $v_d m_2 = v_s m_1$ under steady state, then

$$p_2 = r_1 \quad (15)$$

The above analysis does not take into account the possibility of the exchange of the dissolved component between the bed and the water. This is discussed in the following section, which considers solids resuspension - a condition more likely to enhance exchange of the dissolved component.

2. Type II Analysis - Mixed Bed - Resuspension

The type of analysis described in this section is identical to that of the previous, with the addition of a resuspension term in both the solids and toxic equations. The physical structure of the system is shown diagrammatically in Figure E-1, from which it is apparent that a mass balance equation must be developed for both the water column and the bed, since they are interactive.

a. Suspended Solids

The mass rate of change of solids in the water column is:

$$V_1 \frac{dm_1}{dt} = Qm_1 - Qm_2 - V_s A_s m_1 + V_u A_s m_2 \quad (17)$$

in which

V_1 = resuspension velocity - L/T

m_2 = concentration of solids in the bed - M/L³

and the remaining terms are as previously defined in equation (1) of previous section.

Expressing the input flux of solids Qm_1 as W and dividing through by the volume V_1 , yields

$$\frac{dm_1}{dt} = \frac{W}{V_1} - \frac{m_1}{t_0} - \frac{V_s}{H_1} m_1 + \frac{V_u}{H_1} m_2 \quad (18)$$

in which

H_1 = average depth of the water column

A mass balance of the bed solids includes the influx of the bottom-solids from the water and mass outflow from the bed due to the resuspension and sedimentation:

$$\frac{dm_2}{dt} = \frac{V_s m_1}{H_1} - \frac{V_u m_2}{H_2} - \frac{V_d m_2}{H_2} \quad (19)$$

in which

H_2 = average depth of the bed

At steady-state conditions, $\frac{dm}{dt} = 0$, the concentration in the bed may be expressed in terms of the concentration in the water from (18):

$$m_2 = \alpha m_1 \quad (19)$$

in which

$$\alpha = \frac{v_s}{v_u + v_d}$$

Substitution of which in equation (17) under steady state yields

$$0 = \frac{W}{V} - m_1 \left[\frac{1}{t_o} + \frac{v_s}{H_1} \right] + \frac{v_u}{H_1} \cdot \frac{v_d}{v_u + v_d} m_1$$

Expressing $\frac{v_s}{H} = K_s$ and solving for m_1 , after simplification, gives:

$$m_1 = \frac{W/Q}{1 + \beta K_{s1} t_o} \quad (20)$$

in which

$$\beta = \frac{v_d}{v_u + v_d}$$

The value of α falls between zero and unity. The latter represents the case of no resuspension $v_u = 0$ and $\beta = 1$, reducing (20) to (3) and the former of no sedimentation $v_d = 0$, reducing (20) to

$$m_1 = W/Q \quad (21)$$

In this case the settling flux is exactly balanced by the resuspension flux, resulting in zero net change and the concentration of solids is simply that of a conservative substance, as indicated by (21).

The bed concentration follows from substitution of (20) in (19):

$$m_2 = \frac{\alpha W/Q}{1 + \beta K_{s1} t_o} \quad (22)$$

Algebraic simplification yields

$$m_2 = \frac{W/Q}{\frac{1}{\beta} + \frac{v_d}{H_1} t_o} \quad (23)$$

For lakes or reservoirs of shallow or moderate depth ($H \sim 10M$), moderate high settling velocities ($v_s \sim 3M/DAY$) and low resuspension velocities

($v_u < 1\text{CM/YR}$), the β term is more than an order less than the sedimentation term and (22) reduces to

$$m_2 = \frac{W}{K_{d1} V} \quad (24)$$

in which

$$K_{d1} = \frac{v_d}{H_1}$$

b) Toxic Substances

The equations for the toxic substance are developed in an identical fashion as in the Type I Analysis. Each phase in the water column, the dissolved, c , and the particulate, p , is analyzed separately with adsorption and desorption kinetics in addition to the input, outflow and settling terms. Furthermore, allowance is made for the exchange of the dissolved component between the water and the bed, expressed in terms of the difference in the dissolved concentrations. Addition of the two equations cancels the adsorption-desorption terms and yields:

$$\frac{dc_{T1}}{dt} = \frac{W_{ct}}{V_1} - \frac{c_{T1}}{t_o} - K_{s1} p_1 + K_{u1} p_2 + K_{b1} (c_2 - c_1) \quad (25)$$

in which

the subscript 1 refers to the water column and 2 to the bed

c_{T1} = total concentration of toxic in the water column

$K_{s1} = \frac{v_s}{H_1}$ = settling coefficient (1/T)

$K_{u1} = \frac{v_u}{H_1}$ = resuspension coefficient (1/T)

$K_{b1} = \frac{K_m}{H_1}$ = dissolved exchange coefficient (1/T)

K_m = transfer coefficient of the dissolved between water and bed ($\frac{1}{T}$)

Expressing p and c as fractions of the total concentration (equation 4 of the previous chapter) and combining similar terms yields:

$$\frac{dc_{T1}}{dt} = \frac{W_{cT}}{V} - \left[\frac{1}{t} + f_{p1} K_{s1} + f_{d1} K_{b1} \right] c_{T1} + \left[f_{p2} K_{u1} + f_{d2} K_{b1} \right] c_{T2} \quad (26)$$

the bed equation is developed in a similar fashion

$$-\frac{dc_{T_2}}{dt} = [f_{p_1} K_{s_2} + f_{d_1} K_{b_2}] c_{T_1} - [f_{p_2} (K_{u_2} + K_{d_2}) + f_{d_2} K_{b_2}] c_{T_2} \quad (27)$$

in which

$f_{p_{1,2}}$ = particulate fraction in each segment, 1 and 2

$f_{d_{1,2}}$ = dissolved fraction in each segment, 1 and 2

The working equations for the steady-state condition are developed in a manner similar to that of the solids. Under steady state conditions, the total concentration in the bed is expressed in terms of the total concentration in the water with equation (27). Substitution of (27) in (26) yields the water concentration as a function of the input load, W, and the parameters of the system. Since $m_2 \gg m_1$ and $\eta m_2 \gg 1$, $f_{p_2} \sim 1$ and $f_{d_2} \sim 0$. For this simplification, which is realistic for $\eta > 1000$, the water and bed concentrations are respectively

$$c_{T_1} = \frac{W/Q}{1 + \beta f_d [\eta m_1 K_{s_1} + K_{b_1}]} t_o \quad (28)$$

$$c_{T_2} = \frac{f_p K_{s_2} + f_d K_{b_2}}{K_{u_2} K_{d_2}} c_{T_1} \quad (29)$$

in which

$$\beta = \frac{v_u}{v_u + v_d}$$

$$f_d = \frac{1}{1 + \eta m_1}$$

$$f_p = \frac{\eta m_1}{1 + \eta m_1}$$

$$K_s = \frac{v_s}{H}$$

$$K_b = \frac{K_m}{H}$$

$$K_u = \frac{v_o}{H}$$

$$K_d = \frac{v_d}{H}$$

For the condition of negligible exchange of the dissolved between water and bed ($K_b \sim 0$), the above equations reduce to

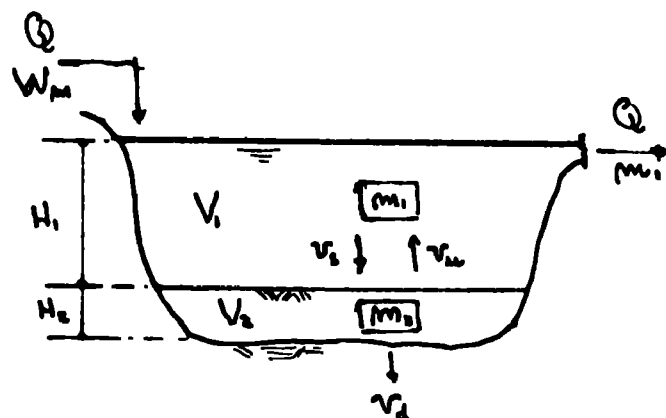
$$c_{T_1} = \frac{W/Q}{1 + \beta f_{p_1} K_{s_1} t_o} \quad (30)$$

$$c_{T_2} = \alpha c_{T_1} \quad (31)$$

in which, in accordance with equation 14

$$\alpha = \frac{v_s}{v_u + v_d}$$

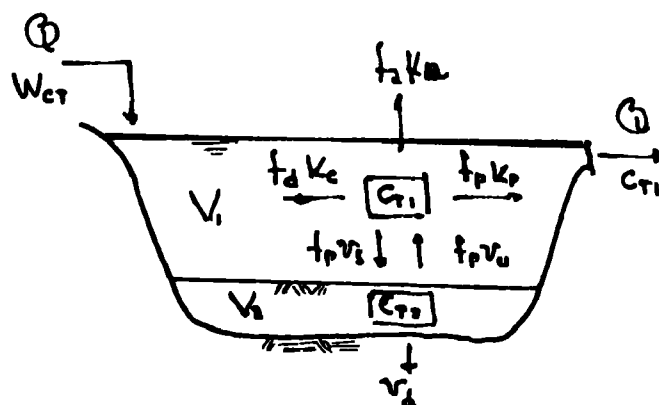
For toxics of high partition coefficient and systems of high solids ($\tau_{m_1} \geq 5$), the above respectively reduce to equations (21) and (19), the equivalent solids equations.



SOLIDS

SUBSCRIPTS

- 1 WATER
- 2 BED



TOXIC

ANALYSIS TYPE RESUSPENSION

- I $v_{rs} = 0$
 - II $v_{rs} > 0$
- Bed Transport zero

LEGEND

UNITS

W	MASS INFLUX	M/T
Q	FLOW	L ³ /T
V	VOLUME	L ³
H	DEPTH	L
m	SOLIDS	M/L ³
C _T	TOXIC-TOTAL	M/L ³
f _d	DISSOLVED FRACTION	-
f _p	PARTICULATE FRACTION	-
v _s	SETTLING VELOCITY	L/T
v _{rs}	RESUSPENSION VELOCITY	"
v _d	SEDIMENTATION VELOCITY	"
K _e	EVAPORATION COEFFICIENT	1/T
K _c	DISSOLVED DECAY	"
K _s	SETTLING COEFFICIENT	"
K _p	PARTICULATE DECAY	"

FIG. B-1 Schematic of Type I & Type II Solids Parameters

TYPE I ANALYSIS

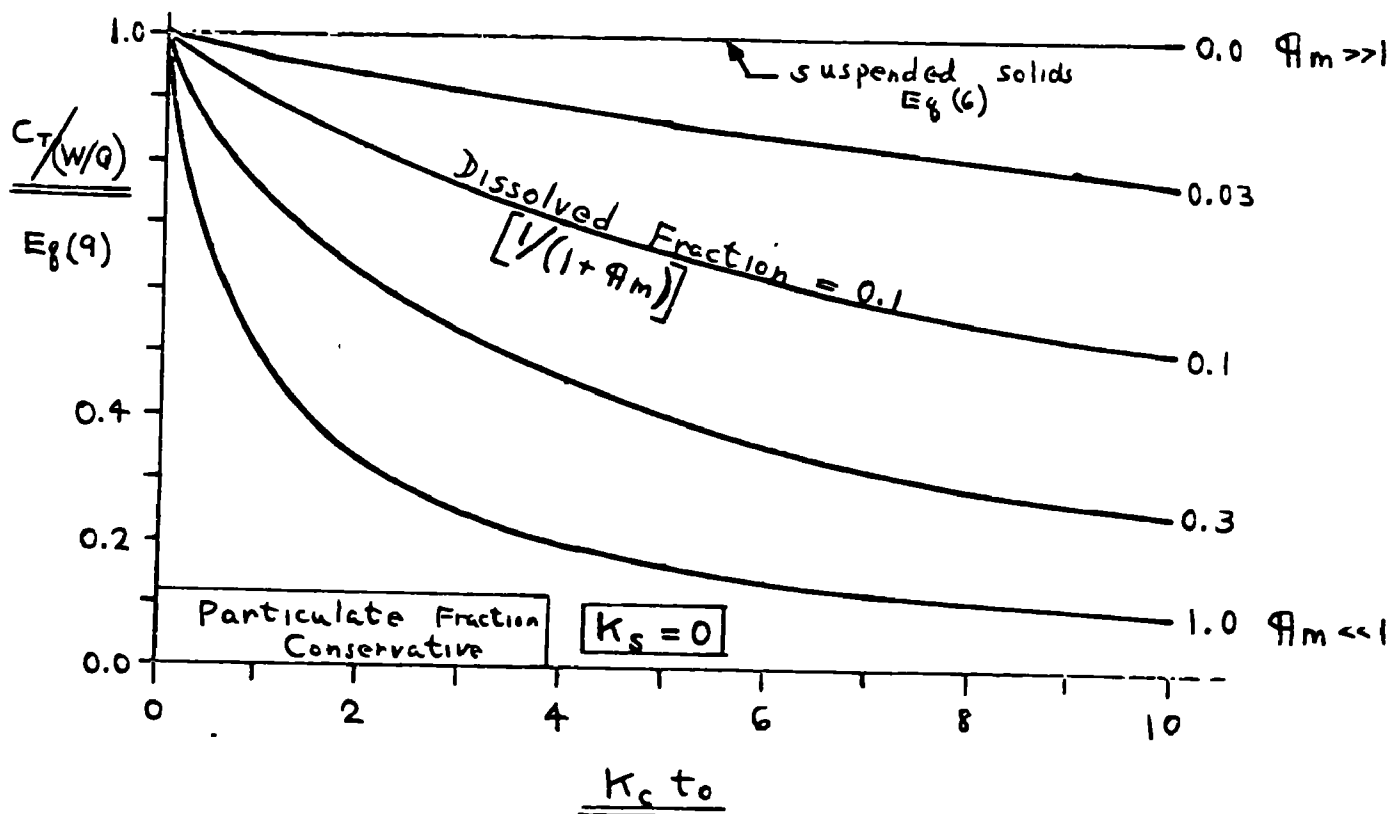
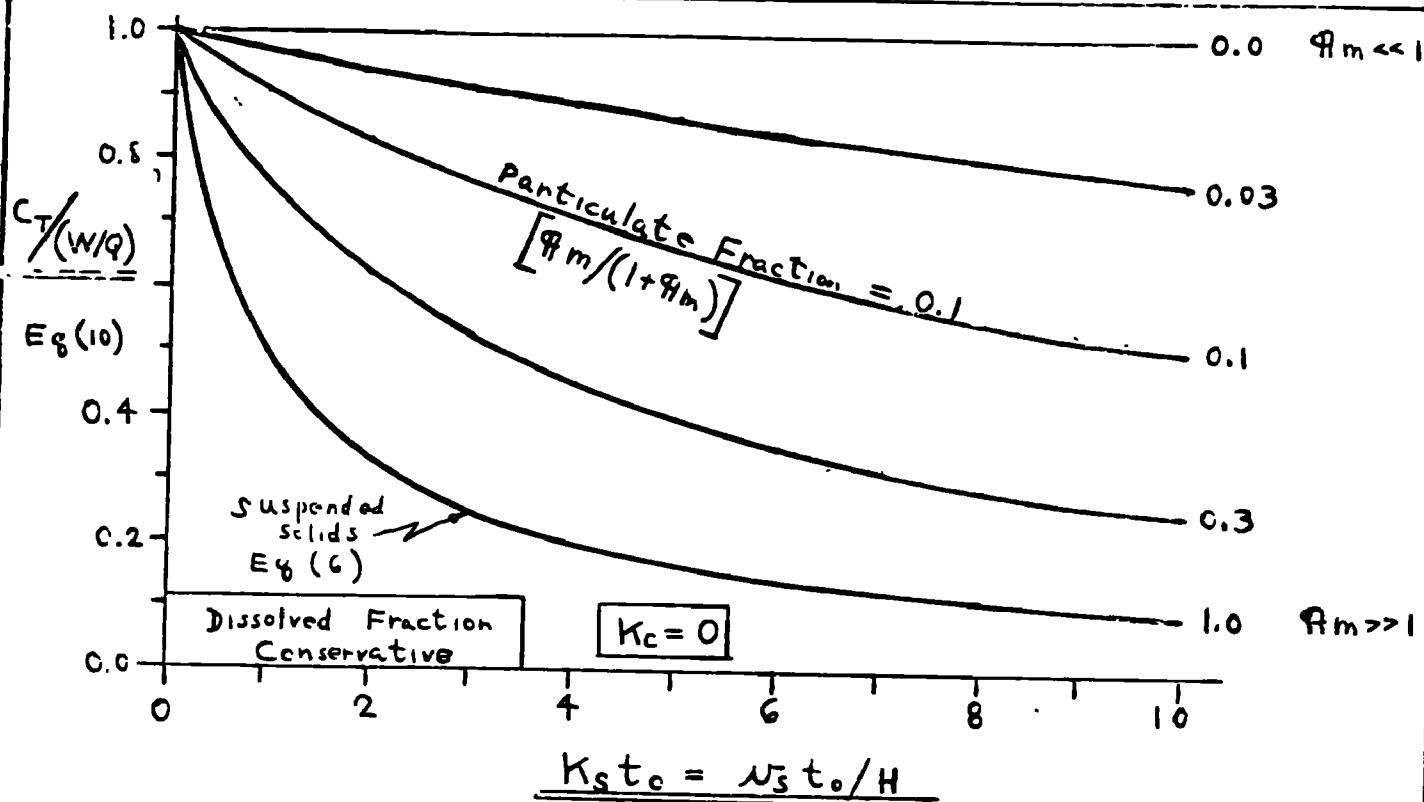


FIG. B-2 Fraction Remaining for Various Detention Times and Kinetic Parameters

TYPE I ANALYSIS

$f_p = 0.02$

$f_p = 0.2$

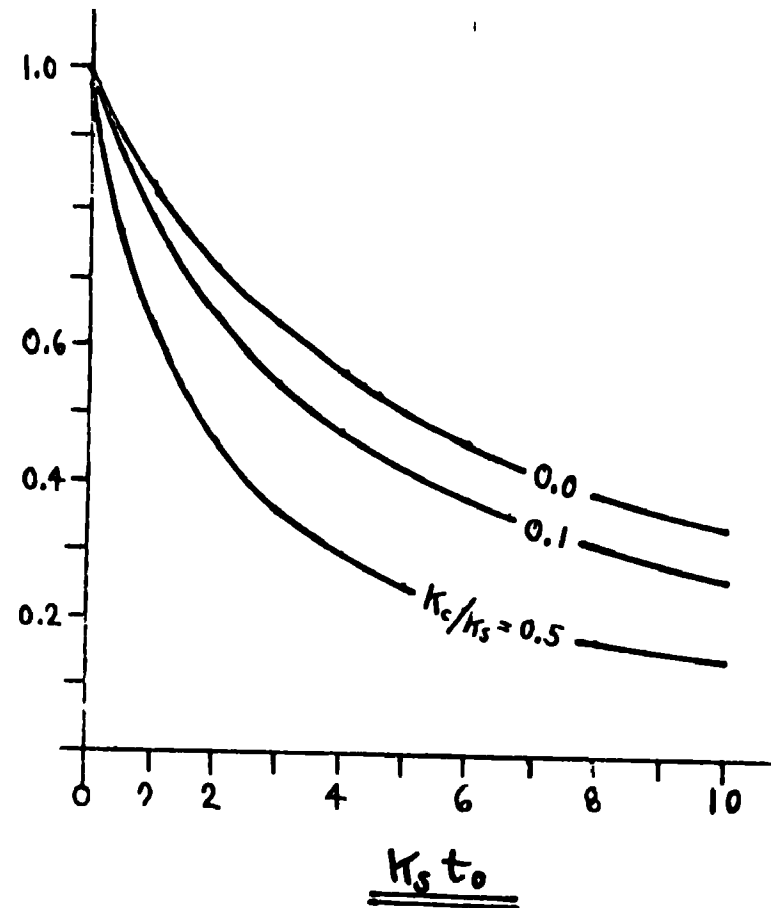
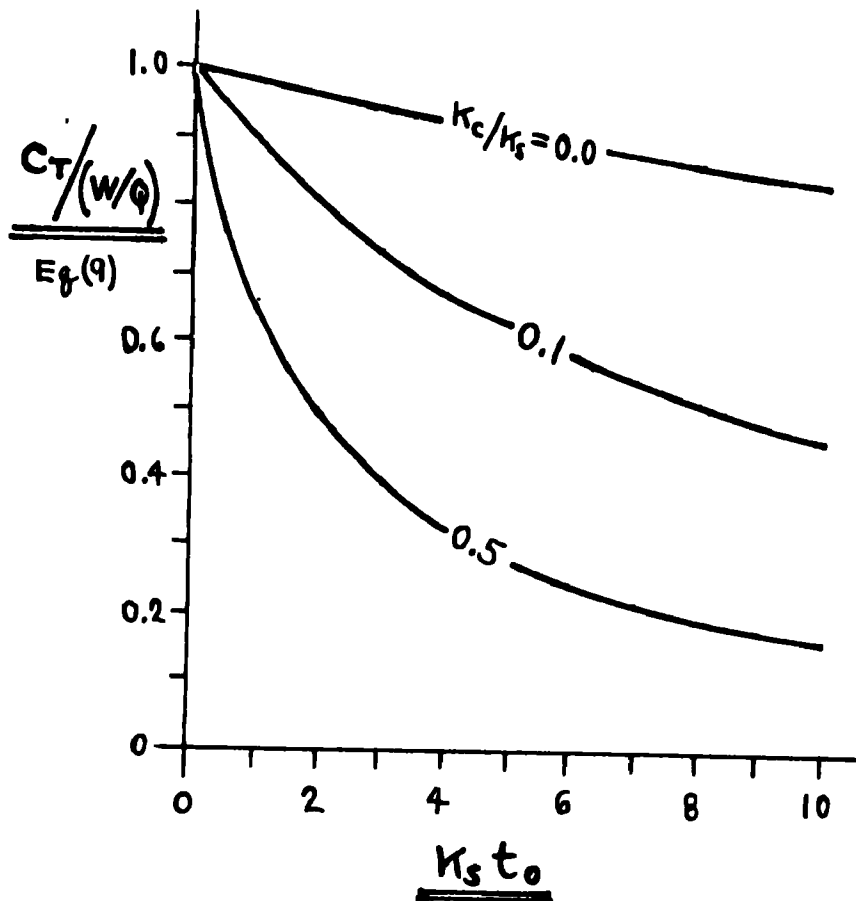


FIG. B-2 (cont'd) Fraction Remaining for Various Detention Times and Kinetic Parameters

Saginaw Bay - Solids and PCB Model*

Steady State Toxicant Model - Theory

In order to understand the interactions between sediments, water column solids and a given toxicant, several time variable models have been employed. These models attempt to incorporate the mechanisms of solids settling, sediment resuspension, net sedimentation and transfer to the deep sediments, interstitial diffusion of dissolved toxicant and other decay and transfer mechanisms. The difficulty with the more complex interactive time variable toxicant models is that the specification of the various parameters (e.g. resuspension velocity and surface sediment solids concentration) is not unique and various combinations of the parameters, within reported ranges, yield a similar calibration.

Consequently, it is desirable that a procedure be developed that utilizes available field data for calibration and that minimizes the number of parameters that must be specified. A simplified steady state approach provides a direction. Since the analysis framework is steady state, questions related to the time it would take to reach a new equilibrium state cannot be answered. Furthermore, the time for the entire system of water column and sediment to reach steady state may be long. On the other hand, as noted above, complex time variable models sometimes tend to obscure the principle mechanisms of net settling and water column-sediment exchanges. A steady state framework, therefore, is a simplified

* Robert V. Thomann and John A. Mueller

first approximation to chemical fate that does not address issues related to temporal questions but does provide a useful model for estimating chemical concentrations in a simpler way.

Suspended Solids Model

Consider first the steady state model for suspended solids in a multi-dimensional system. It is assumed that the bed sediment that is coupled to the water column is stationary. Figure 10 shows a definition sketch. The mass balance equation for the solids in segments #1, and 1s, using backward finite differences is

$$0 = W_1 - Q_{12}M_1 + E'_{12}(M_2 - M_1) - v_{s1}AM_1 + v_{ul}AM_{1s} \quad (10)$$

$$0 = v_{s1}AM_1 - v_{ul}AM_{1s} - v_{sdl}AM_{1s} \quad (11)$$

where M_1 and M_2 = solids concentration in water column segment 1,2
 $[M_s/L^3_{w+s}; L_{w+s}$ = volume of water plus solids]

M_{1s} = solids concentration in sediment segment, 1s
 $[M_s/L^3_{w+s}]$

W_1 = input solids loading $[M_s/T; M_s = \text{mass of solids}]$

Q_{12} = flow from segment 1 to 2 $[L^3_w/T]; A = \text{sediment area } [L^2]$

E'_{12} = bulk dispersion between 1 and 2 $[L^3_w/T]$

v_{s1} = settling velocity $[L/T]$

v_{ul} = resuspension velocity $[L/T]$

v_{sdl} = sedimentation velocity $[L/T]$

A similar set of equations can be written for segments 2 and 2s.

Equation (11) can be solved for the sediment concentration as:

$$M_{1s} = \left[\frac{v_{s1}}{v_{ul} + v_{sdl}} \right] M_1 = \alpha_1 M_1 \quad (12)$$

where $\alpha_1 = \frac{v_{s1}}{v_{ul} + v_{sdl}}$

Substituting eq. (12) into eq. (10) and simplifying gives:

$$0 = W_1 - Q_{12} M_1 + E'_{12} (M_2 - M_1) - w_{s1} AM_1 \quad (13)$$

where w_{s1} is the net loss of solids from water column segment #1 and is given by

$$w_{s1} = \frac{v_{s1} v_{sdl}}{v_{u1} + v_{sdl}} \quad (14)$$

Note that eq. (13) essentially states that for a multi-dimensional system such as Saginaw Bay, the sediment interaction can be substituted out of the equation set and incorporated in the net loss parameter, w_{s1} . A mass balance around the sediment segment then yields

$$v_{sdl} AM_{1s} = w_{s1} AM_1 \quad (15)$$

which simply states that the solids flux into the sediment layer from the water column is balanced by the solids flux leaving the sediment segment due to net sedimentation. In principle, the net sedimentation velocity can be measured so that the solids concentration in the sediment can be calculated from eq. (15). In practice, however, the spatial variability in the sedimentation velocity and the uncertainty in the sediment solids concentration that interact with the water column make it difficult to separate the two quantities. This is a reflection of the occurrence of nepheloid layers or "fluff" layers that are at the boundary between the water column and the bed sediment. As a consequence, in the absence of detailed data on v_{sdl} or M_{1s} , only the net flux to the sediment from the water column can be estimated. This assumes, of course, that all terms in the water column equation (13) are known with more certainty than the sedimentation velocity or the sediment solids.

If now suspended solids data are available for the water column then the equation set represented by eq. (13) can be used to obtain spatially varying estimates of w_{si} for any segment i . Note that the sediment segments are not included directly in the model but are incorporated in the net loss term.

Preliminary estimates of w_{si} may be obtained from eq. (15) or from solving eq. (13) directly for w_{si} with given water column solids concentrations. These estimates, however, may be subject to wide variations, including inconsistency in net sedimentation as a result of small changes in water column concentrations. The procedure finally adopted in this research was to obtain estimates of w_{si} from trial and error calculations of the water column model to calibrate to the observed suspended solids concentrations. A single set of net loss rates is then obtained that balances mass in the water column and sediment but does not require specification of the settling or resuspension velocities.

For the case of net gain from sediment, that is a steady state erosion zone, the water column equation is:

$$0 = W_1 - Q_{12}M_1 + E'_{12} (M_2 - M_1) + v_{uB}AM_{1sB} \quad (16)$$

where v_{uB} is scour velocity and M_{1sB} is sediment solids concentration available for scour.

$$\text{Let } W_1 - Q_{12}M_1 + E'_{12} (M_2 - M_1) = m \quad (17)$$

where $m[M/T]$ is the net production (loss) of solids.

A useful procedure for this case is then:

1) Compute m , the net mass production or loss of solids for each segment

2) If m positive, then

$$m = w_{s1}AM_1 \text{ and}$$

$$w_{s1} = \frac{m}{AM_1}$$

3) If m negative, then

$$m = v_{uB} A M_{lsB}$$

and if desired, v_{uB} the net scour velocity can be calculated.

Toxicant Model

The basic objective of the steady state toxicant model is to obtain a modeling framework that utilizes available field data for calibration, and eliminates the need for directly specifying sediment-water interactions. The approach then is not from first principles of detailed mechanisms of settling, resuspension and interstitial diffusion, but rather from an analysis of field data. It is assumed that laboratory data are available for the following:

- 1) water column rates of degradation, photolysis, vaporization, hydrolysis
- 2) sediment microbial degradation rates
- 3) partition coefficients at water column and sediment solids concentrations.

The available field data are combined with these laboratory data in such a way that overall loss and transfer coefficients are obtained.

The analysis begins from the point where the dissolved and particulate fractions of the chemical have been assumed in local equilibrium, and the total toxicant mass balance equation for a given segment has been obtained. The equation for segment 1 is then:

$$\begin{aligned}
 0 = & W_{T1} - Q_{12} C_{T1} + E'_{12} (C_{T2} - C_{T1}) - v_{s1} A f_{p1} C_{T1} \\
 & + v_{u1} A f_{pls} C_{T1s} + E'_{1s} F_{D1s} C_{T1s} - E'_{1s} f_{D1} C_{T1} \\
 & - K_{11,1} f_{D1} v_1 C_{T1}
 \end{aligned} \tag{13}$$

The equation for the sediment segment, #1s is

$$0 = v_{sl} A f_{pl} c_{Tl} - v_{ul} A f_{pls} c_{Tls} + E'_{ls} f_{Dl} c_{Tl} - E'_{ls} f_{Dls} c_{Tls} - v_{sdl} f_{pls} A c_{Tls} - K_{11,s} f_{Dls} V_{ls} c_{Tls} \quad (19)$$

where W_{Tl} = input toxicant loading $[M_T/T]$

c_{Tl}, c_{T2}, c_{Tls} = total toxicant concentration in segments 1, 2 and 1s respectively $[M_T/L_{w+s}]$

$K_{11,1}$ = overall loss rate of dissolved form (e.g. vaporization, decay) $[1/T]$

$K_{11,s}$ = decay of dissolved toxicant in sediment $[1/T]$

V_1, V_{1s} = volumes of segments 1 and 1s respectively $[L_{w+s}^3]$

E'_{ls} = interstitial water sediment - water column diffusion coefficient $[L_w^3/T]$

The fraction of toxicant in the particulate form is given by

$$f_{pl} = \frac{\pi_1 M_1}{1 + \pi_1 M_1} \quad (20)$$

and the fraction dissolved is

$$f_{Dl} = \frac{1}{1 + \pi_1 M_1} \quad (21)$$

where π_1 is the partition coefficient $[M_T/M_s \div M_T/L_{w+s}^3]$ at ambient water column solids concentrations.

Similar expressions are used for f_{pls} and f_{Dls} , the fraction particulate and dissolved respectively in the sediment segment, 1s, that is,

$$f_{pls} = \frac{\pi_{1s} M_{1s}}{1 + \pi_{1s} M_{1s}} \quad (22)$$

$$\text{and } f_{Dls} = 1 / (1 + \pi_{1s} M_{1s}) \quad (23)$$

where π_{1s} is the partition coefficient at ambient sediment solids concentrations.

If now equations (9) and (10) are added, one obtains an interesting result:

$$0 = W_{T1} - Q_{12} c_{T1} + E'_{12} (c_{T2} - c_{T1}) - K_{11} f_{D1} V_1 c_{T1} - v_{sd1} f_{pls} A c_{T1s} - K_{11s} f_{D1s} V_{1s} c_{T1s} \quad (24)$$

It can be noted that all of the sediment interaction terms are eliminated through the addition of the equations. This is a result of taking the mass balance around the water column and sediment so that the only loss terms are those that are net from the entire system. These net loss terms are fluxes out due to transport and dispersion, decay in water column and sediment and net sedimentation of mass out of the sediment segment. Of course, equation (24) still includes the sediment total toxicant concentration.

Therefore, let

$$\alpha_{T1} = \frac{c_{T1s}}{c_{T1}} = \Pi \frac{M_{1s}}{f_{pls}} \quad (25)$$

$$\text{where } \Pi = \frac{r_{1s}}{c_{T1}} \frac{[M_T/M_s] \text{ sed.}}{[M_T + L_{ws}^3] \text{ water}} \quad (26)$$

where r_{1s} is the toxicant concentration on a solids basis in the sediment.

The variable Π represents an overall partitioning between the solids toxicant concentration in the sediment and the total toxicant concentration in the water column. Note also from the solids balance discussed previously

$$\alpha_{T1} = \left(\frac{w_{s1}}{v_{sd1}} \right) \left(\frac{f_{p1}}{f_{pls}} \right) \left(\frac{r_{1s}}{r_1} \right) \quad (27)$$

where r_1 is the water column toxicant concentration on a solids basis $[M_T/M_s]$. Substituting eq. (25) into (24) and simplifying gives:

$$0 = W_{T1} - Q_{12} c_{T1} + E'_{12} (c_{T2} - c_{T1}) - w_{T1} A c_{T1} \quad (28)$$

where w_{T1} [L/T] is the net loss of toxicant and is given by

$$w_{T1} = K_{11} f_{D1} H_1 + \alpha_{T1} [v_{sd1} f_{pls} + K_{11s} f_{D1s} H_{1s}]$$

where H_1 and H_{1s} are the depths of the water column and sediment respectively.

Equation (28) is a mass balance on the water column toxicant only and all sediment interactions are embedded in the net loss of toxicant w_{T1} . The estimate of this net loss rate can be obtained from the water column field data and a finite segment water quality model without sediment segments. The procedure then is

1) From c_{T1} , estimate w_{T1} for each segment using a water column model

2) From w_{T1} and laboratory data on decay rates in water column and sediment, and partition coefficients, and estimates of net sedimentation from field data and the solids balance model, compute α_{T1} from eq. (29) as

$$\alpha_{T1} = \frac{w_{T1} - K_{11} f_{D1} H_1}{\beta_1} \quad (30)$$

where $\beta_1 = v_{sd1} f_{pls} + K_{11s} f_{D1s} H_{1s}$

3) Calculate the sediment toxicant concentration from eq. (27) as

$$r_{1s} = [\alpha_{T1} \left(\frac{f_{pls}}{f_{pl}} \right) \left(\frac{v_{sd1}}{w_{s1}} \right)] r_1 \quad (31)$$

The latter calculation can be used as an additional calibration for the model if data on r_{1s} , the sediment toxicant concentration are available. Such is the usual case.

A very useful special case is obtained for those toxicants that are highly sorbed to solids and for which sediment decay and diffusion processes are negligible. PCBs are an example. If then it is assumed that K_{11s} and E'_{1s} are zero, then it can be shown that

$$w_{T1} = K_{11} f_{D1} H_1 + f_{pl} w_{s1} \quad (32)$$

and $r_{1s} = r_1$

(3)

This result indicates that for PCB, if the net solids loss to the sediment, w_{s1} can be obtained and information is available on the partition coefficient, then the entire steady state PCB problem can be approached through the simple equations (32) and (33). For the case of no net sedimentation, then $w_{s1} = 0$ and

$$w_{T1} = K_{11} f_{D1} H_1$$

and $r_{1s} = r_1$.

These special case models for $K_{11}=0$ were applied to the PCB distribution in Saginaw Bay.

Application: Saginaw Bay Solids & PCB Model

After a considerable amount of time variable modeling on Saginaw Bay, including long-term calculations for the Great Lakes of Cesium-137, it was determined that the initial thrust on Saginaw Bay could best be accomplished via the steady-state model previously discussed that incorporates horizontal transport, net solids settling and resuspension and sedimentation, and the interaction of the solids with PCBs. Accordingly, the 5 segment Saginaw Bay model was prepared for a steady-state computation.

Segmentation & Transport Coefficients

The segmentation was obtained from the Grosse Ile Laboratory of the EPA under this cooperative agreement, including segment volumes, areas and depths. The dispersive exchange coefficients and the flows between each of the segments and Lake Huron were also obtained from hydrodynamic modeling conducted by the Grosse Ile Laboratory. That work, however, concentrated on the time variable aspects of 1977 and 1979 and, as a result, the coefficients of turbulent exchange and flow have to be modified to represent a long-term steady-state condition. The temporally averaged flows and exchange coefficients that were used in the

steady-state computation for the five segments in the water column are as shown in figure 11 together with the segmentation.

A chloride calibration was then performed using these flows and bulk dispersion values. Chloride data were obtained from STORET for the years 1974 through 1977 and all data found in a segment were averaged for each annual period for that segment. Loadings consisted of the Saginaw River discharge and atmospheric sources (6670 kg/day), the latter values obtained from data in IJC (1977). Saginaw River chloride loadings for 1974 were estimated to be from 1.04 to 1.15 million kg/day according to Grosse Ile and Canale, and the 1977 discharge was 0.8 million kg/day as per Grosse Ile. For the simulation, the 1977 value was used. Boundary conditions were selected to be 6.3 mg/l for both segment 4 and 5 on the basis of available STORET data nearest the open lake boundary of the model. The comparison of calculated concentrations of chlorides with the 1974-1977 data in figure 12 indicates good agreement and, therefore, confirms the transport and dispersion regime as representative of steady state conditions.

Suspended Solids Calibration

The Saginaw River and smaller tributaries to the Bay, shoreline erosion, atmospheric fallout and phytoplankton biomass are the components of solids loads used to calibrate the solids in Saginaw Bay. Grosse Ile provided a long-term estimate of the Saginaw River load, whereas the contributions of other tributary drainage areas were estimated from average flows and a long-term average suspended solids concentration estimated for the Saginaw River. Bank erosion values were derived from county by county erosion volumes in Monteith and Sonzogni (1976) and proportioned to Saginaw Bay on the basis of shoreline length. Volumes of eroded material were converted to mass loadings by assuming a porosity of approximately 60% and a specific gravity of 2.65. To account for immediate settling of heavier fractions, a 50% reduction was used to obtain the final estimates. Atmospheric sources were obtained from the IJC report cited previously. Phytoplankton biomass was obtained from a algal model simulation performed

by the Grosse Ile Laboratory. A summary of all segment loads by class is contained in Table 2. The predominance of the Saginaw River and phytoplankton loadings is apparent.

Boundary conditions, consistent with limited available data, were selected primarily on the basis of trial and error. Preliminary computations indicated that initial estimates of approximately 2 mg/l solids at the open lake boundary were too low since calculated solids concentrations in segments 4 and 5 were well below observed values and mass balances of these segments indicated that the boundary fluxes dominated these segments. Final values of 4.3 mg/l for segment 4 and 5.5 mg/l for segment 5 were selected. The former value is thought to be more associated with advective flow entering the Bay from Lake Huron and the latter value more representative of observed segment 5 concentrations leaving the Bay with the net advective flow (see net circulation, figure 11).

Net removal rates of the suspended solids were then assigned to segments 2, 4, and 5 where solids deposition zones are either documented to occur (segment 2) or estimated to occur (segments 4 and 5). No net removal rates were assigned to segments 1 and 3 since sedimentation appeared to be minimal there on the basis of sediment solids and PCB data in sediment cores. Initial values of the net removal rates were made from mass balances of each segment using observed water column solids concentrations. There were then input to the 5 segment Saginaw Bay model, using the transport coefficients previously calibrated, and adjusted until the calculated and observed suspended solids concentrations were in agreement. As seen in figure 13, the calculated values in the water column are in good agreement with the observed data of 1976 through 1979, when values of the net removal rate of 12.7, 13.8 and 9.7 meters/year are used for segments 2, 4 and 5 respectively. Sensitivity analyses indicate that the differences in the net loss rates in segments 2, 4 and 5 are not significant. Equally acceptable calibrations are obtained for values between 10 and 20 m/yr. for segments 2, 4 and 5.

With the estimated net removal rate of solids w_s from the water column, the flux of solids into the bed is calculated as $w_{sl} AM_1$ [M_s/T]. This is equal to the sedimentation flux which is calculated as $v_{sdl} AM_{1s}$. Since both v_{sdl} and M_{1s} vary with sediment depth, no single value can be specified. However, from eq. (15) the relationship between v_{sdl} and M_{1s} is unique. If v_{sdl} is selected, then M_{1s} is a predetermined value. Log-log plots of the relationships between the sedimentation rate and the bed solids concentration are included in the bottom of figure 13.

A considerable amount of effort was expended in determining the sediment concentrations of solids drawing on the work of Robbins (1980). From sediment cores located primarily in segment 2 of the Saginaw Bay model, a selected number of cores were examined for the sediment solids concentration at the midpoints of a 10 cm well-mixed layer and at the midpoints of two deeper 5 cm layers. The results are summarized in Table 3. For the well-mixed surface sediment layer, sediment concentrations average approximately 390,000 mg/l for nine cores with a range of approximately 230,000 to 900,000 mg/l. This range is shown in figure 13 for segment 2. If the lower value of the range is used, the corresponding sedimentation rate for the 10 cm well-mixed layer would be approximately 0.8 mm/yr., somewhat less than a previously reported value of 3 mm/yr. (Robbins, 1980).

These results indicate the utility of the simple steady state solids balance. The water column data are known with some accuracy and do not exhibit marked spatial gradients. Note that the maximum spatial differences in the average water column suspended solids is about a factor of four. In contrast, the spatial heterogeneity of the sediment is quite marked with regions of deposition, scour and no apparent net deposition. Suspended solids may then vary markedly in a given segment horizontally, but, most importantly, vertically. Boundary layer sediment solids "fluff" layers may be available for interaction with the surface water column at concentrations less than sediment data from cores. Conversely, estimated net

sedimentation velocities are often cited only for those regions of deposition and not over an area equivalent to a model segment of Saginaw Bay. The calculation discussed above provides a good estimate of the net flux to the sediment over the segment area. The trade off between net sedimentation over the segment area and sediment solids concentrations is shown in the lower figures of figure 13. If, as noted above, the solids data from the sediment cores are used, then the net sedimentation velocity varies from 0.25 to 0.8 mm/yr. or almost one order of magnitude less than the 3mm/yr. previously cited. If on the other hand, an average net sedimentation over the entire area of segment 2 is fixed at say 3 mm/yr., then the sediment solids concentration that is consistent with that sedimentation velocity is about 45,000 mg/l or one order of magnitude less than the average sediment solids in the top 5 cm of the cores. The results indicate, therefore, that with only the net flux of solids to the sediment as known with some confidence, then it is not possible to uniquely specify the net sedimentation or boundary layer sediment solids. Additional tracers (of which the radionuclides or PCBs are examples) would provide additional information that could aid in specifying the net sedimentation and sediment solids concentrations.

A mass balance of suspended solids for the entire model is presented in figure 14 for three flux categories: the external and internal loads, the net flux removed from the water column and the boundary transport. In the lower right panel, it is seen that 2,970,000 lb/day of solids enter the model, 40% (1,190,00 lb/day) is incorporated into the sediments, and the remaining 60% (1,780,000 lb/day) leaves the Bay and enters Lake Huron.

PCB Calibration

With the horizontal transport and net loss rate of suspended solids calibrated, analysis of the PCB concentrations can proceed. Total PCB loadings were obtained from the Grosre Ile Laboratory for 1979, the first year for which total PCB field data were available. As noted in Table 4, the Saginaw River load is approximately 75% of the total load and atmospheric

sources contribute an additional 25%. Although open lake concentrations are reported to be in the 1 ng/l range, the boundary condition was selected as 10 ng/l - the value needed to calibrate observed data in segments 4 and 5.

Partition coefficients were selected on the basis of observed dissolved and particulate fractions and values of 10,000, 50,000 and 100,000 $\mu\text{g/kg}$ per $\mu\text{g/l}$ were selected for segments 1, 2 and 3, and 4 and 5, respectively. These are in accord with values calculated from field measurements, as seen in Table 5. With the partition coefficients selected, the removal rates of total PCB are then calculated as the particulate fraction of the suspended solids net settling rate (see eq. (32) for $K_{11}=0$). For segment 2, for example, the net removal rate w_{T2} is:

$$w_{T2} = w_{s2} \times f_{p2}$$

$$\text{where } f_{p2} = \frac{2M_2}{1 + 2M_2} = \frac{(.05)(11.2)}{1 + (.05)(11.7)} = 0.37$$

$$\text{and then } w_{T2} = (12.7)(.37) = 4.7 \text{ m/yr.}$$

Similarly, the net total PCB removal rates for segments 4 and 5 are 4.8 and 3.5 m/yr., respectively.

With the loads, boundary conditions and net removal rates described above, together with the horizontal transport, the steady state model is used to calculate total PCB concentrations in the water column. The top panel of figure 15 shows the agreement between calculated values and data observed in 1979. Dissolved and particulate fractions also agree well with observed data, as noted in the next two panels of the figure. The bottom panel displays the particulate PCB per unit weight of solids and, again, agreement between observed means and calculated values is good for the water column.

In the previous theoretical section of this report, it was shown that, for depositional areas, and areas where settling and resuspension were equal, the PCB per unit weight of solids in the water column (r_1) - a reproduction of the

bottom panel of figure 15. Directly below, is a plot of the PCB in the sediment (r_{1s}), where the solid line is the calculated value of r_{1s} assuming $r_{1s} = r_1$. The data are segment averaged sediment concentrations for 1979, provided by the Grosse Ile Laboratory. Agreement between calculated and observed means is good for segments 1 and 2. It is hypothesized that segment 3 may be a net erosion zone (see suspended solids calibration, figure 12) in which case the assumption that $r_{1s} = r_1$ is not appropriate.

A mass balance of total PCB is shown in figure 17 for the Saginaw River and atmospheric loads, net settling fluxes and boundary fluxes. As noted in the lower right panel, approximately 30% of the total PCB entering Saginaw Bay from external loads is incorporated into the sediments of the Bay and approximately 70% is exchanged with Lake Huron.

The separate effects of the external PCB loads (Saginaw River and atmospheric) and the boundary conditions are illustrated in figure 18. The total PCB due to both external loads and boundary conditions is compared with observed data in the top panel of the figure, where the peak concentration in segment 1 is seen to be approximately 24 ng/l. Of the 24 ng/l, approximately 6 ng/l is due to the boundary condition (center panel) and the remaining 18 ng/l is the effect of the loads. Thus, complete removal of the Saginaw River loads and maintenance of the boundary at 10 ng/l would result in at least a 75% reduction in the segment 1 PCB concentration under this new steady-state condition. Additional reduction would occur since some significant fraction of the boundary concentration is probably caused by the loads. Therefore, reducing the boundary concentration to lower open Lake Huron levels would reduce the concentration in segment 1. If, for example, the boundary decreased to a value of 5 ng/l, the concentration in segment 1, under the no-load situation, would be approximately 3 ng/l.

A mass balance of PCB for the external loads alone (figure 19) shows that approximately 10% of the load entering the Bay is incorporated in the sediment and 90% enters Lake

Huron - the bulk of it from segment 5. A similar balance for the boundary condition reveals a net source from Lake Huron into segment 4, and a net sink into the Bay sediments before the remaining mass returns to Lake Huron from segment 5 (figure 20).

Conclusion

A simplified procedure for estimating the concentrations of PCB in the water column and sediment of a water body due to external sources of PCB has been applied to Saginaw Bay. Due to its simplicity, many insights can be gained with respect to the factors governing the distribution of toxicant in a natural water system, including the net pathways of the material.

Further work is proceeding on testing the sensitivity of the results to the net removal rates and the impact of the PCB boundary conditions. The PCB simulation will be redone using 1979 flow and dispersion coefficients in order that transport and loading information would be synchronous.

TABLE 2

ESTIMATED LONG-TERM AVERAGE SUSPENDED SOLIDS INPUTS

Model Segment	Tributary Loads (lb/day)	Bank Erosion (lb/day)	Atmospheric Loads (lb/day)	Phytoplankton Mass (lb/day)	Total Loading (lb/day)
1	1,232,000*	28,200	10,100	132,200	1,402,500
2	123,900	92,600	31,400	341,600	589,500
3	34,900	63,900	15,100	143,300	257,200
4	21,900	124,100	23,700	176,300	346,000
5	43,700	50,700	24,700	251,300	370,400
Total	1,456,400	359,500	105,000	1,044,700	2,965,600

*Saginaw River 1,208,000

TABLE 3
SEDIMENT SOLIDS CONCENTRATIONS (1)Core Solids Concentrations (mg/l (Bulk))
at Following Depths

Station (2)	5 cm	12.5cm	17.5 cm
1A	510,000	1,350,000	1,130,000
6A	250,000	700,000	730,000
11A	230,000	560,000	620,000
24-1	280,000	390,000	507,000
37-1	900,000	1,040,000	730,000
43-1	340,000	420,000	450,000
46-1	280,000	450,000	850,000
50-A	250,000	340,000	420,000
28-A	450,000	790,000	1,070,000
Mean	390,000	670,000	720,000
Std.Dev.	200,000	320,000	240,000

(1) Data from Robbins (1980)

(2) Stations all in Saginaw Bay model segment 2.

TABLE 4
ESTIMATED TOTAL PCB LOADING FOR 1979⁽¹⁾

Segment	Tributary Loads (lb/day)	Atmospheric Loads (lb/day)	Total Loading (lb/day)
1	1.61 ⁽²⁾	0.05	1.66
2	-	0.16	0.16
3	-	0.07	0.07
4	-	0.12	0.12
5	-	0.12	0.12
Totals	1.61	0.52	2.13

(1) Source: USEPA ERL Grosse Ile

(2) Saginaw River

TABLE 5
Total PCB PARTITION COEFFICIENTS⁽¹⁾

Segment	Partition Coefficient (π) from Observed Concentrations		π Used in Model
	<u>Mean</u>	<u>Approx. Range</u>	
1	10,000	700- 30,000	10,000
2	80,000	7,000-190,000	50,000
3	60,000	20,000-160,000	50,000
4	90,000	10,000-250,000	100,000
5	280,000	10,000-920,000	100,000

(1) All values in $\mu\text{g}/\bar{\text{K}}\text{g}$ per $\mu\text{g}/\text{l}$

Data from Grosse Ile Laboratory (1979)

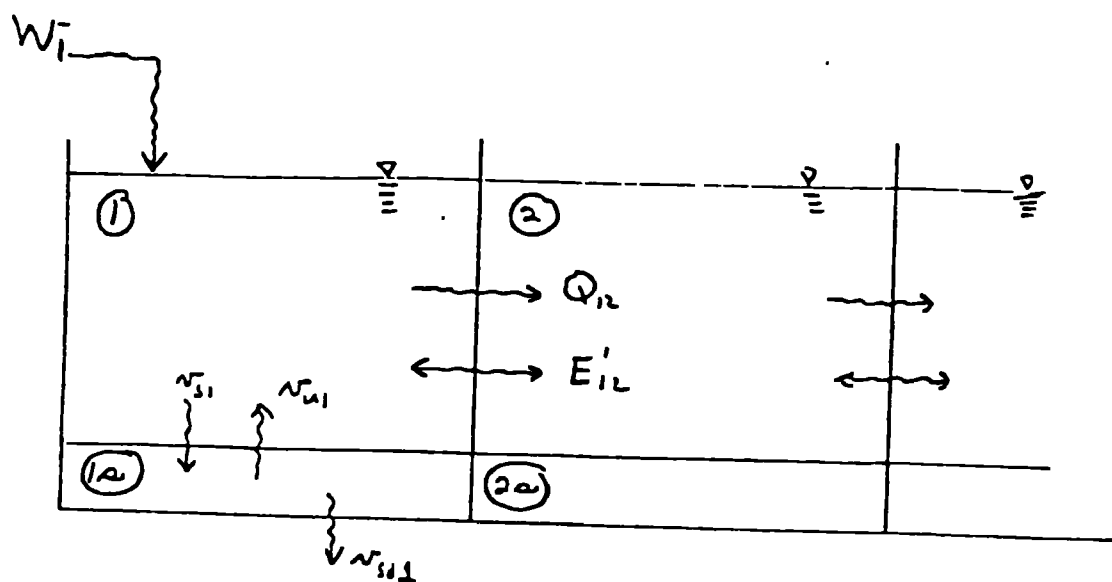


Fig. 10 Definition sketch for steady state model.

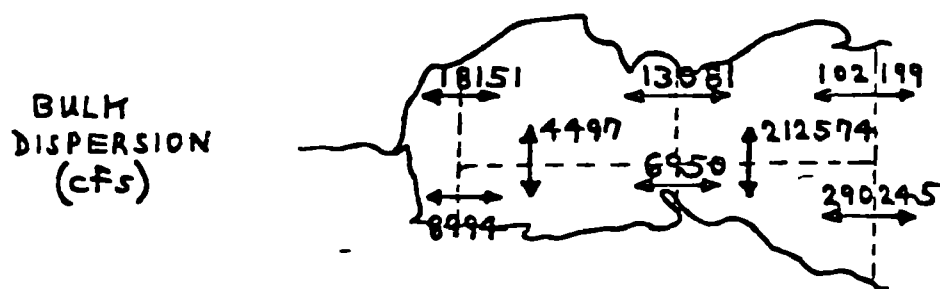
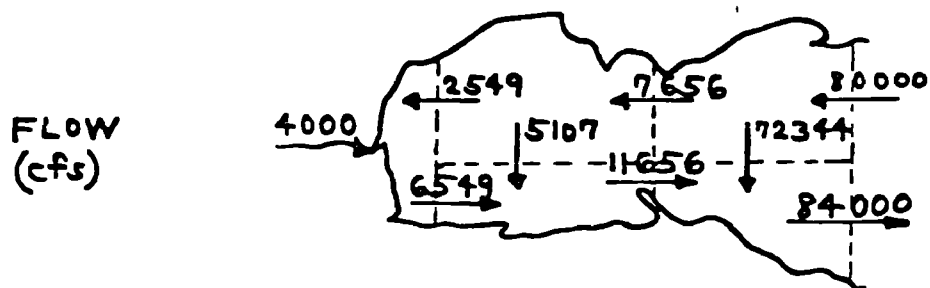
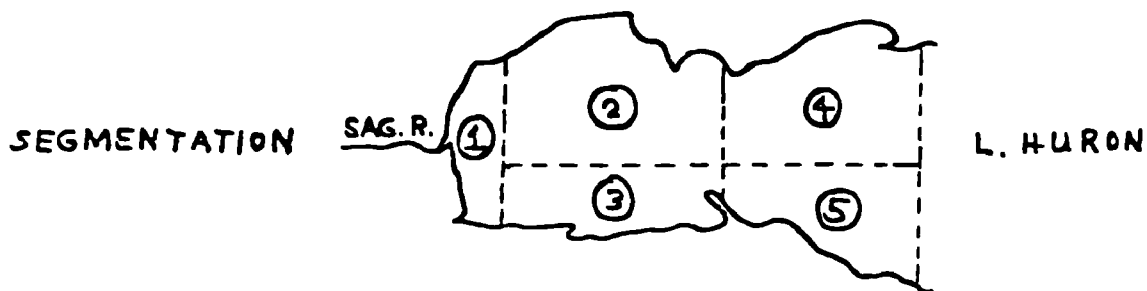


FIGURE II SEGMENTATION & ESTIMATED LONG-TERM
AVERAGE TRANSPORT COEFFICIENTS IN
SAGINAW BAY

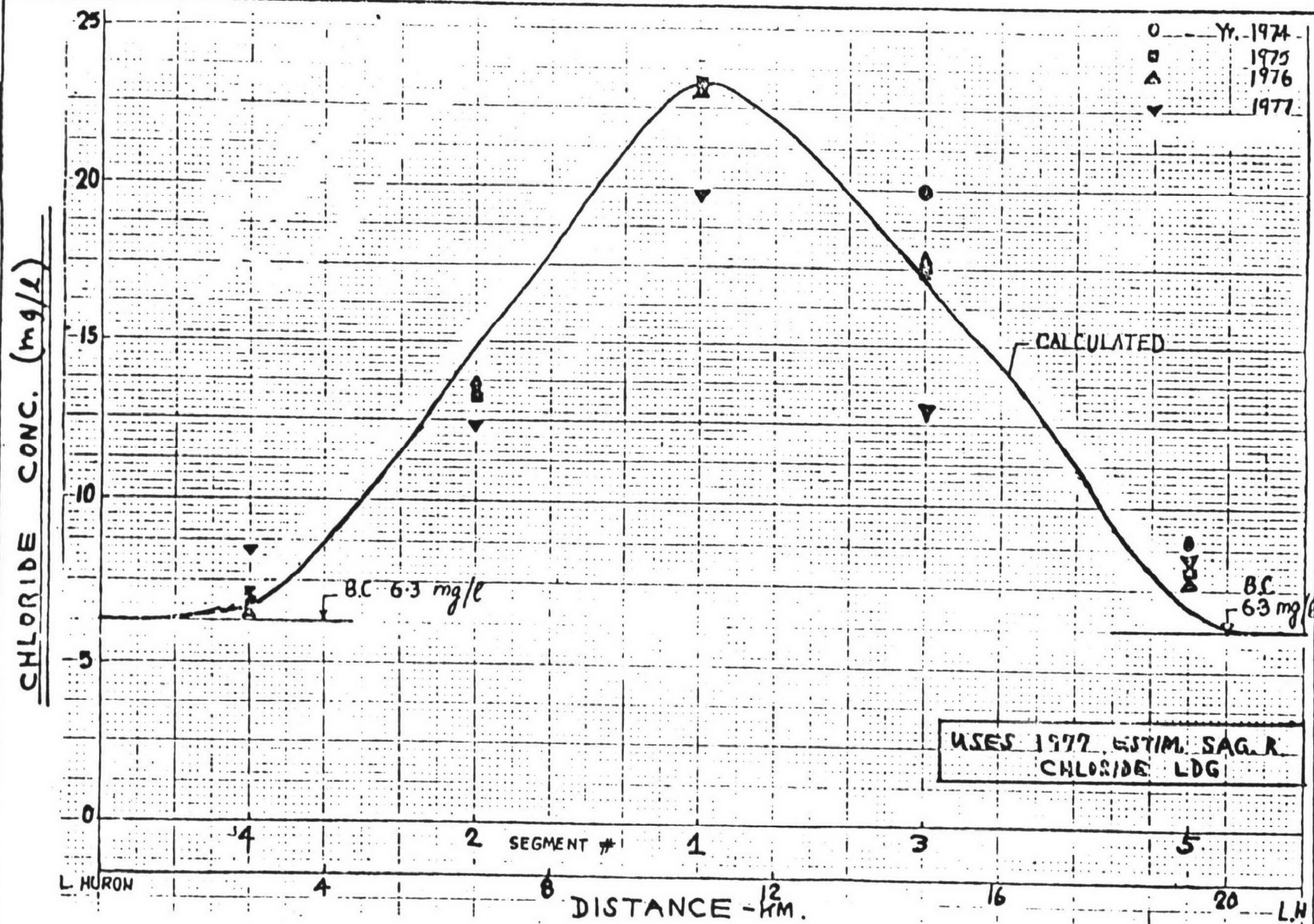


FIGURE 12 TRANSPORT CALIBRATION USING LONG-TERM AVERAGED CHLORIDE DATA

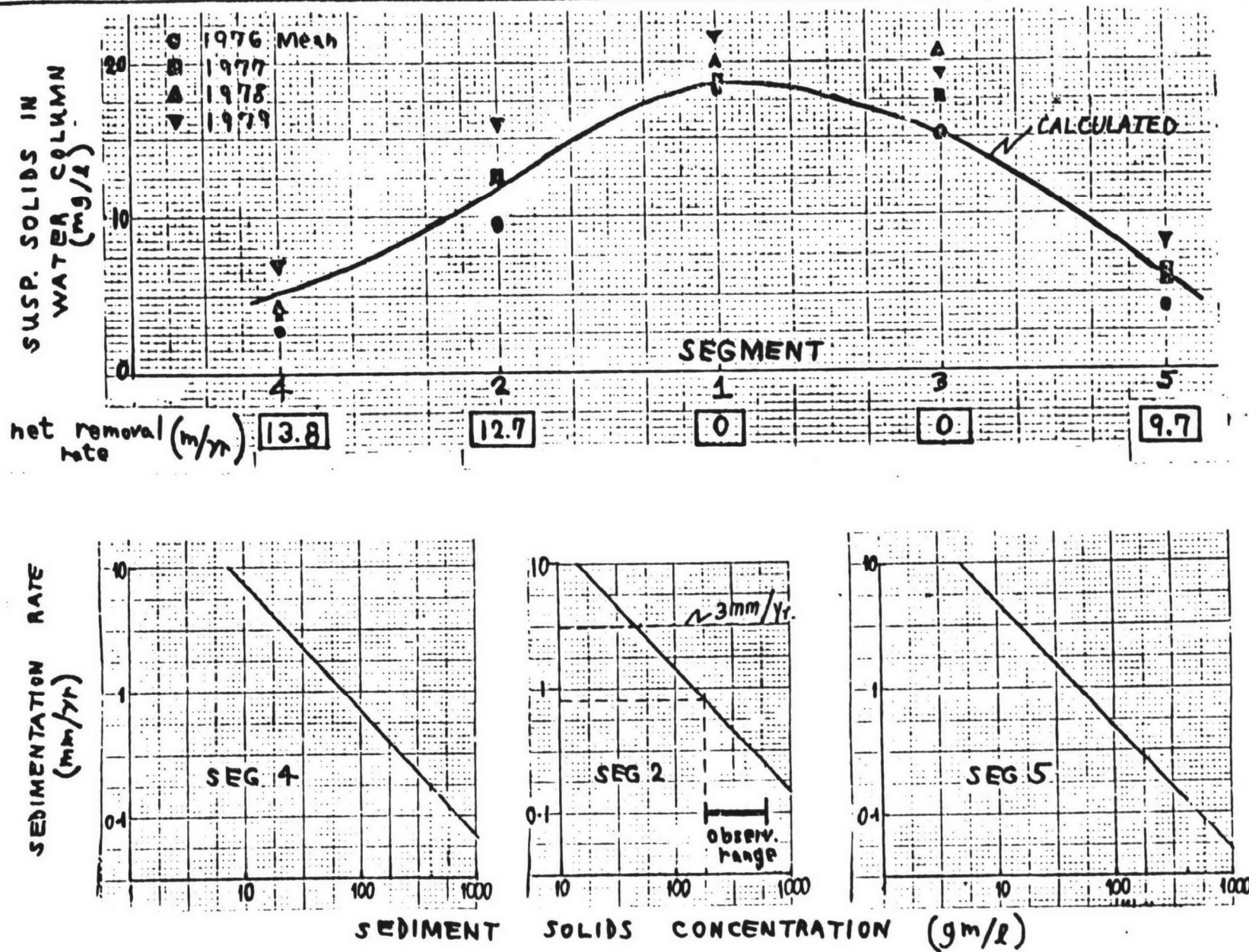
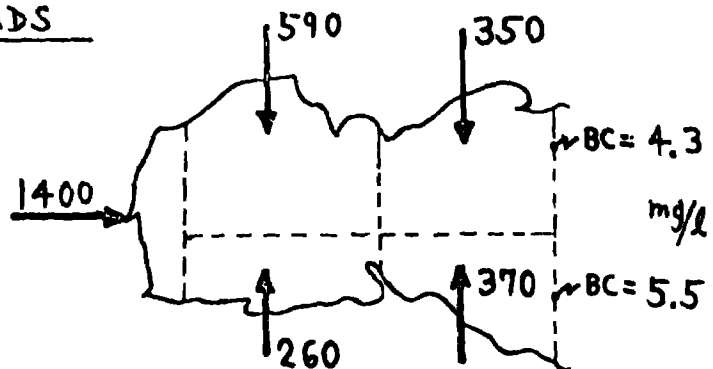
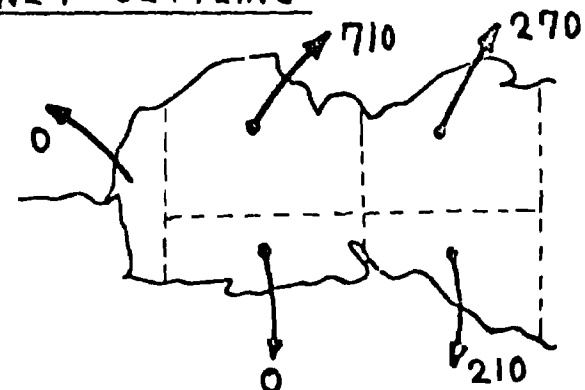


FIGURE 13 SOLIDS CALIBRATION USING LONG-TERM SOLIDS DATA

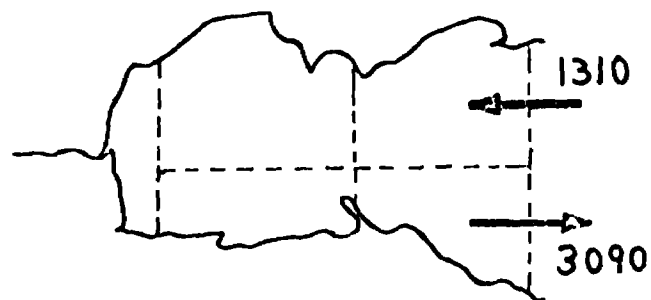
LOADS



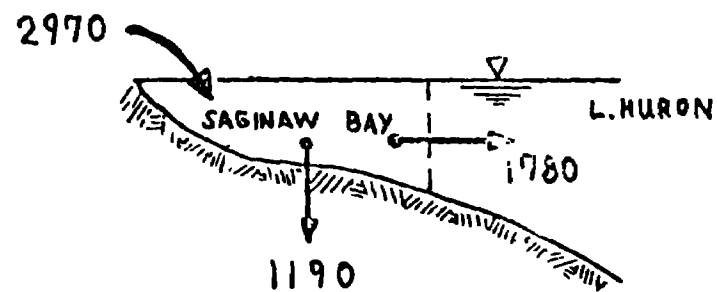
NET SETTLING



BOUNDARY TRANSPORT



SUMMARY



Note: All values in 1000 lb/day

FIGURE 14

MASS BALANCE of TOTAL SUSPENDED SOLIDS
UNDER LONG-TERM AVERAGE CONDITIONS

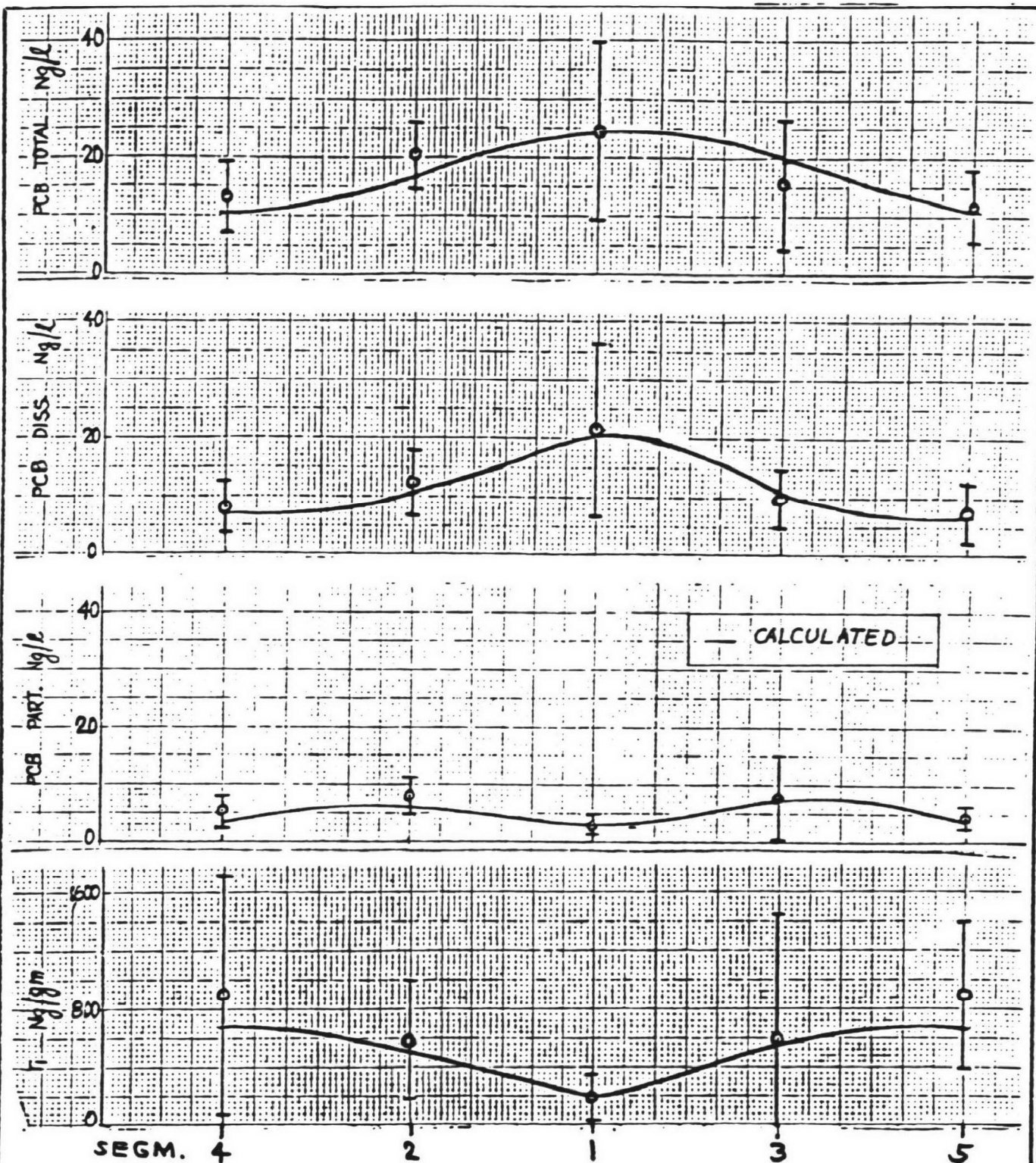


FIGURE 15 COMPONENTS of PCB IN WATER COLUMN - 1979

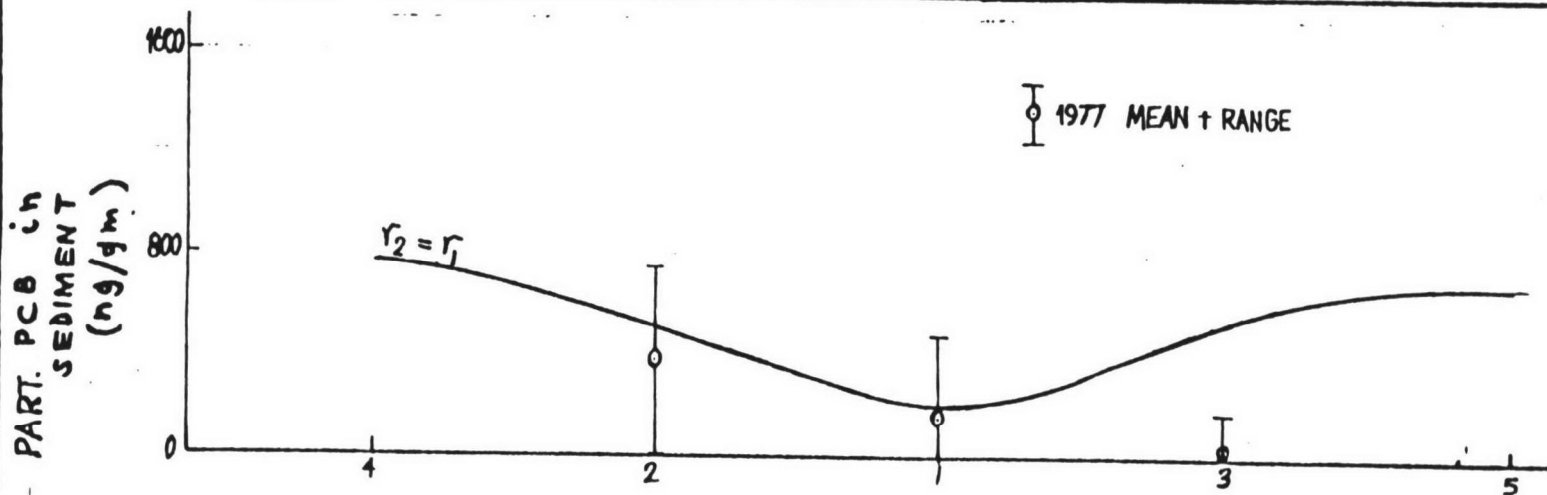
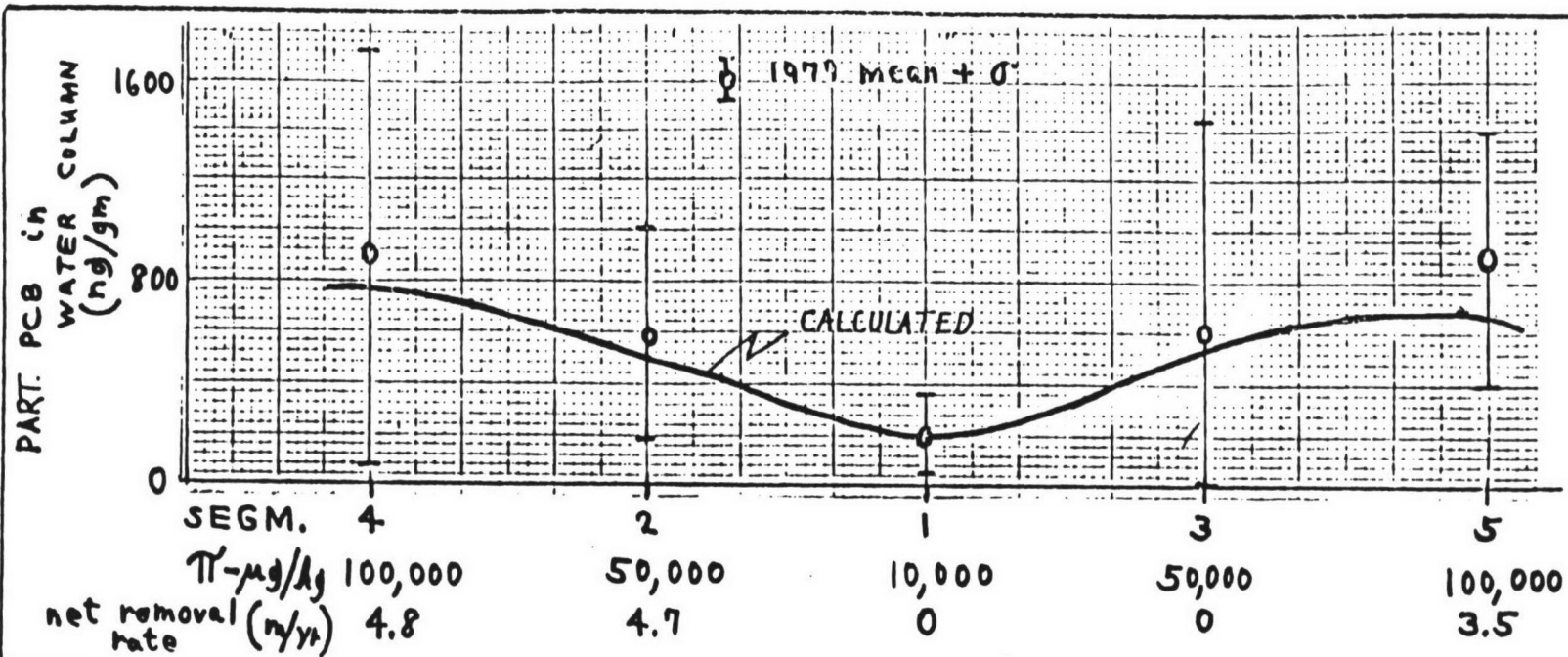
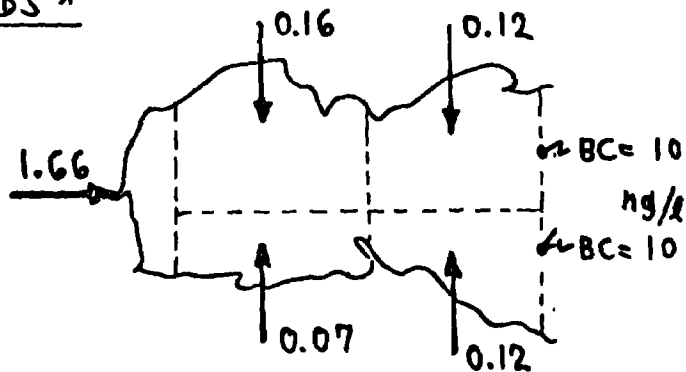


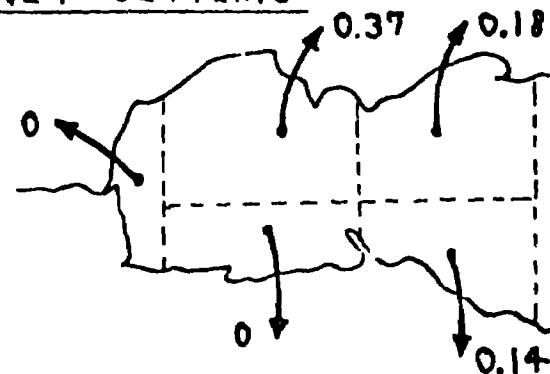
FIGURE 16 PART. PCB CALIBRATION USING 1979 LOADS + DATA

LOADS *

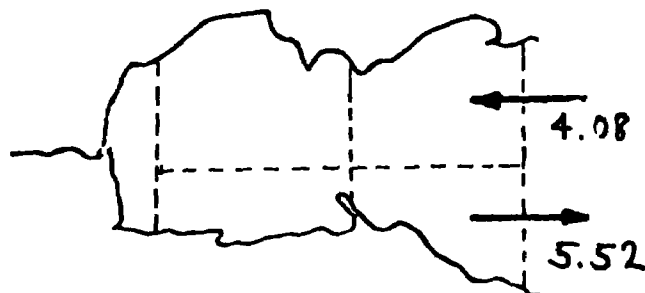


* Estimated 1979 values

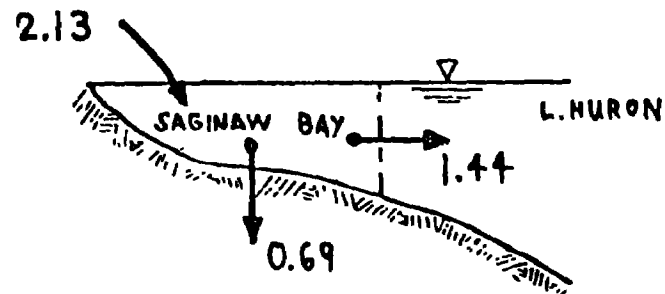
NET SETTLING



BOUNDARY TRANSPORT



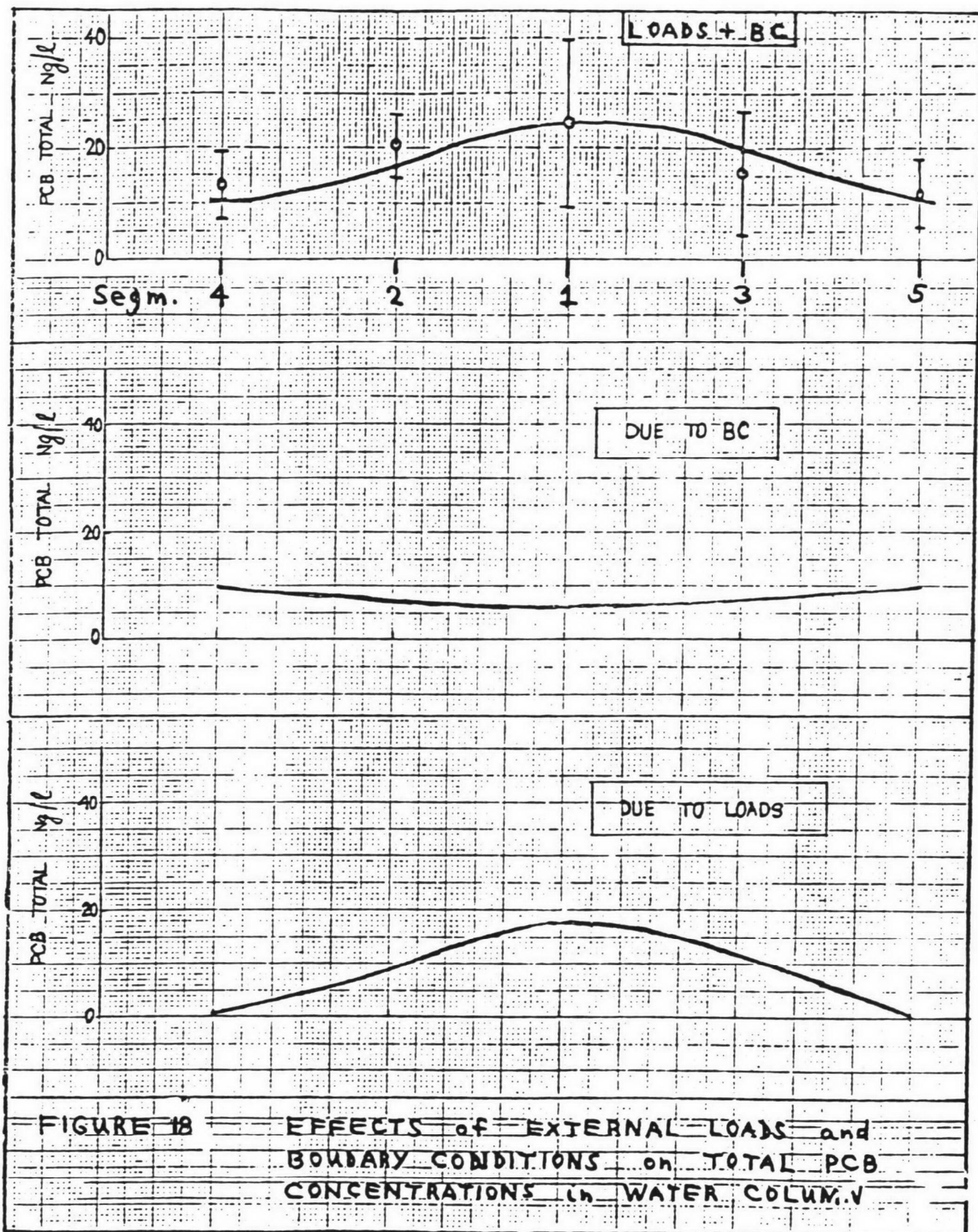
SUMMARY

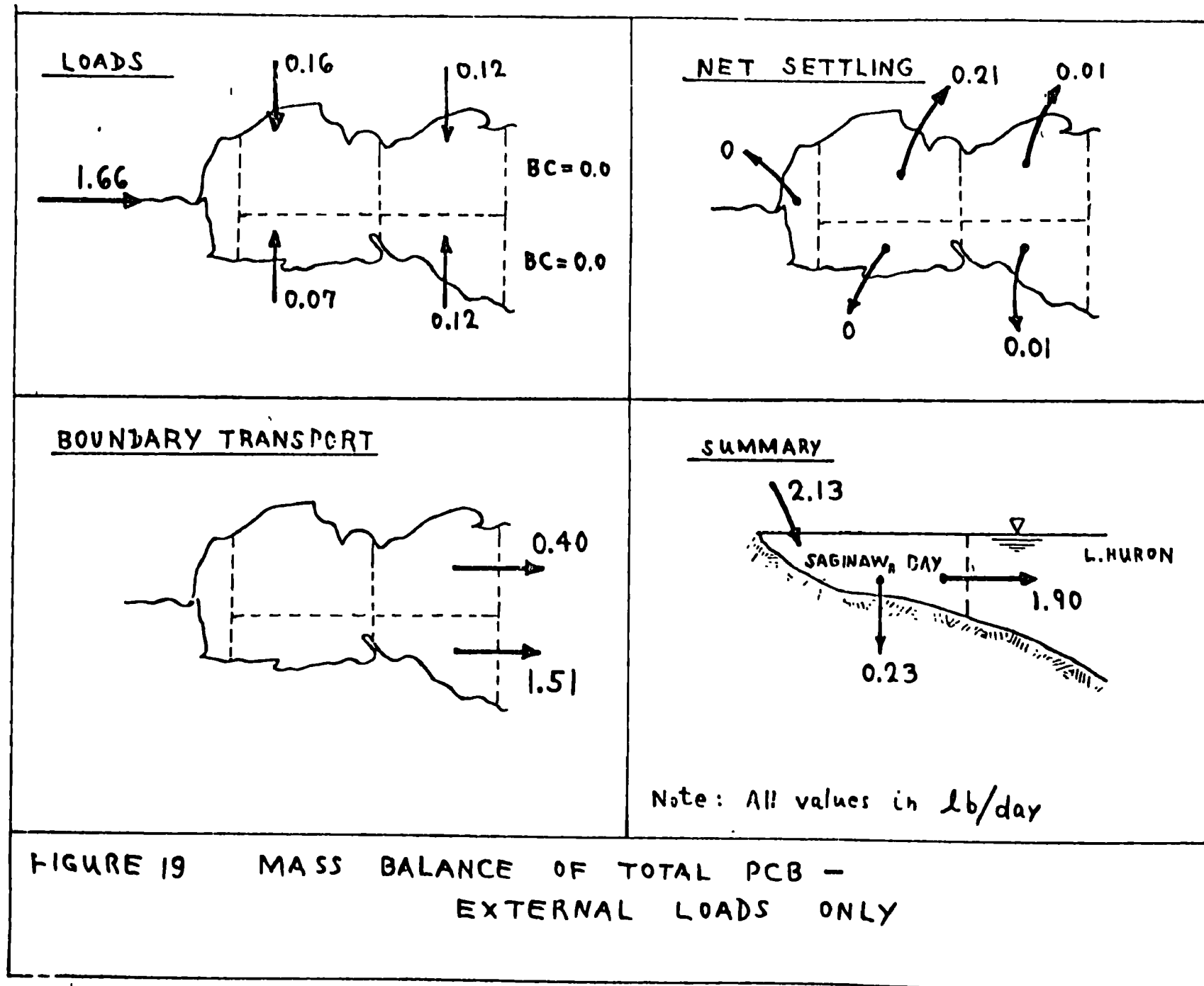


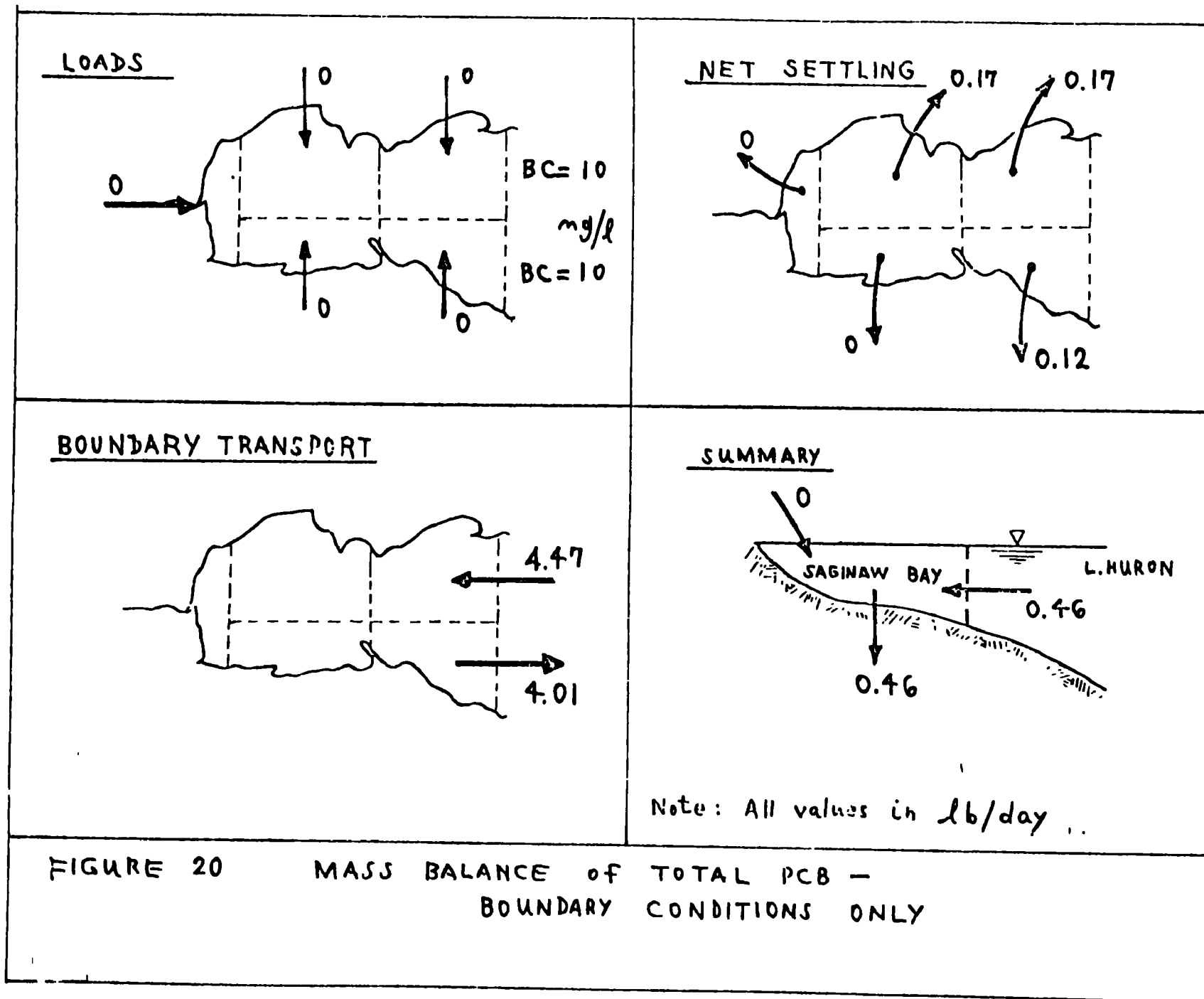
Note: All values in lb/day

FIGURE 17

MASS BALANCE of TOTAL PCB
UNDER LONG-TERM AVERAGE CONDITIONS







STREAM & RIVER MODELS

A. INTRODUCTION*

This chapter of the notes describes the distribution of toxic substances in fresh water streams & rivers. The characteristic feature of these water bodies is the longitudinal advective motion induced by gravity due to the slope of the natural channel or by a head differential due to a backwater effect of a dam. In either case, the transport is due primarily to the advective component, rather than the dispersive component. In a steady-state analysis of the systems, the latter can frequently be neglected without introducing significant error. For those cases in which the dispersive component may be significant, reference is made to the following chapter of these notes. This section deals exclusively with streams and rivers, in which the advective translation is the significant transport mechanism of the water column.

The water flow and the various substances contained therein interact in varying degrees with the bed, which are classified in accordance with the three general types of bed conditions, as described previously. Type I is a stationary non-interacting bed receiving settling solids, with no resuspension. Type II treats a mixed bed with a net zero horizontal motion, but which is interacting with the water column. The shear produced by the flowing water causes mixing and resuspension of the interfacial bed layer, but is insufficient to induce bed motion. Type III covers the case in which the shear is of sufficient magnitude to induce both scour and bed transport. The following sections of this chapter cover Types I & II and Type III is dealt with in the estuary chapter.

*Donald J. O'Connor

B. LONGITUDINAL ANALYSIS*

The advective transport component, which is simply the flow velocity in fresh water streams and rivers, is common to the various types of analysis described above. Consequently, the discussion is first focused on this aspect, which is best considered in light of the concentration of a dissolved tracer, such as total dissolved solids or chlorides. The source of ions, such as these, is invariably the ground water inflow and possibly the waste-water input, itself, which in addition to containing the toxic substance also may have an appreciable concentration of dissolved solids.

1. TRANSPORT

Consider the case of an upstream tributary, in which the ground water inflow is an appreciable fraction of the river flow. An inflow of this nature produces a spatially increasing flow in the downstream direction. Consider further a variable cross sectional area, which in general also increases in the downstream direction. The mass balance takes into account inflow, ground water input and outflow. Assuming lateral homogeneity of concentration, the balance is taken about an elemental volume of cross sectional area $A(x)$ and length Δx . The basic differential equation for the dissolved solids is

$$A \frac{\partial s}{\partial t} = \frac{\partial}{\partial x} (Qs) + s_g \frac{\partial Q_g}{\partial x} + s_s \frac{\partial Q_s}{\partial x} \quad (1)$$

in which

s = concentration of a dissolved tracer

Q = flow

and the subscripts g and s refer to the ground water and surface runoff components, respectively.

Under steady state low flow conditions, the surface runoff is zero and the above equation, after expanding the first term on the right-hand side, reduces to:

$$\frac{ds}{dx} = \frac{s}{Q} \frac{dQ}{dx} + \frac{s_g}{Q} \frac{dQ}{dx} = q [s_g - s] \quad (2)$$

in which

$$q = \frac{1}{Q} \frac{dQ}{dx} = \text{exponential flow increment}$$

The subscript is dropped from the flow since the only source of flow is the ground water. The solution is

*Donald J. O'Connor

$$s = s_g [1 - e^{-qx}] + s_o e^{-qx} \quad (3)$$

in which

$$s_o = \frac{W}{Q_o}$$

W = mass input of dissolved solids at $x = 0$

Q_o = flow at $x = 0$

Depending on the relative magnitudes of the ground water concentration and the concentration due to the waste input, the spatial distribution of dissolved solids increases or decreases to an equilibrium value, s_g .

2. TYPE I ANALYSIS - STATIONARY NON-INTERACTIVE BED

The condition of a stationary, non-interactive bed occurs under low flow conditions in streams and rivers. The vertical mixing of the flowing water is sufficiently low to permit the settling of the suspended solids and to preclude motion and scour of the bed material. It is recognized that some fraction of the solids is probably maintained in suspension - e.g. the smaller clay sizes and/or the flocculent organic particles of low specific gravity. However the majority of the solids are susceptible to settling and accumulation in the bed.

a. Suspended Solids

As in the case of the dissolved solids, discussed above, consider an upstream tributary in which the ground water inflow is the source of water for the stream flow. However, in this instance, the concentration of suspended solids in the ground water is negligible. The basic differential equation, allowing for settling is therefore,

$$\frac{\partial m}{\partial t} = \frac{1}{A} \frac{\partial}{\partial x} (Qm) - K_s m \quad (4)$$

in which

m = concentration of suspended solids

K_s = settling coefficient = $\frac{v_s}{H}$

v_s = settling velocity

H = average depth of the stream

Expanding the first term on the right hand side of the above equation and simplifying, the steady state form is

$$\frac{dm}{dx} = - \left(\frac{K_s}{U} + q \right) m \quad (5)$$

in which

U = velocity = $\frac{Q}{A}$

q = exponential flow increment = $\frac{1}{Q} \frac{dQ}{dx}$

the solution is

$$m = m_0 e^{-\left(\frac{K_s}{U} + q\right)x}$$

in which

m_0 = boundary concentration at $x = 0$.

It is assumed that the incremental flow is balanced by the increasing area resulting in a constant velocity, U . The boundary concentration may be due to the input of suspended solids from a point source - e.g. a treatment plant or tributary - or to an input from the upstream river segment of different hydraulic characteristics. The concentration approaches zero for large x .

In the subsequent development the effect of incremental flow due to ground water is not included. It may be readily introduced in the final working equations as an additional exponent as shown in the above equation. An example of this effect is discussed subsequently.

b. Toxic Substances

The equation for toxic substance are developed in a similar fashion, using the mass balance principle. The dissolved component includes the transport with adsorption - desorption interaction with the particulate and allowance is made for a reaction or transfer effect. In this case, assume the transfer term is an evaporation loss:

$$0 = -U \frac{dc}{dx} - K_0 m c + K_2 p - K_a c \quad (7)$$

in which

K_a = evaporation coefficient

The particulate form is described in a similar fashion with a settling term

$$0 = -U \frac{dp}{dx} + K_0 m c - K_2 p - K_s p \quad (8)$$

Addition of these equations yields

$$0 = -U \frac{dc_T}{dx} - K_a c - K_s p \quad (9)$$

Substitution of the dissolved and particulate fractions for c and p gives

$$0 = -U \frac{dc_T}{dx} - c_T [f_d K_a + f_p K_s] \quad (10)$$

in which

$$f_d = \frac{1}{1 + \eta_m}$$

$$f_p = \frac{\eta_m}{1 + \eta_m}$$

Assuming the river stretch is segmented such that each element may be approximated by a constant concentration of suspended solids; the solution

of the above is straightforward.

$$C_T = C_{To} e^{-[f_d K_a + f_p K_s] \frac{x}{u}} \quad (11)$$

in which

$$C_T = \frac{W_T}{Q}$$

W_T = mass discharge of total toxic ($\frac{M}{T}$)

Q = river flow ($\frac{L^3}{T}$)

Knowing the total concentration, the dissolved and particulate may be readily determined from the f_d and f_p equations.

If the effect of incremental flow is significant, the above equation is written in the following form:

$$C_T = C_{To} e^{-[(f_d K_a + f_p K_s)U^{-1} + q]x} \quad (12)$$

3. Type II Analysis - Mixed-Interactive Bed

This case describes a bed which is receiving solids due to the settling flux from the water column and returning solids by resuspension. The toxic substance in particulate form is transported by similar routes. The water column concentration is designated by subscript 1 and the bed by subscript 2. The analysis of each is discussed separately.

a) Suspended Solids

The basic equation for the solids is similar to that previously developed and in addition, includes a source term due to resuspension. The steady-state equation is:

$$0 = -U \frac{dm_1}{dx} - K_{s1}m_1 + K_{u1}m_2 \quad (13)$$

in which

$$K_{u1} = \text{resuspension coefficient} = \frac{v_u}{H_1}$$

m_2 = concentration of solids in the bed

v_u = resuspension velocity

The solution of this equation is:

$$m_1 = \frac{K_{u1}m_2}{K_{s1}} \left[1 - e^{-K_{s1} \frac{x}{U}} \right] + m_0 e^{-K_{s1} \frac{x}{U}} \quad (14)$$

If the ground water flow is significant, the above is expressed as

$$m_1 = \frac{K_{u1}m_2}{K_{s1} + qU} \left[1 - e^{-\left(\frac{K_{s1}}{U} + q\right)x} \right] + m_0 e^{-\left(\frac{K_{s1}}{U} + q\right)x} \quad (15)$$

The first term describes the build-up to spatial equilibrium of solids and the second term the decay by settling of the boundary solids. The spatial equilibrium concentration is

$$m_{e1} = \frac{K_{u1}m_2}{K_{s1}} = \frac{v_u m_2}{v_s}$$

The spatial distribution of solids will either build-up or decrease to the equilibrium values depending on the relative magnitudes of m_e and m_0 .

The equation for the concentration of the solids in the bed includes a sedimentation term. Under steady-state:

$$0 = K_{s2}m_1 - K_{u2}m_2 + K_{d2}m_2 \quad (16)$$

in which

$$K_{d2} = \text{sedimentation coefficient} = \frac{v_d}{H_2}$$

H_2 = depth of the bed.

It is apparent that the sedimentation term, which reflects the thickness of the bed, may be either positive or negative, depending on the magnitudes of the settling and resuspension terms. Thus, the bed increases or decreases along the length of the river in accordance with the decrease or increase in the spatial distribution of suspended solids. At spatial equilibrium the bed thickness is constant and the equilibrium concentrations in water and bed are maintained in accordance with the above equation defining m_{1e} .

b) Toxic Substances

The basic equation for the toxic substance follows from the above considerations. The dissolved component is identical to that for the Type I analysis:

$$0 = -U \frac{dc_1}{dx} - K_{o1}c_1 + K_2p - K_a c_1 \quad (17)$$

in which, as in the previous case, allowance is made for a decay or transfer. A volatilization transfer is assumed in the above.

The particulate component has an additional term due to the resuspension effect:

$$0 = -U \frac{dp_1}{dx} + K_{a1}c_1 - K_2p_1 - K_{s1}p_1 + K_{ul}p_2 \quad (18)$$

Addition of the dissolved and particulate components yields the equation for the total concentration.

$$0 = -U \frac{dc_T}{dx} - K_{a1}c_T - K_{s1}p_1 + K_{ul}p_2 \quad (19)$$

Substitution of the dissolved and particulate fractions for c and p are replacing $p_2 = r_2 m_2$.

$$0 = -U \frac{dc_T}{dx} - \alpha c_T + K_{ul}r_2 m_2 \quad (20)$$

in which $\alpha = f_d K_a + f_p K_s$

For the condition of spatial equilibrium of solids for which $m_1 = m_{e1}$ and

$K_{ul}^m = K_{sl}^m$, the solution is:

$$c_T = \frac{K_{sl} r_{2el}^m}{\alpha} [1 - e^{-\frac{\alpha x}{u}}] + c_{To} e^{-\frac{\alpha x}{u}} \quad (21)$$

Simplification of the first term yields

$$\frac{K_{sl} r_{2el}^m}{\alpha} = \frac{r_{2el}^m}{f_p + f_d \frac{K_L}{v_s}} \quad (22)$$

in which K_L = evaporation transfer coefficient = $K_a H_1$ (L/T)

v_s = settling velocity of solids = $K_{sl} H_1$ (L/T)

For the case of spatially varying solids, the above equation may be used as an approximation by segmenting the system into a number of elements, such that the solids are approximately uniform in each, but varying from one to the other in accordance with the solids equation.

If the ground water flow is significant, the appropriate equation is

$$c_T = \frac{K_{sl} r_{2el}^m}{\alpha} [1 - e^{-(\frac{\alpha}{u} + q)x}] + c_{To} e^{-(\frac{\alpha}{u} + q)x} \quad (23)$$

It is to be noted that a direct simple analytical solution results for the condition of spatial equilibrium of the solids. For the case of spatially varying solids, however, the differential equation is

$$0 = -u \frac{dc_T}{dx} - \left[\frac{K_{al} + K_{sl} \phi(x)}{1 + \phi(x)} \right] c_T + K_{sl} r_{2el}^m \quad (24)$$

in which $\phi(x) = \eta_{m_{el}} (1 - e^{-\frac{K_{sl} x}{u}})$

Finite difference forms of the equation may be used to calculate the distribution of toxic chemical, in which the necessary solids concentrations both in the bed and water column are inputs to each segment of the system. The solids equations are solved for the appropriate concentrations, which are introduced into the toxic distribution.

Application to PCBs in the Hudson River *

INTRODUCTION AND GENERAL PROBLEM FRAMEWORK

The focus of this review is the description of the distribution and fate of polychlorinated biphenyls (PCBs) in the Hudson River and Estuary using a simplified model of the physical-chemical system. (An analysis of the fate of PCBs in the food chain is given in Chapter 10 of the Notes). A settlement between the New York State Department of Environmental Conservation (NYSDEC) and the General Electric Company (GE) concerning the contamination of the Hudson River by PCBs discharged by GE's facilities at Fort Edward, New York, called for an overall study of the Hudson. A more complete treatment of the model discussed here is given in (1). This model treats the entire river estuarine and harbor regions of the Hudson system in a simplified manner and does not address the details of estuarine sediment transport and exchange. The model is intended to provide some guidance on the order of magnitude response that may be anticipated under different environmental controls. Considerable research in this area is continuing and the results of that research may influence the conclusions drawn herein.

Figure 1 is a schematic of the Hudson River which indicates the mile points (MP) of key locations and also shows the divisions of the Hudson into reaches for the physical transport analysis and reaches for the biological analysis. From the Federal Dam at Troy to the Ocean, the Lower Hudson is tidal and depending on the average freshwater flow, the end of the salt water intrusion oscillates approximately between the Tappan Zee Bridge (MP 25) and Poughkeepsie (MP 75) and under severe drought conditions, it may reach as far north as MP 80. The long term monthly average discharge and the 1976 monthly average discharge from the Upper Hudson to the Lower Hudson are 13,270 cfs and 22,100 cfs respectively.

ANALYSIS OF WATER COLUMN AND SEDIMENT PCB DATA

The principle of the conservation of mass permits a first approximation to describing the spatial distribution of the various components of PCBs. The following assumptions are made: a) the mass of PCB in the food chain

* Robert V. Thomann

is small relative to that in the water column; b) a local equilibrium prevails between the particulate and dissolved phases of the PCBs; c) the adsorption phenomena is linear; d) the river system is in temporal steady state (although longer term trends may be present); and e) losses from the water column are principally through sedimentation, although some evaluations of losses due to evaporation and biodegradation has been made.⁽¹⁾

The general equation for the total PCB concentration, c_T ($\mu\text{g/l}$) in a dimensional system can be written as:

$$\frac{u}{dX} \frac{dc_T}{dX} - E \frac{d^2 c_T}{dX^2} + \left[\frac{\eta m}{1+\eta m} K_s + \frac{K_a + K_n + K_d}{1+\eta m} \right] c_T = [W_{TB} + W_{TA} + W_{TE}] \quad (1)$$

where x is distance downstream, u is the river or estuary velocity (cm/sec), E is the tidal dispersion (m^2/day), m is the mass of suspended solids (mg/l), " a " is a partition coefficient between the particulate and dissolved phases ($\mu\text{g/g} \div \mu\text{g/l}$), K_s , K_a , K_n , K_d are coefficients [day^{-1}] representing sedimentation, evaporation, photooxidation, and biodegradation, respectively; and W_{TB} , W_{TA} and W_{TE} are total input loads (kg/l-day) of PCB from bottom sediment interactions, atmospheric sources and other external sources, respectively. For the Upper Hudson area, W_{TA} can be assumed close to zero and W_{TB} can be given from the resuspended bed sediment load as $W_{TB} \approx r_b W_{ss}$ where r_b is the concentration of PCBs in the resuspended sediment ($\mu\text{g PCB/g sediment}$, a measurable quantity) and W_{ss} is the sediment input ($\frac{\text{kg sediment}}{\text{liter-day}}$). A mass balance on the suspended solids is therefore also required and is given by

$$\frac{u}{dX} \frac{dm}{dX} - E \frac{d^2 m}{dX^2} + K_s m = W_{ss} \quad (2)$$

With m from (2) and estimates of the coefficients for (1), c_T can be calculated. Since the total concentration is the sum of the particulate and dissolved, the dissolved concentration, c_D , can be calculated from:

$$c = c_T / (1 + \eta m) \quad (3)$$

The concentration then provides an estimate of the dissolved form of PCB which may be available for uptake and bioconcentration by the aquatic food chain. The approach to analyzing the PCB column data was to first fit the suspended solids data using Equation (2) which provides an estimate of K_s and W_{ss} (but not uniquely). Then using field data of r_B and the determined distribution of m and K_s , the PCB data are calibrated using Equation (1). In using this latter equation, a knowledge of the partition coefficient η is needed. The limited available data for the Upper Hudson River show a large variation from 20-500 $\mu\text{g/g}$ per $\mu\text{g/l}$. Dexter² in his work examined the partitioning of PCB in the two phases and reported values from 13-75 $\mu\text{g/g}$ per $\mu\text{g/l}$. A value of 100 $\mu\text{g/g}$ per $\mu\text{g/l}$ was chosen for this work. The reaches for the physical analysis of PCBs are shown in Figure 1.

For the Upper Hudson (north of Federal Dam), the model was applied to PCB surveys of March 18 and March 29-31, 1976. The resulting profiles and the survey data are shown in Figure 2 and as shown, the agreement between the observed data and the calculation is good. However, background and tributary PCBs had to be assigned based on rather meager data.

Figure 3 shows the calculation profile for the entire length of the Hudson to the Battery. In the lower Hudson, data on total PCBs were available only for the reach for MP 65 - MP 90. In the top graph of Figure 3 are shown two profiles resulting from different assumptions on bottom PCB concentration as shown in the bottom graph. The dashed line therefore in the water column PCB calculation corresponds to an assumption of 1 μg PCB/g sediment for the lower Hudson. It is estimated based on Figure 3 that the total PCB concentration from MP 0 to MP 110 ranges from 0.1 - 0.5 $\mu\text{g/l}$. The average dissolved PCB concentration (not measured) is estimated at about 0.1 $\mu\text{g/l}$ (100 ng/l).

ANALYSIS OF DREDGING OF UPSTREAM SEDIMENTS

Various schemes have been suggested for reducing the effect of the upstream PCB sediments, including the removal of the contaminated sediment by dredging. Therefore, two dredging alternatives were considered and their impacts on the water column PCB were calculated.

Under the first alternative, only the Thompson Island pool at Fort

Edward is dredged to a bottom sediment PCB concentration of 1 $\mu\text{g/g}$. Under the second dredging alternative all pools of the Upper Hudson are dredged to a bottom sediment PCB concentration of 1 $\mu\text{g/g}$.

Figure 4A shows the results of the calculation under the two dredging alternatives and assuming that the bed sediment PCB concentration remains the same as at present. The average PCB concentration for the Upper Hudson is calculated to be appreciably reduced from approximate present levels of 0.5 $\mu\text{g/l}$ to 0.28 $\mu\text{g/l}$ and 0.14 $\mu\text{g/l}$ under the two alternatives. This represents an approximate 20% and 70% reduction of level from the Upper Hudson to the Lower Hudson. These results assume no change in the estuary PCB sediment concentration. However, at the mean annual flow, the estuarine sediment PCBs are the primary source of estuarine water column PCBs. Therefore, if the contaminated sediment of the Upper Hudson were not partially or totally removed or inactivated, such sediment would continue to add to the contamination of estuarine sediments via the naturally occurring sediment discharged over the Troy Dam.

Recognizing this indirect effect and an approximate range of 20-70% reduction in load at Troy depending on the degree of dredging, it has been assumed that the bed sediment-bed load input may drop by 50%. The results of the calculation under this assumption are shown in Figure 4B. In this case the calculated total PCB concentration is almost halved and in the biologically active region, the average dissolved PCB concentration is estimated at 0.05 $\mu\text{g/l}$.

THE NO-ACTION ALTERNATIVE - UPPER HUDSON

If no action were taken, some notion of the time span required for the reduction of the PCB load to the estuary from the Upper Hudson may be gained by means of a mass balance. The mass balance is considered around the water column of the Upper Hudson for the March 18, 1976 survey, as shown in Fig. 5A. From the inputs to the calculated profile the load to the Upper Hudson due to the upstream conditions is 5 lb/day, due to the tributaries 2 lb/day, and at the flow of 12,700 cfs the load to the Estuary is 17 lb/day. This causes a net loss of 10 lb PCB/day from the bottom sediment. From a similar

mass balance at 48,700 cfs from the calculated profiles, for the March 29-31, 1976 profile, there is a net loss of 225 lb PCB/day from the bottom sediment. Using these net losses at the given flows (Fig. 6) and the long term monthly hydrograph, an approximate average daily net bottom PCB loss can be computed for the typical year. Following this procedure the approximate daily net bottom PCB loss is 15 lb/day on a yearly average. Then, for the estimated 450,000 lb of PCB in the entire volume of sediments of the upper Hudson, it would take at least several decades for these sediments to be "flushed out". This assumes the entire sediment volume would be flushed out. If only a fraction of the mass were "available" for scouring, then the response time would be reduced accordingly. In addition, other effects such as evaporative losses and biodegradation may reduce this time.

Evaporative losses can be computed by assuming that (1) the soluble component only will be depleted by means of gas transfer process and (2) that the PCB in the air is negligible when compared to the soluble component. Assuming that this gas transfer is liquid film controlled, the evaporative loss will be:

$$N = K_L A c$$

where

N = evaporative loss in (M/T)

K_L = liquid film coefficient in (L/T)

c = The dissolved PCB concentration in (M/L³)

A = The surface area through which the transfer occurs (L²)

the liquid-film coefficient was taken as 0.07 m/h, and the dissolved component for the March 18, 1976 survey is 0.2 µg/l averaged over the entire Upper Hudson. With this parameter, the evaporative loss is estimated at 15 lb/day.

If biodegradation is included at an assumed rate of $K_d = .25 \text{ (day)}^{-1}$, then there is an additional loss of 5 lb/day. It is also assumed in these calculations that the biodegradation process depletes only the dissolved component, but this is not known. A biodegradation process depleting the particulate component could also be postulated with, perhaps, different

rate. Thus if these processes for the dissolved component are included in the mass balance, the total net bottom loss is increased to 30 lb/day (Fig. 5B). Since these additional losses are depleting the dissolved component, it is of interest to consider the dissolved input. Assuming that the interstitial water is saturated with PCB, then the soluble input can balance approximately 40% of the PCB loss due to evaporation and biodegradation. Fig. 5C. The response time to "flush out" the Upper Hudson sediments is therefore reduced by a factor of about 2 when evaporative and biodegradation losses are included. Sediment burial and subsequent interstitial diffusion rates may also markedly reduce the time to flush out the Upper Hudson. Such a calculation would require a detailed model of the bed sediment PCB and interactors with the overlying water.

ACKNOWLEDGEMENT

Special thanks are due to Messrs. John St. John, Thomas Gallagher and Michael Kontaxis of Hydro Qual, Inc. (formerly Hydrosience, Inc.) for their valuable assistance and input into the work described herein. This project was part of a contract between Hydrosience, Inc. and the New York State Department of Environmental Conservation.

REFERENCES

1. HYDROSCIENCE, INC. 1978. Estimation of PCB reduction by remedial action on the Hudson River ecosystem. Prepared for New York State Department of Environ. Conservation by Hydroscience, Inc., Westwood, N.J.: 107.
2. DEXTER, R.N. 1976. An application of equilibrium adsorption theory to the chemical dynamics of organic compounds in marine ecosystems, Ph.D. Diss. Univ. of Wash. Seattle, Washington: 181.

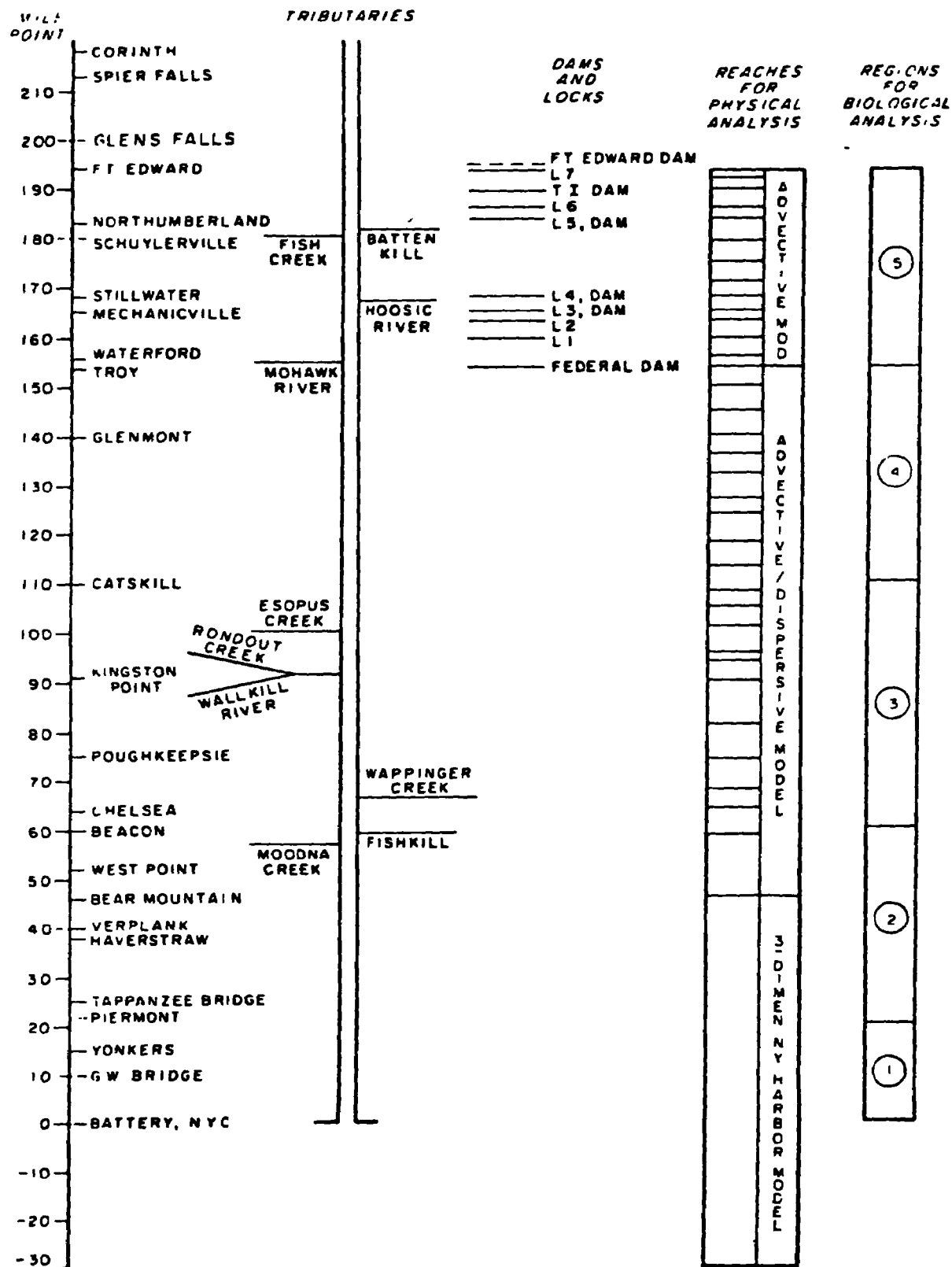


FIGURE 1
SCHEMATIC OF THE HUDSON RIVER AND SEGMENTATION
USED IN PCB ANALYSIS (BIOLOGICAL AND PHYSICAL)

-401-

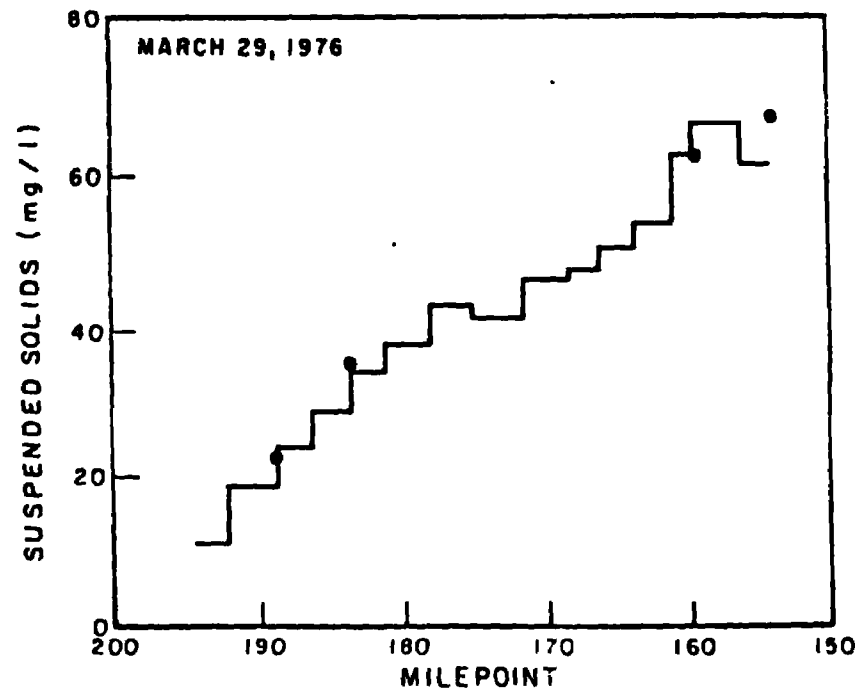
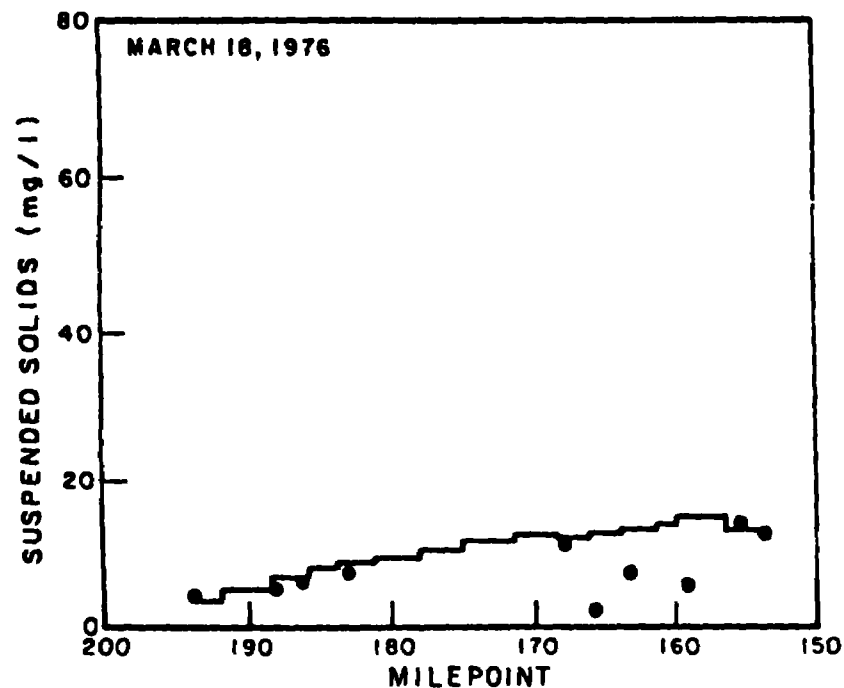
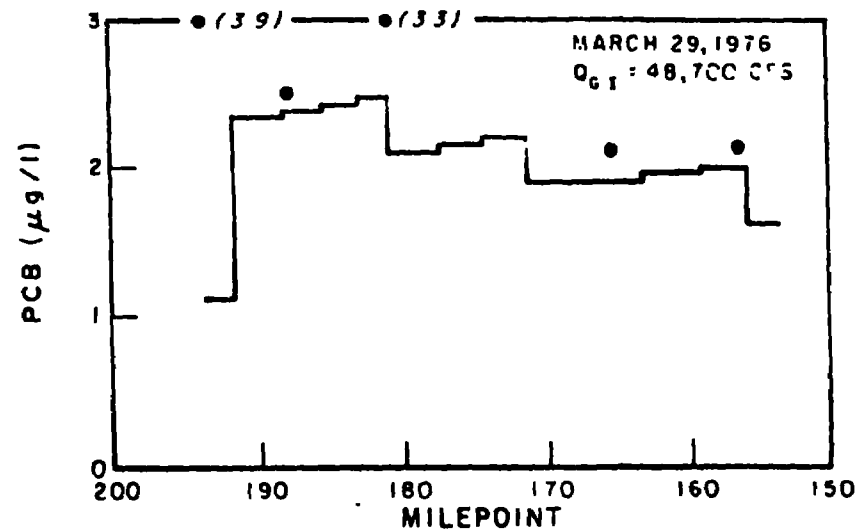
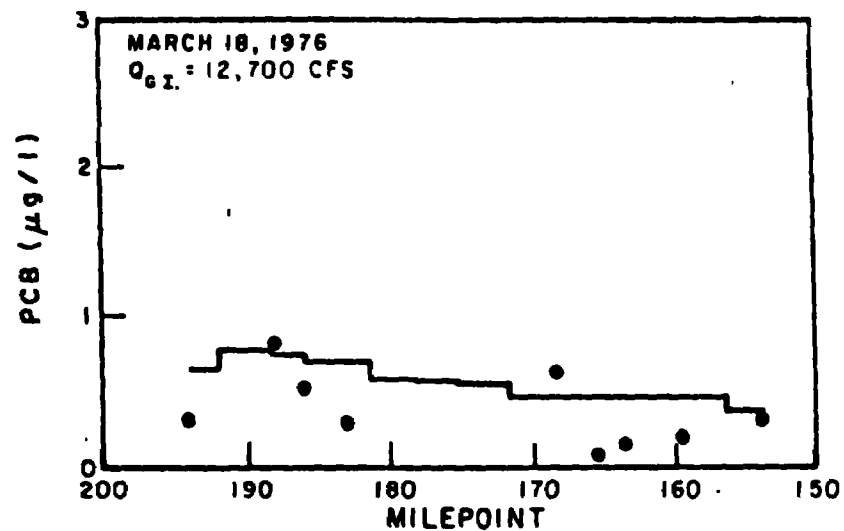


FIGURE 2
TOTAL PCB AND SUSPENDED SOLIDS CALCULATED PROFILES.
(UPPER HUDSON RIVER)

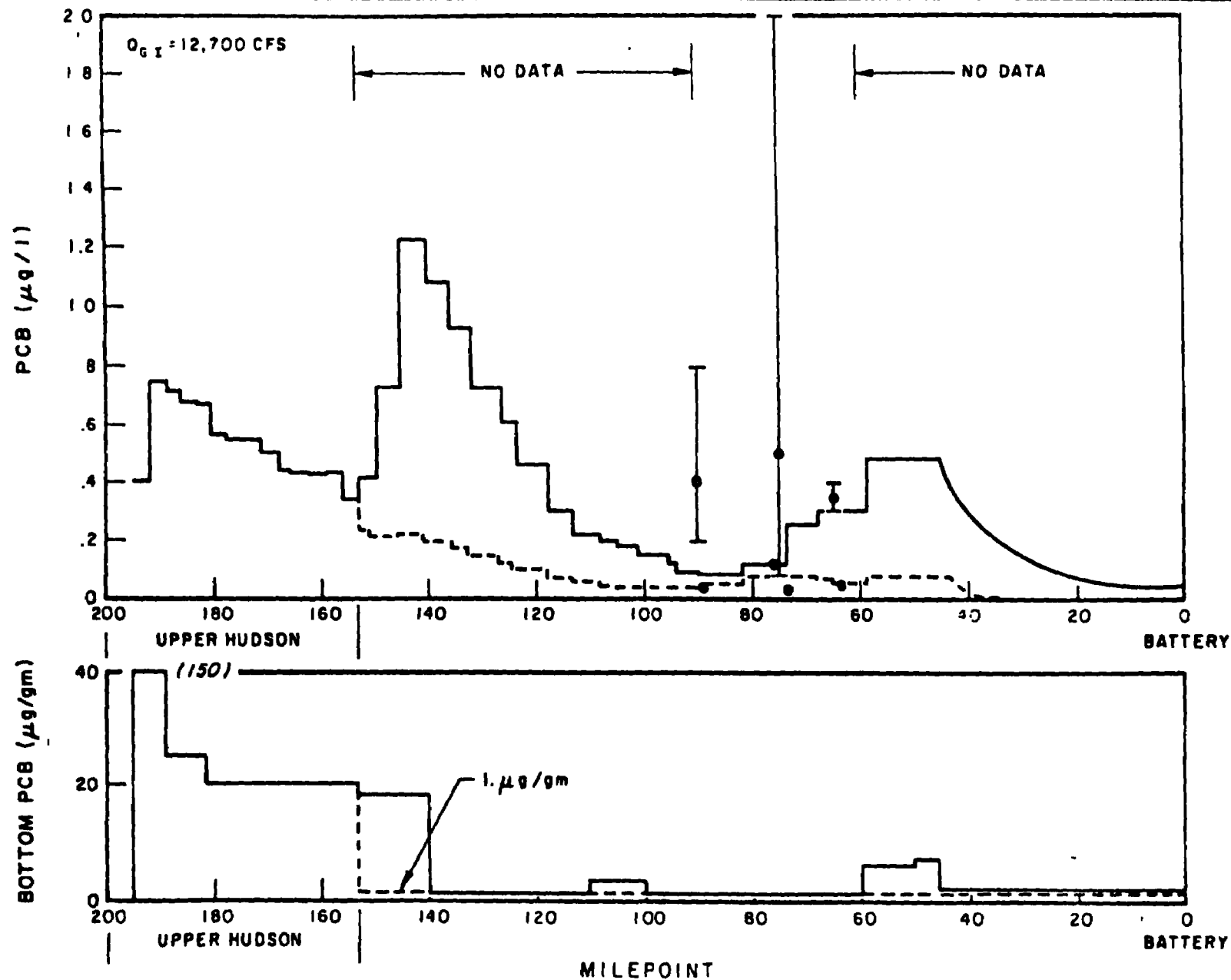


FIGURE 3
TOTAL PCB CALCULATED PROFILE AND BOTTOM PCB DISTRIBUTION

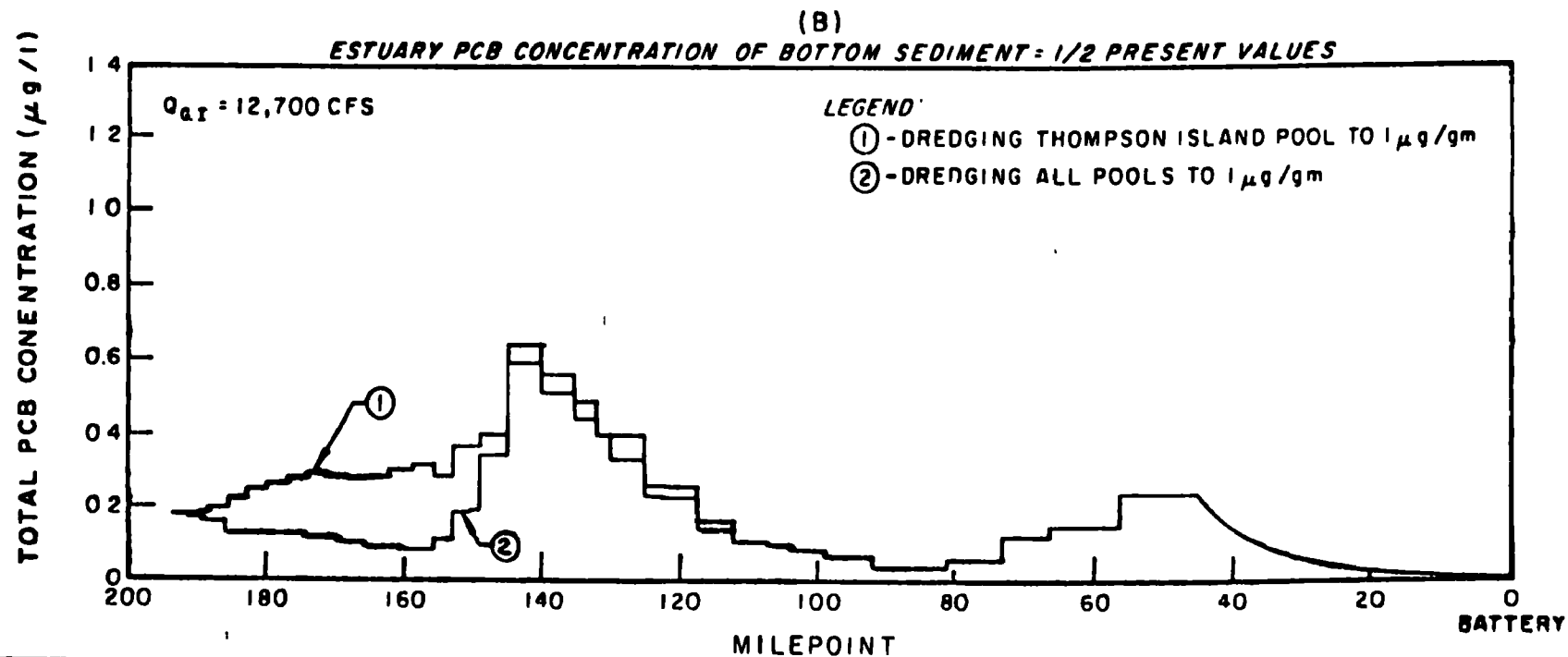
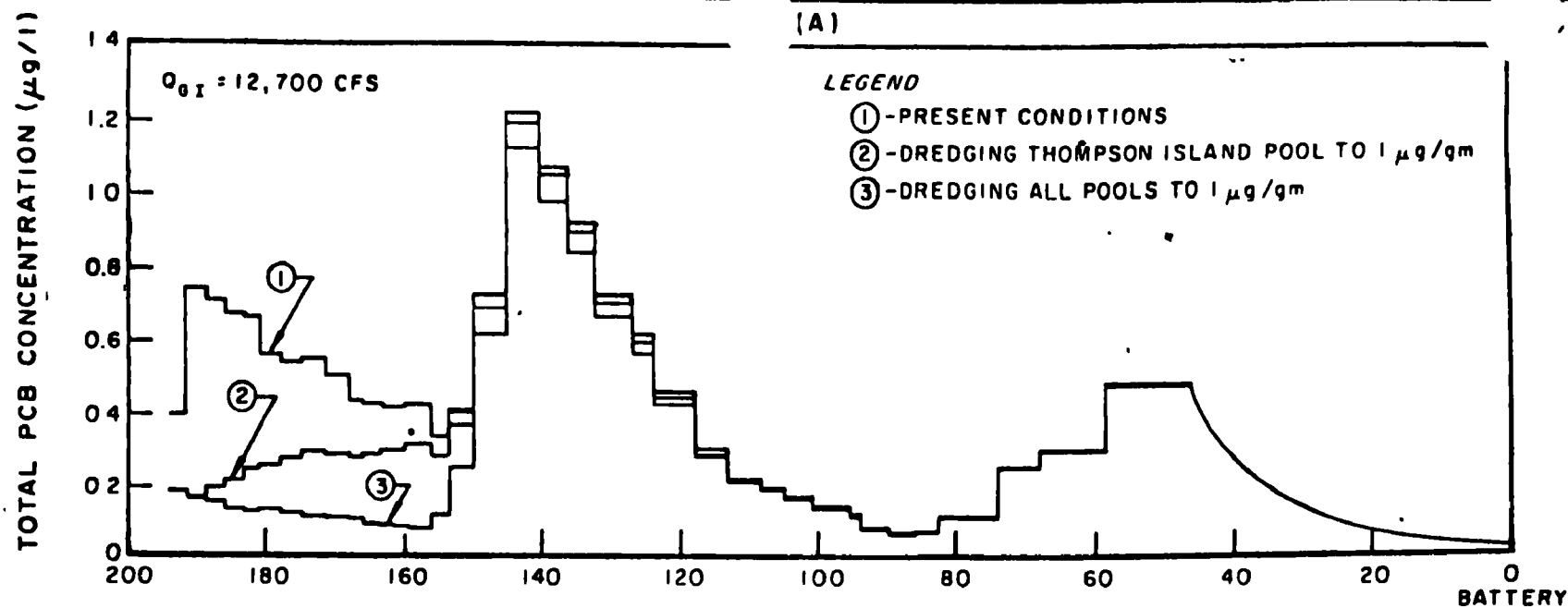


FIGURE 4
EFFECT OF REMEDIAL ACTION
ON PRESENT AND POSSIBLE FUTURE ESTUARINE CONDITIONS

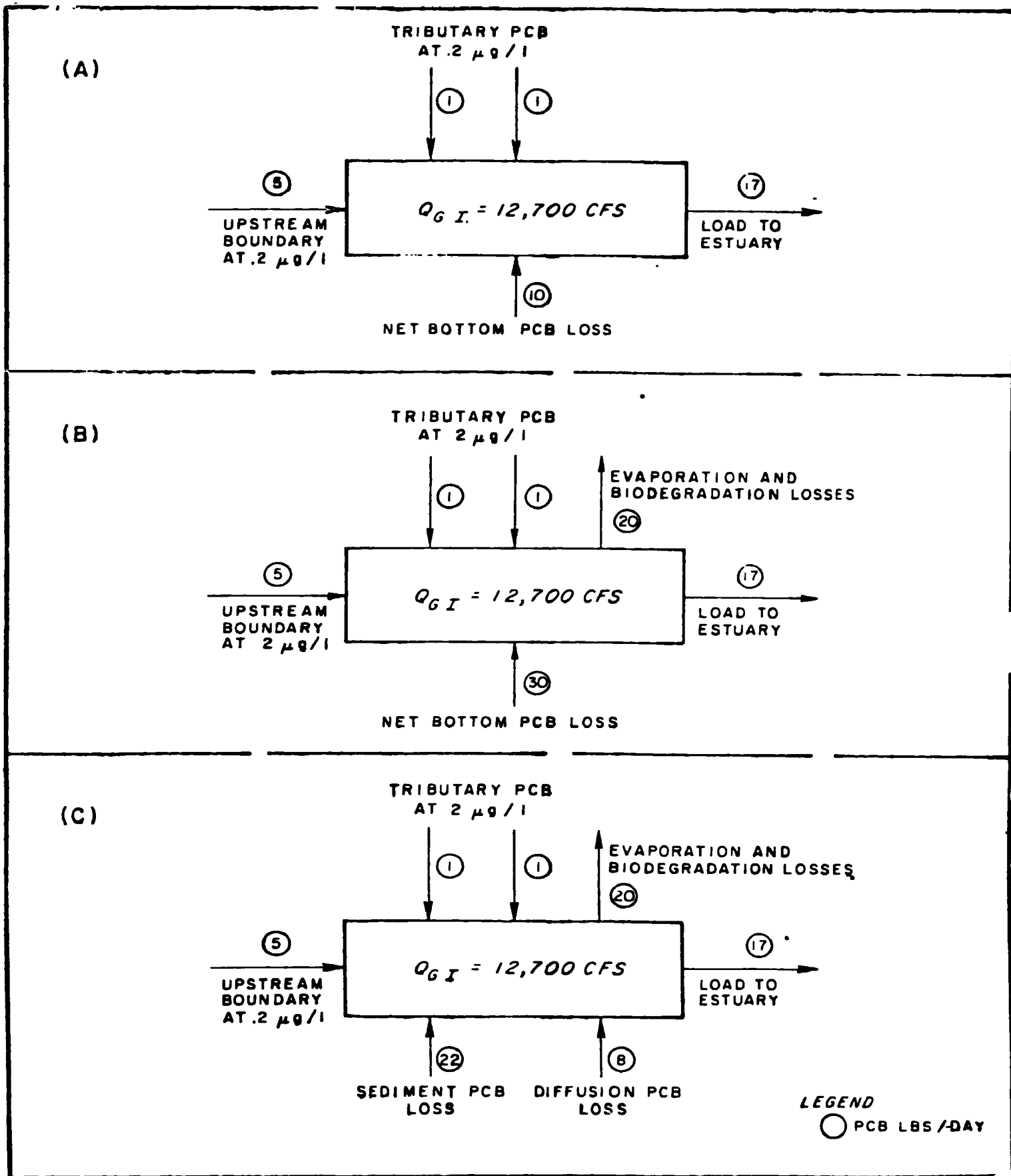


FIGURE 5
PCB MASS BALANCE
(UPPER HUDSON RIVER)

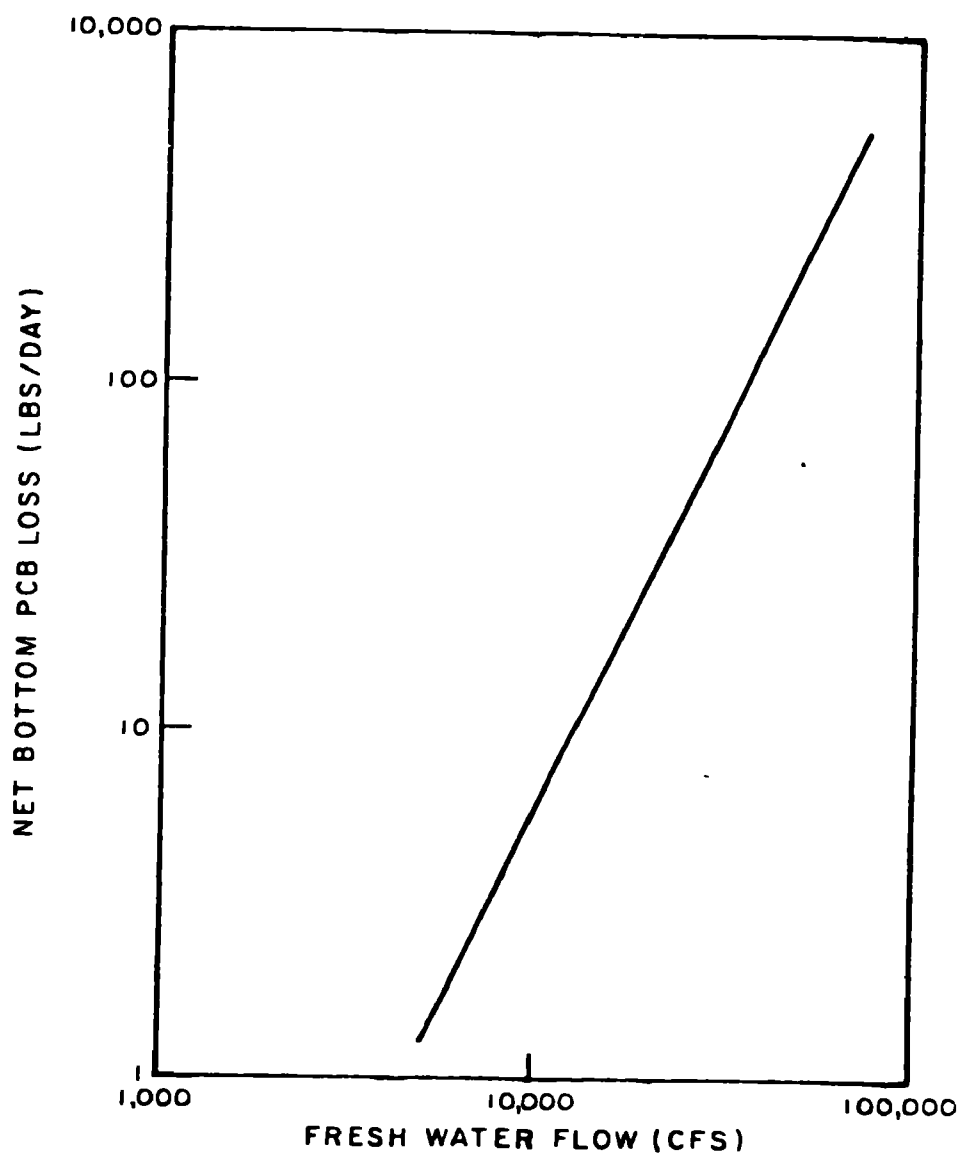


FIGURE 6
NET PCB LOSS FROM BOTTOM SEDIMENTS
(UPPER HUDSON RIVER)