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**FRESHWATER ECOSYSTEM WATER QUALITY MODELLING**

by

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## Abstract

This paper presents a review of recent (1978-1988) water quality models which have been developed for predicting the impacts, pathways, fate and effects of nutrient and toxic chemicals in freshwater systems. The principal characteristics and applications of 38 nutrient and 35 toxic chemical models are summarized in tabular form. These tables should be particularly useful for directing research and management model users towards suitable models and model components which can be used to solve water quality problems. Detailed reviews of model structures, process representations and applications are presented for 2 nutrient models and 3 toxic chemical models.

## RÉSUMÉ

Ce document passe en revue les modèles récents (1978-1988) de qualité de l'eau qui ont été mis au point afin de prévoir les impacts, les voies, le sort et les effets de substances nutritives et de produits chimiques toxiques dans les réseaux d'eau douce. Les principales caractéristiques et applications de 38 modèles de matières nutritives et de 35 modèles de produits chimiques toxiques sont présentées sous forme de tableaux. Ces tableaux pourraient se révéler particulièrement utiles pour orienter les utilisateurs de modèles de gestion et de recherche vers des modèles et éléments de modèles mieux appropriés et qui peuvent servir à régler des problèmes de qualité de l'eau. Des revues détaillées des structures de modèles, des représentations des processus et des applications de deux modèles de matières nutritives et de trois modèles de produits chimiques toxiques sont présentées.

## Management Perspective

Ecosystem management requires predictions to be made about the pathways, fate and effect of contaminants. In a management mode, the models can be used to optimize proposed control measures which are proposed to meet water quality standards. This chapter presents a review of the recent (1978-1988) state-of-the-art models which have been developed for predicting the impacts, pathways, fate and effects of nutrient and toxic chemicals in freshwater systems. The authors were asked to write this chapter as a contribution to a CRC Press book entitled "Focus on Modelling Marine Systems, Volume II., in recognition of their significant contributions to water quality modelling and because of the modelling concepts which have been developed for freshwater systems which are incorporated into marine water quality models. The principal characteristics and applications of 38 nutrient and 35 toxic chemical models are summarized in two tables. These tables should be particularly useful for directing both research and management model users towards suitable models or model components which can be used to solve water quality problems.

## PERSPECTIVE-GESTION

La gestion des écosystèmes nécessite la formulation de prévisions où il est question des voies, du sort et des effets de contaminants. Dans un mode de gestion, les modèles peuvent servir à optimiser les mesures proposées de dépollution pour l'atteinte de normes de qualité de l'eau. Ce chapitre fait la revue des modèles récents et raffinés (1978-1988) qui ont été mis au point pour prévoir les impacts, les voies, le sort et les effets de substances nutritives et de produits chimiques toxiques dans les réseaux d'eau douce. Les auteurs ont été priés de rédiger ce chapitre qui doit être incorporé dans un ouvrage de la CRC Press et qui sera intitulé "Focus on Modelling Marine Systems, Volume II"; ces auteurs ont été pressentis à cause de leur importante contribution à la modélisation de la qualité de l'eau et parce qu'ils ont trouvé des concepts de modélisation des réseaux d'eau douce qui ont été incorporés dans des modèles de la qualité de secteurs marins. Les principales caractéristiques et applications de 38 modèles de substances nutritives et de 35 modèles de produits chimiques toxiques sont présentées en résumé dans deux tableaux. Ces tableaux pourraient se révéler particulièrement utiles pour orienter les utilisateurs de modèles de gestion et de recherche vers les modèles et éléments de modèles mieux appropriés qui peuvent servir à régler des problèmes de qualité de l'eau.

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## 1. INTRODUCTION

Mathematical modelling of ecological systems is a multidisciplinary field of research. The models are based upon fundamentals of climatology, meteorology, chemistry, biology, geology, hydrology and physics. All models are developed with the goal of being able to simulate real-world behaviour under varying conditions. The complexity of the model and its input and output data depend on the spatial and temporal scales of interest. The main thrust behind the development of water quality models has been the need to predict the results of man-made influences on our water resources, ranging from rainwater to seawater. Until recently, the oceans have been treated as a system that, because of its enormous size, could continue to dilute any contaminants that were introduced into it. However, freshwater systems, such as rivers, lakes and groundwaters, have had more rapid and more visible impacts on their water quality by both natural and man-made processes. For this reason, much more effort has been directed over the past several decades toward the development of water quality models and the associated data collection activities for freshwater systems. Consequently, any book which deals with the development of models for the oceans should also include a review of freshwater models. Such a review could benefit ocean modelling since many of the underlying concepts are applicable in both systems. Indeed, for estuary models it is necessary to combine the two systems.

There have been a number of excellent reviews of the developments in environmental modelling of freshwater systems.<sup>1-7</sup> In this chapter a review of more recent (1978-1988) state-of-the-art freshwater modelling is presented. Due to the extremely diverse range of freshwater models, this chapter is restricted to a discussion of nutrient and toxic chemical water quality models only.

## 2. MODEL DESIGN

All environmental models are designed as a compromise representation of a natural system. Some models are designed to be applied to a specific type of site and problem while others are

designed as general, multimedia models, which have a flexible number of compartments and processes which can be selected by the model user. However, it is well accepted that there will never be a single environmental contaminant model that can be developed which will be suitable for all applications. It is apparent that classes of models with specific applications will continue to be developed. One way to efficiently utilize these models is to incorporate them into an expert system<sup>8</sup> framework that would allow the user to pick and choose the best model or model components for the particular application. Once the conceptualization of a modelling problem has been made, the model developer or user must determine the relevant variables that are required for describing the desired water quality characteristics of the system and the appropriate mathematical expressions. Without the help of an expert system, the choice of the model's spatial, temporal and ecological aggregation must be made on the modeller's or model user's personal experience. There is no guarantee that these initial choices will turn out to be the best choices in the later stages of the modelling procedure. Any model should be designed to be flexible enough in design to allow subsequent modifications to be made without major changes being required in the model's programming structure. The nature of the model will be determined by the end use; as a research model or as a management model.

Empirical and statistically-based models are normally based on data collected from a specific site or ensemble of sites and employ mathematical estimation techniques to determine model functions. In many cases these models are not transferable to other areas and the spatial and temporal detail used in the models leads to less exact results than could be obtained using a physically-based model.

Deterministic models are based on physical and chemical processes which are derived from theory rather than from mathematical analysis of data which is used for statistical models. Deterministic models can be based on the assumption of steady-state or they can employ a dynamic approach which allows the consideration of the variable time. The main problem with steady state models is that, in most cases, they can not be used for management as they do not generate temporal



response predictions. Time variable deterministic models are particularly useful in water quality modelling where input loads can vary over short time periods. Deterministic models are also assumed to have greater applicability for establishing cause-effect relationships among the processes modelled. However, all models rely to some extent on empiricism and require field data for model calibration and verification.

The more complex models will require more extensive field data for model calibration and verification than the other models. This data is usually only available for a small number of sites, which will limit the utility of the more complex models. Also, data collection is rarely carried out which considers the basic needs of modelling. In the case of complex deterministic models, the verification step can be a very difficult task since model verification can only be performed with a data set independent from that used during model calibration. In both the model calibration and verification steps, the "goodness" of fit must be adequately addressed. There are a number of quantitative methods that can be used to examine the fit between the predicted and observed data. Reasonable verification statistics however do not guarantee that any model will accurately predict future water quality.<sup>9</sup> Some uncertainty will always be present which results from the model coefficients, variables, and from the model structure itself.<sup>10</sup> The uncertainty of the values used in a model are normally reflected in the model results. Techniques such as first-order error analysis and Monte Carlo analysis can be used to calculate these values, as outlined in Reckhow and Chapra<sup>11</sup> and Chapra and Reckhow.<sup>12</sup>

### 3. WATER QUALITY MODELS

Tables 1 and 2 list some of the more recent nutrient and toxic chemical water quality models along with summaries of their principal characteristics and applications. As in a previous compilation<sup>4</sup> of existing models, these tables are not exhaustive in their scope but are presented as a starting point from which the reader can proceed in his/her search for a model or model components which can be used to solve a particular problem. In the first column of the tables the model name and its developer(s) are listed along with the associated model literature reference

number (#). In the time domain column the deterministic models are characterized as being either steady-state (S-S) or dynamic (Dyn). The time step is further defined as being variable (var), daily or annual. The empirical models are specified as having long term average (LTA), annual average (AA) or summer average (SA) data. As can be seen from the third column of the tables, the models represent a wide range of possible spatial domains. The models can simulate a system in one dimension (1-D), such as a whole lake (WL); in two dimensions (2-D) or in three dimensions (3-D). One dimensional models are capable of simulating either the vertical or longitudinal behaviour of water bodies. These models are used when simplifying assumptions can be justified to allow the other dimensions to be ignored. However, this necessitates a limit in the generality of the model. For a water body such as a lake, one dimensional models cannot predict the horizontal differences in water quality due to physical processes such as wind driven currents, the influences of nearshore processes, and variable bed sediments. The patterns of distribution or circulation that cover large space and time scales are normally determined by the shape of the lake or by short-term factors such as point source loadings that are characterized by much shorter space and time scales. These different scenarios would require the use of two and three-dimensional models that would be capable of simulating the processes over a wide range of scales.

The chemicals which are simulated in the models are presented in column 4. Some of the models were designed for specific chemicals while others were designed to simulate many different types of chemicals, such as metals or organics. The number of chemical state variables required in a model is basically determined by the nature and the number of significant interactions that occur with the key chemical or chemicals of interest. Some models<sup>17,67,69,87</sup> include generalized thermodynamic sub-models which allow an extensive number of interactions to be evaluated. However, proper application of some of these models requires specialized expertise because kinetic limitations may prevent many thermodynamically possible reactions.

In column 5 of the tables the input data necessary to run the models are listed. For some of the empirical models, input data for only one or two variables are required (i.e. Smith Blue-Green

Algal Model<sup>33</sup>) whereas some of the more complex deterministic models (i.e. WASP4<sup>34</sup>) may require input data for hundreds of model variables and parameters. Some of the models have been developed as theoretical exercises and have never been applied to natural systems. Other models have been calibrated and verified by application to a number of independent system data sets. The natural systems the models have been applied to and the associated time periods are presented in column 7. In the last column some of the key assumptions and features of the models are presented. The model user must be aware of the assumptions and limitations of the models used. Failure to take these factors into account before applying a model to a new system will inevitably result in inaccurate model output. For any new application, a recalibration of the model is necessary and in some cases a change in model structure is required. The models which are designed for managers and other such users are now being designed with features to make them more user-friendly. These models are typically designed to be able to be run on personal computers and have menu driven software. For a model to be useful to persons other than the developer, it must also be well documented. For many of the existing models, such documentation is not available or it is not written in a manner to make it useful for the wide range of potential model users. For the users with little or no modelling experience, the documentation should point out those areas in the model program that can be modified and those that should not be altered. A model may also be designed that operates in an interactive mode so that the documentation and operation are combined. It is also common practice to include benchmark example input and output files with the model documentation to ensure that the model is operating properly on the user's computer system, which may not be fully compatible with the design of the model computer coding. In order for a model to maintain its utility, it must continuously be revised. This includes modifications of mathematical representations of physical-chemical processes as well as modifications to incorporate the ever changing state-of-the-art in computer technology. For example, model set-up can be improved by new sophisticated input techniques. Output can now be displayed more efficiently using computer graphics. The process of linking different models

together for application to a problem is becoming more widely used. For example, a hydrodynamic model might be linked with a chemical model, which might in turn be linked with a biological model to assess the effect of a chemical spill.<sup>13</sup>

#### 4. MODEL CASE STUDIES

The bulk of the water quality models which have been developed over the past few decades have been directed toward the problem of eutrophication which has been caused by the significant increase in the loadings of nutrients, particularly phosphorus, to both large and small lakes. Eutrophication of rivers has not been as serious a problem due to the short residence time of the water. In rivers, one of the major problems has been the concentration of dissolved oxygen, which is controlled by the rate of production of oxygen by algae, the nitrogen cycle, and other biochemical processes. Also, the direct relationship between eutrophication and algal concentrations has allowed the development of empirical models to proceed more rapidly. Consequently, these empirical models have found a much wider use in lake management than they have in river management. In this chapter, it is impossible to describe all of the models in detail. The major characteristics of some of the recent water quality models have been presented in Table 1. A number of models have been selected from Table 1, which represent a reasonably wide range of water quality models, for more in-depth review. A similar approach has been followed for toxic models.

##### 4.1 Nutrient Models

###### 4.1.1 Introduction

Numerous studies have determined that the concentration of total phosphorus in lakes can be used as an indicator of lake trophic status (Vollenweider<sup>92</sup>, Dillon<sup>93</sup>), algal population densities as measured by chlorophyll a concentrations (Dillon and Rigler<sup>94</sup>, Jones and Bachman<sup>95</sup>) and water clarity (Dillon and Rigler<sup>96</sup>). Simple empirical models have been developed to predict total lake phosphorus concentrations using data such as annual phosphorus inputs, lake morphometry,

hydraulic flushing rates and temperature (Chapra<sup>97</sup>, Vollenweider<sup>98</sup>, Kirchner and Dillon<sup>99</sup>, Jones and Bachmann<sup>95</sup>, Larsen and Mercier<sup>100</sup>, Reckow<sup>101,102</sup>). These empirical models are based on data from numerous field studies and require only a limited amount of input data which makes them particularly useful for lake managers.

An example of an empirical model that has been developed to predict total phosphorus concentrations, chlorophyll a, and Secchi depths is that of Canfield and Bachmann.<sup>97</sup> Although the model coefficients are based on data collected from a wide variety and number of lakes, the model is based upon the general model proposed by Vollenweider<sup>103</sup>:

$$TP = L/D_s(\sigma + h) \quad (1)$$

where

TP = total phosphorus concentration in lake water (mg/m<sup>3</sup>)

L = annual phosphorus loading per lake area (mg/m<sup>2</sup>/y)

D<sub>s</sub> = mean lake depth (m)

σ = phosphorus sedimentation coefficient (1/y)

h = hydraulic flushing rate (1/y)

The successful application of such a model is greatly dependent on how well the loss of phosphorus to the sediments is estimated. Dillon and Rigler<sup>104</sup> chose to rewrite the Vollenweider equation and work with the phosphorus retention coefficient of a lake rather than the phosphorus sedimentation coefficient:

$$TP = L(1 - R_p)/w_a \quad (2)$$

where w<sub>a</sub> = annual areal water loading (m/y), and R<sub>p</sub> = phosphorus retention coefficient (difference between annual phosphorus inputs and phosphorus outputs divided by the annual phosphorus input).

Chapra<sup>97</sup> used a different parameter, the apparent settling velocity (v), which is equal to the product of the mean depth and the sedimentation coefficient:

$$R_p = v/(v + w_a) \quad (3)$$

where v is assumed to be a constant. Reckow<sup>102</sup> later proposed that v varied with w<sub>a</sub>:

$$v = 11.6 + 0.2w, \quad (4)$$

Larsen and Mercier<sup>100</sup> and Vollenweider<sup>105</sup> independently determined that phosphorus retention coefficients could be better estimated by the reciprocal of 1 plus the square root of the hydraulic flushing rate. Canfield and Bachmann<sup>37</sup> have evaluated the general applicability of these relationships to both natural and artificial lakes by applying them to a large data base for 704 natural and artificial lakes (Jones and Bachmann,<sup>95</sup>; Larsen and Mercier,<sup>100</sup>; U.S. EPA National Eutrophication Survey (EPA-NES).<sup>106</sup> Phosphorus sedimentation coefficients were estimated from the data by assuming steady state and by rearranging the terms of Equation 1 (Jones and Bachmann,<sup>95</sup>)

$$\sigma = ((L/D_p)/TP) \cdot h \quad (5)$$

The authors attempted to avoid the problems associated with developing and testing a model with the same data by randomly sorting the lakes into two data sets. One data set (model development) which included 151 natural and 210 artificial lakes was used to determine the limnological factors that influence phosphorus sedimentation rates. The other data set (model verification), which included 139 natural lakes and 233 artificial lakes, was used to evaluate the accuracy of the model predictions.

A statistical analysis showed that the best estimate for the sedimentation coefficient ( $\sigma$ ) in the Vollenweider equation was

$$\sigma = 0.162(L/D_p)^{0.458} \text{ for natural lakes} \quad (6)$$

$$\sigma = 0.114(L/D_p)^{0.589} \text{ for artificial lakes} \quad (7)$$

Two other models were developed to reflect the rapid sedimentation of particulate phosphorus carried into a lake by inflowing streams. The first assumes that a constant fraction ( $f_p$ ) of the inflowing total phosphorus will flow into the open waters to be acted on by a constant sedimentation coefficient, following a rapid, initial sedimentation of particulate phosphorus near the tributary inlets. The model is represented by the equation

$$TP = f_p L/D_p (\sigma + h) \quad (8)$$

A second similar model combines the initial rapid sedimentation with a sedimentation coefficient that varies with the volumetric loading

$$TP = f_s L / D_s (a(L/D_s)^b + h) \quad (9)$$

For natural lakes,  $a = 0.0942$ ,  $b = 0.422$ , and  $f_s = 0.8$  and for artificial lakes,  $a = 0.0569$ ,  $b = 0.639$ , and  $f_s = 0.8$ . However, the model results gave no indication about the relative importance of immediate sedimentation of particulate phosphorus versus sedimentation in open waters because both equations gave similar results.

Canfield and Bachmann<sup>37</sup> also examined the phosphorus-chlorophyll a and chlorophyll a-Secchi relationships for the natural and artificial lake data. Their results indicate that the relationships are stronger for the natural lakes than for the artificial lakes. Factors other than phosphorus were suggested to be limiting algal levels in many artificial lakes and the results also support the common observation that nonalgal turbidities are important as factors of water clarity in artificial lakes.

To improve the accuracy of the predictions, the empirical models must be modified so as to reduce the number of simplifying assumptions that do not always hold. However, increasing the complexity of the models must be carried out so that the new variables that are added are effective in reducing the errors while maintaining the generality of the models. A determination of model complexity enters the modelling process at two stages. The first is during the initial stage when the modeller must choose a certain level of complexity before attempting to verify the model against measured data and the second is during the final phases when the modeller must decide whether the model has been verified and has sufficient complexity for its intended application. Simple models, such as the empirical model, can be used as a first approximation analysis upon which to build a more complex model that can take advantage of more detailed field data.

#### *4.1.2 Steady-State Eutrophication Model*

Schnoor and O'Connor<sup>30</sup> developed a steady-state model which built upon the previous empirical models, but because it was not developed empirically, it has the advantage of being applicable to

lakes and reservoirs of varying morphology and locality. This type of model also allows the analyst to quantitatively relate nutrient concentrations to phytoplankton concentrations. The principal disadvantage of this type of model is that various rate constants required in the model must be estimated.

An initial simplification is made by assuming that the lake or reservoir can be considered as being completely mixed. Figure 1 is a schematic of the kinetics and transport of the nutrient-phytoplankton system simulated in the model. Inorganic nutrient input ( $W_i$ ) is derived from natural and manmade sources, and is formed by the mineralization of organic nitrogen,  $K_m$ . It is lost through washout,  $1/t_o$ , and by phytoplankton uptake,  $K_p$ , via a Lotka-Volterra<sup>105</sup> kinetics. Phytoplankton are lost due to washout and by the conversion to organic nutrient via  $K_c$ . Phytoplankton is also lost from the water column by settling, at a rate,  $K_s$ . It is assumed that total organic nutrient is mineralized at a constant rate,  $K_m$ . In this model, inorganic nutrient recycling from the sediments must be included in the external input term  $W_i$ . The mass-balance equations for the system are:

$$dN_i/dt = K_m N_o - K_p N_i N_p - N_i/t_o + W_i/V \quad (10)$$

$$dN_p/dt = K_p N_i N_p - K_c N_p - N_p/t_o - K_s N_p \quad (11)$$

$$dN_o/dt = K_c N_p - K_m N_o - K_s N_o - N_o/t_o + W_o/V \quad (12)$$

where

$N_i$  = inorganic nutrient concentration,  $ML^{-3}$

$N_p$  = phytoplankton nutrient concentration,  $ML^{-3}$

$N_o$  = organic nutrient concentration,  $ML^{-3}$

$t_o$  = mean hydraulic detention time, T

$W_i$  = input rate of inorganic nutrient,  $MT^{-1}$

$W_o$  = input rate of organic nutrient,  $MT^{-1}$

$V$  = lake volume,  $L^3$

Summing equations (10) - (12) results in the equation:



$$dN_T/dt = -N_T/t_o - K_r N_o + W_T(t)/V - K_p N_p \quad (13)$$

where

$$N_T = N_i + N_p + N_o$$

$$dN_T/dt = dN_i/dt + dN_p/dt + dN_o/dt$$

$$W_T = W_i + W_o$$

At steady-state, the non-linear, ordinary differential equations (10)-(12) are reduced to the following set of algebraic equations:

$$N_i = (K_c + (1/t_o) + K_p)/K_r \quad (14)$$

$$N_p = (\alpha(N_q - N_i) + (N_i K_m / K_c)) / t_o (\alpha K_p N_i - K_m) \quad (15)$$

$$N_o = (N_p + (N_i / t_o K_c)) / \alpha \quad (16)$$

where

$$\alpha = (K_m + K_r + (1/t_o)) / K_c$$

$$N_i = W_o t / V = \text{average inflow organic nutrient concentration}$$

$$N_q = W_i t / V = \text{average inflow inorganic nutrient concentration}$$

Assuming that measurements for  $N_i$ ,  $P$ , and  $N_o$  are available and that  $K_r$  can be calculated from productivity measurements, equations (10)-(12) can be solved for  $K_c$ ,  $K_p$ ,  $K_m$ .

$$K_c = K_p N_i - 1/t_o - K_r \quad (17)$$

$$K_p = (W_T/V - N_T/t_o) (1/(N_o + N_p)) \quad (18)$$

$$K_m = 1/N_o (K_p N_i N_p + N_i/t_o - W_i/V) \quad (19)$$

From equation (17) it can be seen that at steady state, the overall growth rate minus the outflow and settling rate is equal to the total loss of phytoplankton,  $K_c$ . Equation (18) shows that the mass rate of sedimentation  $K_p(N_o + N_p)$ , is equal to the mass rate of total nutrient minus outflow. The mass rate of nutrient recycled,  $K_m N_o$ , increases with primary production ( $K_p N_i N_p$ ) and decreases with the inorganic input minus the outflow of inorganic nutrient, according to equation (19). The model was applied to Lake Lyndon B. Johnson, which is the third of a series of seven

impoundments in the Highland Lakes chain of Central Texas. It was calibrated using 1972 data and verified using 1973 data. The model was also applied to Lake Ontario data for the period 1967 - 1973.

A general observation that can be made from examining the model equations is that the sedimentation coefficient,  $K_s$ , and the nutrient loading determine the total phosphorus in a lake or reservoir. The kinetic coefficients  $K_p$ ,  $K_c$ , and  $K_m$  determine the nutrient partitioning among the various organic, inorganic, and phytoplankton fractions.

#### 4.1.2 Lake Erie Model (Lam et al. <sup>18,19</sup>)

Lake Erie has been the focus of several water quality modelling studies for the last two decades (Vollenweider,<sup>92</sup>; DiToro and Connolly,<sup>108</sup>; Lam et al.<sup>19</sup>; Snodgrass<sup>109</sup>). Major pollution abatement on phosphorus loading was implemented in Lake Erie in the early seventies, but anoxia still occurs intermittently in the central basin hypolimnion. Several modelling approaches were proposed to explain why phosphorus removal alone cannot eliminate anoxic occurrences totally. Some, e.g. Burns<sup>110</sup>, attributed the occurrences to the physical conditions in the lake. He used three thermal layers (epilimnion, mesolimnion and hypolimnion) to calculate oxygen exchanges across layers. While he showed that the physical effects were important, the data he used were too crude to accurately pinpoint the water oxygen demand (WOD) and sediment oxygen demand (SOD). Others, e.g. DiToro and Connolly<sup>108</sup> elaborated on the biological and chemical processes (using 15 variables) to define these rates but parameterized the stratification with a simple diffusivity. While they derived interesting theoretical values for WOD and SOD, they found it necessary to revise the hypolimnion depth which was assumed constant in order to fit the observed oxygen data for 1975.

The shortcomings in these models indicated that physical, chemical and biological processes all play a role in the oxygen depletion problem in Lake Erie. The question is which processes should be included in the model and which should not. Lam et al.<sup>19</sup> proposed the use of a hierarchy of models to deal with this situation. For the case of Lake Erie, a model consisting of nine boxes

representing the three basins and the three thermal layers which change their depths in time were found to be adequate in terms of the spatial resolution. An oxygen-phosphorus model with three variables is incorporated in these boxes and comparison to 16 years of data was reported in Lam et al.<sup>11</sup>. The following is a summary of the model components and their interactions.

#### *Nine-Box Model Structure*

A detailed discussion of the mathematical equations for the nine-box model is given in Lam et al.<sup>18</sup> Briefly, Table 3 summarizes the three basic mass balance equations, Equations (20) to (22), for the three variables, soluble reactive phosphorus (SRP), organic phosphorus (OP), and dissolved oxygen (DO), respectively. For each of the three layers, namely epilimnion, ( $i=1$ ), mesolimnion ( $i=2$ ), and hypolimnion ( $i=3$ ), in each of the three basins, appropriate areas ( $AB_i$ ) and volumes ( $V_i$ ) must be used in these equations (Table 3). Note that  $AB_i$  and  $V_i$  are assumed to vary with time. The source term,  $F_i$ , used in these equations refers to the loading as well as the inputs and outputs of the variable into and out of the  $i$ th layer as a result of five major physical processes. Again, briefly, Figure 2 shows a schematic description of the five physical processes considered. The hydraulic flow represents the inflow at the Detroit River and the outflow at the Niagara River, resulting in a general west-to-east flow in the lake. The water transport across the boundary between the western basin and the central basin as well as that across the boundary between the western basin and the eastern basin is conservative. Thus, depending on the cross-sectional areas of these boundaries in each layer, the velocities due to the hydraulic flow are adjusted to obey mass conservation within each box.

For simplicity, it is assumed that the interface between epilimnion and mesolimnion and the interface between mesolimnion and hypolimnion are at the same depths in all three basins. This assumption facilitates the calculation of vertical entrainment and avoids the complication of further adjusting the hydraulic flows to mis-matched interfaces in different basins. Under this assumption, when one of the interfaces moves up, that part of the water in the upper layer traversed by the interface is mixed into the lower layer. In this way the concentrations in the new upper layer

remain undisturbed. This entrainment mechanism<sup>111</sup> differs from the so-called diffusion process in which the concentrations in both layers are mutually disturbed due to an exchange mechanism. Indeed, the incorporation of the vertical entrainment sets the model apart from other models using fixed thermal interfaces (e.g. DiToro and Connolly<sup>108</sup>) in which only the diffusion process can occur. In the model, both entrainment and diffusion processes are possible. Due to the fact that the nine-box model uses the lake bottom as the reference point, changes in water level must be taken into account to transfer these processes properly. The water level can affect the heat storage in the lake and hence the thermal layer structure. As the water level rises, so do the thermal interfaces with respect to the lake bottom, and vice versa.<sup>111</sup>

Wind driven circulation can cause interbasin transports (Figure 2) in addition to the hydraulic flow. For simplicity, two vertical gyres are assumed in the nine-box model. The first gyre connects the epilimnion and mesolimnion in the central and eastern basins and the second connects the mesolimnion and hypolimnion (Figure 2). Of particular interest is the possibility that under certain wind conditions, there could be interbasin transport from the eastern basin hypolimnion to the central basin hypolimnion, bringing oxygen-rich water from the former to replenish the oxygen depleted in the latter.

#### *Phosphorus Oxygen Submodel*

The nine-box model structure provides the dynamic framework for defining the boundaries of the boxes as well as the movement of substances among the boxes. Within each box, a set of biological and chemical processes also takes place. The Simons and Lam model<sup>10</sup> has been refined by the addition of an oxygen compartment for this purpose, i.e., a three-variable model of soluble reactive phosphorus (SRP), organic phosphorus (OP), and dissolved oxygen (DO). Figure 3 shows the schematic for the biochemical kinetics of the three variables for a typical basin with a three-layered structure. Table 3 summarizes the governing equations (Equations 20-22). In the epilimnion, the oxygen is produced by phytoplankton photosynthesis in the photic zones and by reaeration at the air-water surface. Most of the time, oxygen is saturated or even super-saturated in

this layer, with the saturation being a function of the water temperature calculated using the thermocline model.<sup>111</sup> In the mesolimnion and hypolimnion, oxygen can be produced by photosynthesis, since these layers may still be within the photic zone, particularly during the early part of the stratification period. However, as in the case of Lake Ontario,<sup>10</sup> plankton respiration activity is reduced and hence less oxygen is consumed in the hypolimnion because of lower temperature and smaller cell size.

The sediment oxygen demand (SOD) is one of the major factors responsible for removing oxygen from the overlying waters in the central basin hypolimnion. The values of SOD measured by, e.g., Lucas and Thomas,<sup>113</sup> Snodgrass,<sup>109</sup> Charlton<sup>114</sup> and Herdendorf<sup>115</sup> in this basin range from 0.18 g O<sub>2</sub>/m<sup>2</sup>d to 0.88 g O<sub>2</sub>/m<sup>2</sup>d, depending on the instrument design and sampling method. Snodgrass<sup>109</sup> examined three SOD submodels with varying degrees of complexity and concluded that the simplest one produced essentially the same results as the most complex. This model uses the Monod kinetic

$$J_o = s_o (DO)/(DO + k_o) \quad (23)$$

where  $J_o$  is the oxygen flux into the sediment (g O<sub>2</sub>/m<sup>2</sup>d),  $s_o$  is the sediment oxygen demand rate (g O<sub>2</sub>/m<sup>2</sup>d), DO is the oxygen concentration of the overlying water (mg/L), and  $k_o$  is the Michaelis constant (mg/L) for oxygen. The Monod kinetic has been found<sup>109</sup> to simulate successfully the biological sediment oxygen demand as well as the water oxygen demand. The chemical sediment oxygen demand is found<sup>109</sup> to be relatively small and can be sufficiently described by first order kinetics. Snodgrass<sup>109</sup> reported  $k_o = 1.2$  mg/L for biological sediment oxygen demand. In the case of equation (23), with the two Monod expressions combined into one, the Michaelis coefficient  $k_o$  is found to be 1.4 mg/L. Lam et al.<sup>111</sup> examined the SOD submodel and found that, as a first order approximation,  $s_o$  could be written as

$$s_o = L(TP) \times 10^{-5} \quad (24)$$

where  $L(TP)$  is the lakewide total phosphorus load in MT.

#### 4.2 Toxic Chemical Models

#### 4.2.1 Introduction

The presence of a wide range of toxic chemicals in the waters, sediments and biota of lakes has become increasingly evident. These toxics represent uncertain human and aquatic health effects. Effective remedial action and management of these contaminants requires careful examination of the complex cause and effect mechanisms that ultimately determine chemical fate, longevity, and toxicity. The behaviour of the contaminant can be simulated by the use of models which incorporate processes which describe its partitioning characteristics and the rate at which it may be transported between compartments and broken down by various chemical and biochemical reactions.

Deterministic computer models which are developed to predict the distribution of toxic chemicals (heavy metals, organic chemicals and radionuclides) in the aquatic environment are based on the use of mass balance equations which describe a toxic substance's physical transport, adsorption, volatilization and decay in the system. In the most simple case, the lake or reservoir is assumed to be spatially uniform (completely mixed system), in which the transport, transfer, and kinetic components are described in terms of bulk coefficients. The equations which follow have been examined and developed by O'Connor.<sup>116,117</sup> They define the steady-state distribution of toxic substances in a freshwater system which is shown in Figure 4. In this model, it is assumed that the mass of toxicant in the food chain is not significant. It is also assumed that the rates of adsorption and desorption between the dissolved and particulate components are much faster than the other kinetic processes, i.e. decay, volatilization, settling, and exchange with the bed.

#### *Partition Coefficient*

A partition coefficient is typically used to describe the equilibrium distribution of the toxic chemical between the dissolved and solid phase. This distribution describes the reversible reaction which includes the composite effect of specific adsorption, ion exchange, and complexation. The partition coefficient is the ratio of the solid and dissolved phases:

$$P = r/C \quad (25)$$

where  $r$  is the solid phase concentration and  $C$  is the dissolved phase concentration. The total

concentration  $C_T$  in the system may be defined as the sum of the dissolved  $C$  and particulate component  $p$ :

$$C_T = C + p \quad (26)$$

The latter is the product of the solid phase concentration and that of the adsorbing solids  $m$ :

$$p = r m \quad (27)$$

The dissolved concentration  $C$  includes both the free and bound fractions. The bound fraction is defined as the nonparticulate concentration, which in equilibrium with the solid phase is the basis of the operational definition of the partition coefficient. Substitution of equations 25 and 27 into equation 26 results in the expressions for the dissolved  $f_d$  and particulate  $f_p$  fractions:

$$f_d = C/C_T = 1/(1 + Pm) \quad (28)$$

$$f_p = p/C_T = Pm/(1 + Pm) \quad (29)$$

The partition coefficient  $P$  is usually expressed as  $\mu\text{g per kg r per } \mu\text{g per litre C}$  or litres per kilogram, L/kg. The product  $Pm$  is thus a dimensionless parameter. The partition coefficient varies from approximately 500 - 500,000 L/kg and the concentration range of particulate solids also varies over many orders of magnitude (<10 mg/L of suspended solids to > 100,000 mg/L in bed sediments). Considering the high concentration of solids in the bed, the component fractions may be approximated as

$$f_{ps} \approx 1 \quad (30)$$

$$f_{ds} \approx 1/P_s m_s \quad (31)$$

where the subscript  $s$  denotes the sediment.

Many factors are responsible for influencing the magnitude of the partition coefficient. In the case of heavy metals and inorganic chemicals, factors such as pH, redox conditions, ionic strength, and complexing capacity are significant. For organic chemicals, solubility and molecular structure are important. The influence of solids concentration on the partition coefficient has also been observed (O'Connor and Connolly,<sup>118</sup>; Hasset and Anderson,<sup>119</sup>). It is consequently recommended that the partition coefficient of a given chemical be determined over a range of concentrations of solids

and organic matter that exist for a specific water body.

*Kinetic Equations*

The rate of adsorption between the dissolved and particulate components of a substance is a function of both the concentration in the dissolved phase and the number of available sites on the adsorbing solids. The latter is proportional to the maximum adsorption capacity of the solid  $r_c$  minus the amount of the solute adsorbed  $r$ . The rate of desorption is proportional to the amount of solute adsorbed. If we assume that the solid phase concentration  $r$  is significantly less than the adsorptive capacity of the solids, then the rate equation is

$$dC/dt = -K_1C + K_2p \tag{32}$$

and  $K_1 = K_a r_c m$ ;  $K_a$  = adsorption coefficient;  $r_c$  = adsorptive capacity;  $m$  = concentration of solids; and  $K_2$  = desorption coefficient. At steady-state, equation 32 becomes

$$r/C = K_a r_c / K_2 = P \tag{33}$$

and  $K_1 / K_2 = Pm \tag{34}$

If we consider a system where only the dissolved and particulate components are present and where the dissolved component is subject to volatilization, the kinetic equations are

$$dC/dt = -(K_1 + K_v)C + K_2p \tag{35}$$

$$dp/dt = +K_1C - K_2p \tag{36}$$

in which  $K_v = K_l / D_a$  = volumetric volatilization coefficient;  $K_l$  = surface volatilization coefficient and  $D_a$  = average depth. Addition of 35 and 36 yields

$$dC_T/dt = -K_v C \tag{37}$$

For the solutions of equations 35 and 36 to be valid at steady-state equilibrium, it is apparent that the rates of adsorption must be much greater than the rate of volatilization. Substitution of equation 28 into equation 37 gives the dissolved concentration as a function of  $C_T$ :

$$dC_T/dt = -K_v C_T / (1 + Pm) = -f_d K_v C_T \tag{38}$$

For a nonvolatile chemical whose dissolved and particulate components decay at different rates,  $K_d$  and  $K_p$ , respectively, the rate equation for the total concentration is



$$dC_T/dt = -(f_d K_d + f_p K_p) C_T \quad (39)$$

Again, for the solution to be valid at equilibrium, the adsorption-desorption rate must be much greater than the rate of decay. The error introduced by this assumption has been studied by O'Connor<sup>16</sup>, and can be determined by the dimensionless number  $K_2 K_d / K_T^2$ , in which  $K_T = K_1 + K_2 + K_d$ . O'Connor<sup>16</sup> has shown that equation 38 is valid for  $(K_2 K_d / K_T^2) < 0.005$  (error < 1 %). This would suggest that the above approach would not be valid for toxic chemicals whose rate of decay is very rapid, such as short-lived radionuclides.

### *Suspended and Bed Solids*

If nearshore conditions are neglected then O'Connor<sup>16</sup> has shown that a mass balance of the solids can be represented by:

$$V dm/dt = -v_s A_s m - Qm + W \quad (40)$$

where:

$W$  = total mass input of solids to the lake

$A_s$  = sediment area

$v_s$  = solids settling velocity

$m$  = solids concentration in the water column

$V$  = volume of water

$Q$  = outflow rate

Dividing by the volume reduces equation 40 to:

$$dm/dt = m/t_o - m(1/t_o + K_s) \quad (41)$$

where:

$m_i$  = average concentration of total inflow =  $W/Q$

$t_o$  = detention time =  $V/Q$

$K_s$  = settling coefficient =  $v_s/D_s$

$D_s$  = mean depth =  $V/A$

At steady state, the solution is

$$m_j/m_i = 1/(1 + K_s t_o) \quad (42)$$

where  $m_e$  = equilibrium suspended solids concentration. If bed scour is significant, the solids equation is

$$dm/dt = m_j/t_o - m(1/t_o + K_s) + K_s m_s \quad (43)$$

where  $K_s$  is the scour coefficient and  $m_s$  is the bed solids concentration. At steady state, equation (43) reduces to

$$m_j/M_i = 1/(1 + K'_s t_o) \quad (44)$$

where  $K'_s = K_s(1 - \phi_e)$ ,  $\phi_e = (K_s m_s / K_s m_e) = (j_b / v_s m_e)$ . The term  $j_b$  is the entrainment flux and is =  $v_s m_s$ , where  $K_s = v_s / D_s$ , which is the entrainment coefficient. The term  $v_s$  is the scour coefficient of the bed solids.

If it is assumed that on a seasonal or annual basis there is a net sedimentation in a lake, then  $m = m_e$ , and bed thickness ( $D_s$ ) is described by

$$(D_s m_s) / (v_s m_e) = 1 - \phi_e \quad (45)$$

For  $\phi_e \leq 1$ , the rate of change of bed elevation is +ve.

For  $\phi_e = 0$ , scour is negligible.

For  $\phi_e = 1$ , scour balances settling and there is no net sedimentation.

### Chemical Equations

The total concentration in the water column for a lake in which scour is a significant process<sup>116</sup> is given by:

$$dC_T/dt = W/V - C_T/t_o - f_d(t)K_d C_T - f_p(t)K_p C_T + K_d[f_a C_{T_s} - f_d(t)C_T] + K_p C_{T_s} \quad (46)$$

The term  $K_t$  is the transfer coefficient of the dissolved component. If biodegradation or chemical reaction occurs, then the equation becomes

$$dC_T/dt = W/V - C_T/t_o - f_d(t)(K_d + K_s)C_T - f_p(t)(K_p + K_s)C_T + K_d[f_a C_{T_s} - f_d(t)C_T] + K_p C_{T_s} \quad (47)$$

The total concentration in a fixed bed, where diffusion down to deeper sediment is negligible, is given by

$$d(V,C_T)/dt = f_p(t)v_r A_s C_T - v_s f_{ps} A_s C_T - v_r A_s [f_{ds} C_T - f_d(t)C_T] \quad (48)$$

#### 4.2.2 Physical-Chemical Model of Toxic Substances in Lakes

The model must represent the following processes:

- 1) particulate sorption-desorption
- 2) sediment-water interactions
- 3) atmosphere-water interactions
- 4) transport of toxicant by advection, dispersion and mixing
- 5) biochemical decay and photolysis

##### *Suspended Solids Model*

In the Thomann and DiToro<sup>120</sup> suspended solids model, only a single class of solids is considered (i.e. lumps together the inorganic and organic particulates). This is a problem when considering the sorption of hydrophobic compounds such as PCB's, since they sorb differently to organic particles than they do to inorganic particles.

##### Water Column

In the water column, the mass balance equation for suspended solids is

$$Vdm/dt = W_m - Qm - v_s A_m + v_m A_m, \quad (49)$$

where:

$V$ = volume of the water column	$(L^3)$
$m$ = solids concentration in the water column	$(M/L^3)$
$m_s$ = solids concentration in sediment layer	$(M/L^3)$
$W_m$ = mass input of solids	$(M/T)$
$Q$ = advective flow transport	$(L^3/T)$
$v_s$ = particulate settling velocity	$(L/T)$
$A$ = interfacial area	$(L^2)$

$v_{rs}$  = particulate resuspension velocity (L/T)

### Sediment Layer

In the sediment layer, the mass balance equation is

$$V_s d_m/dt = v_r A m_s - v_{rs} A m_s - v_n A m_s \quad (50)$$

where:

$V_s$  = bulk volume of the sediment (L<sup>3</sup>)

$v_n$  = net sedimentation velocity of the sediment (L/T)

If it is assumed that the solids are at steady state, then  $dm/dt = d_m/dt = 0$ . The net sediment velocity ( $v_n$ ) can be defined as:

$$v_n = w_n m / q(1 - \Theta_s) \quad (51)$$

where:

$w_n$  = net loss of sediments from the water column (i.e.  $w_n = v_r v_r / v_n + v_n$ )

$q$  = solids density

$\Theta_s$  = sediment porosity

For a toxic chemical model, it is necessary to separate the solids concentration from the net sedimentation flux. The solids concentration in the sediment represents the bulk density and consequently, the concentration is given by:

$$m_s = q(1 - \Theta_s) \quad (52)$$

### Toxic Substances Model

In this model, it is assumed that the sorption-desorption kinetics are faster than the time step so that the dissolved and particulate toxicant are considered to be in a "local equilibrium" with each other. The dissolved form,  $C_d$  is the mass of toxicant per volume of water and the total toxicant concentration,  $C_t$ , is the mass of toxicant per volume of water plus solids, ( $C_p$ ). The porosity of the volume must be multiplied by  $C_d$  to obtain the porosity-corrected dissolved form of the toxicant,

$C_d$ : The porosity-corrected partition coefficient  $p'$  can be defined as:

$$p' = r/C_d \quad (53)$$

where  $r$  is the concentration of the chemical on a per unit solids basis. The fraction of the toxicant that is dissolved,  $f_d$ , is

$$f_d = (1 + p'm)^{-1} \quad (54)$$

and the particulate fraction,  $f_p$ , is

$$f_p = p'm/(1 + p'm) \quad (55)$$

For a continuously stirred tank reactor (CSTR), the mass balance equation for the total toxicant is expressed by:

$$VdC_T/dt = W - QC_T - v_n Af_p C_T + v_n Af_{ps} C_{Ts} + K_D A(f_d C_T/\phi_s - f_d C_T/\phi) - KVC_T + k_i A(C_a/H_c - f_d C_T/\phi) \quad (56)$$

where:

$W$ = mass loading rate of toxicant	$(M_T/T)$
$C_T$ = total toxicant concentration	$(M_T/L^3)$
$C_{Ts}$ = sediment total toxicant concentration	$(M_T/T)$
$K_D$ = sediment water diffusive transfer coefficient	$(L/T)$
$k_i$ = volatilization transfer rate coefficient	$(L/T)$
$K$ = overall loss rate of toxicant	$(1/T)$
$C_a$ = atmospheric toxicant concentration	$(M_T/L^3g)$
$H_c$ = Henry's constant	$((M_T/L^3g)/(M_T/L^3w))$

where:  $K = K_d f_d + K_p f_p$

$K_d$  = loss rate of the dissolved forms

$K_p$  = loss rate of the particulate forms

The mass balance equation for the toxicant in the sediment segment is represented by the equation:

$$V_s dC_T/dt = WAf_p C_T - v_n Af_{ps} C_{Ts} + K_D A(f_d C_T/\phi - f_{ds} C_{Ts}/\phi_s) - v_n Af_{ps} C_{Ts} - K_2 V_s C_{Ts} \quad (57)$$

where:  $K_2 = K_d F_{ds} + K_{ps} f_{ps}$

The above model was applied by Thomann and DiToro<sup>120</sup> to the prediction of <sup>239</sup>Pu and PCB levels in the Great Lakes. The model was first applied to the plutonium data so that the effects of sediment resuspension and interaction with the water column could be calibrated. The settling and resuspension parameter values were then used in the application of the model to PCB's. The model predictions of PCB in the water column and sediment were found to be, at best, an order of magnitude calculation. This was due to the following:

- 1) uncertainty in input loads
- 2) uncertainty in volatilization rates
- 3) wide range of reported water column and surface sediment concentrations
- 4) variability in the estimates of the coefficients.

#### 4.2.3 Mass Balance Model of Metals in Lakes

Dolan and Bierman<sup>121</sup> used a three-stage approach in the development of a metals mass balance model for Saginaw Bay, Lake Huron. In the first stage, the advection and dispersion components of the model were calibrated using conservative tracers. In the second stage, the output from the first stage was used to obtain a dynamic mass balance for suspended solids in both the water column and sediment. In the final stage an equilibrium partition coefficient was used to couple the metals mass balance to the suspended solids mass balance. A schematic diagram of this coupled model is shown in Figure 5.

##### *Advection and Dispersion*

In the model the effects of advection and dispersion are described using the equation:

$$Vdm/dt = \sum_{i=1}^N F(Q_i, E_i, m_i) + W_m \quad (58)$$

where:

$Q_i$  = the advective flow across the  $i$ th interface of a segment ( $m^3/sec$ )

$E_i$  = the dispersion at the  $i$ th interface of a segment ( $m^3/sec$ )

$m_i$  = the neighbouring segment concentration ( $ug/L$ )

$W_m$  = loading of suspended solids (MT/day)

$V$  = volume of water in a segment ( $m^3$ )

$N$  = total number of neighbouring segments

The function,  $F$ , which represents the net effect of advection and dispersion in the water column, is the same as that used by Richardson<sup>122</sup>. The model was calibrated by adjusting flow rates and dispersions among model segments until calculated concentrations of tracer matched the observed values.

#### *Suspended Solids Mass Balance*

The approach used by Lorenzen et al.<sup>123</sup> for total phosphorus was modified for the suspended solids and metals mass balance. The modifications include:

1. Loading rates were considered time-variable.
2. Particulate sedimentation was considered to depend on a power function, not a first-order function.
3. The resuspension term was considered to be a function of wind speed.

The mass balance equation for each water column segment is represented by:

$$V dm/dt = \sum_{i=1}^N F(Q_i, E_i, m_i) + W_m - (V m v_s)/D + (V_s m_s v_{rs})/D_s \quad (59)$$

where:

$m$  = suspended solids concentration in the water column,  $kg/L$

$v_s$  = settling velocity in  $m/sec$

$D$  = segment depth in meters

$V_s$  = volume of sediment in a segment in  $m^3$

$m_s$  = concentration of solids in the sediment in  $kg/L$

$v_{rs}$  = sediment resuspension velocity in  $m/sec$

$D_s$  = depth of sediment in a segment in meters

For each sediment compartment, the solids concentration in the sediment was determined using an equation of the form:

$$V_s \frac{dm_s}{dt} = V m v_s/D - (V_s/D_s)m_s(v_{s_s} + kb) \quad (60)$$

where  $kb$  is the sediment burial rate in meters/sec. Equations (59) and (60) were coupled through the two variables for suspended solids concentrations,  $m$  and  $m_s$ .

The variable settling velocity,  $v_s$ , is used to account for differences in settling velocities among the various size fractions of suspended solids in the water column. In the model, the settling velocity at any time is represented by:

$$v_s = ks m^G \quad (61)$$

where  $ks$  is the normalized settling velocity in m/sec and  $G$  is an empirical constant (unitless).

A threshold mechanism was used to determine the time-variable sediment resuspension rate. If the average daily wind speed was below a specified threshold value, the apparent net resuspension velocity of the sediments was assumed to be zero. If the wind speed exceeded this threshold, the value of the apparent net resuspension velocity was determined by the use of a calibration curve.

As shown in Figure 5., the sediment was divided into two layers. The upper layer is the "active" layer which is subject to potential resuspension. In the model, the depth of this layer was assumed to be a constant 10 cm, based on the depth of benthic activity.

#### *Equilibrium Partitioning*

In natural systems, the adsorptive capacity of the solids is almost invariably an order of magnitude greater than the solid phase concentration. Also, the suspended solids concentration is at least an order of magnitude greater than any of the metals. The equilibrium equation of Wolfe et al.<sup>124</sup>:

$$C_d = C_T/(P * C + 1) \quad (62)$$

has been used in the model, where  $P$  is the partition coefficient, in L/kg. Under the above conditions, negligible competition between different trace metals can be assumed and the equation



becomes identical to a linear adsorption equation (Oakley et al.<sup>125</sup>).

#### *Metals Mass Balance*

In the model, a mass balance equation for total metal in the water column is defined as:

$$V \frac{dC_T}{dt} = \sum_{i=1}^N F(Q_i, E_i, C_{Ti}) + W - (V(C_T - C_d)v_s)/D + (V_s v_n C_{Ts})/D_s \quad (63)$$

where  $W$  is the loading of total metal (mg/day),  $C_T$  is the concentration of total metal in the water column (ug/L),  $C_d$  is the concentration of dissolved metal in the water column (ug/L), and  $C_{Ts}$  is the concentration of total metal in the sediment in ug/L. The mass balance equation for total metal in the sediment is :

$$V_s \frac{dC_{Ts}}{dt} = (V(C_T - C_d)v_s)/D - (V_s C_{Ts}(v_n + kb))/D_s \quad (64)$$

The mass balance for dissolved metals follows from the differentiation of equation 62:

$$V \frac{dC_d}{dt} = V \frac{dC_T}{dt} (1/(P C + 1)) - V \frac{dC}{dt} (P C_T)/(P C + 1)^2 \quad (65)$$

In the model, particulate metal was assumed to track with suspended solids in the water column. It was also assumed that all metal in the sediments was associated with solids and consequently no explicit consideration was made of the dissolved metal concentrations in the sediments. As a result, identical settling velocities, resuspension and sediment burial rates were used for metals and for suspended solids.

Sensitivity analyses performed on the model indicate that suspended solids exert significant control on metal concentrations. Total metals concentrations in the water column were found to be most sensitive to settling rates of suspended solids. Dissolved metals concentrations were found to be most sensitive to the value of the partition coefficient. Metals concentrations were found to be least sensitive to the long-term burial rate of the surficial sediment layer. In order to obtain a reasonable degree of success in predicting metals concentrations as a function of external loadings, it was found that it is not sufficient to know only the partition coefficient and the water circulation regime. In addition, suspended solids loading, wind regime, system morphometry, depositional zones, and sediment concentrations need to be determined.

#### 4.2.4 Fugacity Concept

The fugacity concept is an approach which is inherent to many models which employ partition coefficients to predict the fate of nonionic, organic hydrophobic compounds, whose distribution in the environment is controlled by the equilibrium between the substances's vapour pressure and solubility. The main advantage of the fugacity concept is standardization of concentration units between the different phases which allows a user to obtain a comprehensive picture of the state of equilibrium between all compartments of a system. Recently, Mackay et al.<sup>126-128</sup> have developed and applied this concept to toxic chemicals in lakes.

##### *Atmosphere*

For real, nonideal gases and gas mixtures, partial pressure is replaced by an idealized pressure, called fugacity  $f$  by G.N. Lewis. The fugacity approaches the partial pressure of the component as the mixture becomes infinitely dilute. Fugacity is related to partial pressure,  $P_p$ , by the expression

$$f = x_r P_p \quad (66)$$

where  $x_r$  is the fugacity coefficient. Only for high pressures is the value of  $x_r$  significantly different from 1. Fugacity can be regarded as the "escaping tendency" that a substance exerts from any given phase, with units of pressure ( i.e. Pa or atm). Concentration  $C_v$  ( $\text{mol/m}^3$ ), in the vapour phase, is related to partial pressure through the gas law:

$$C_v = n/V_v = P_p/RT = f/RT = f Z_v \quad (67)$$

where  $n$  is the number of moles of substance and  $Z_v$  is called the fugacity capacity, and has units of ( $\text{mol/m}^3\text{atm}$ ). The fugacity capacity quantifies the capacity of the phase for fugacity. Since  $Z_v$  is simply  $1/RT$ , where  $R$  is the ideal gas constant,  $Z_v$  is independent of the nature of the solute or the composition of the vapour (for nonassociating solutes and low or atmospheric pressure conditions).

##### *Water*

In aqueous solutions, the relationship between  $f$  and  $C$  for infinite dilution conditions are

represented by the equations:

$$Z_w = C/f = C/P_p = 1/H \quad (68)$$

where H is Henry's Law constant. H describes the linear proportionality between partial pressure and liquid concentration and has units of atm m<sup>3</sup>/mol. Henry's Constant is usually quite constant at low concentrations and, for low solubility substances it can be estimated from the ratio of the substance's vapour pressure and solubility. It must be pointed out that the above relationships are only valid if the solute is in completely dissolved forms less than or equal to saturation.

The air-water equilibrium concentration ratio is expressed as:

$$C_a/C = H/RT \quad (69)$$

Since RT is a constant for a given temperature, it can be seen that it is H which determines the partition equilibrium. Compounds of high H partition preferentially into the atmosphere while those of low H partition preferentially into the water.

#### *Sorbed Phases*

Mackay and Paterson<sup>126</sup> have shown that the sorbed-phase fugacity capacity,  $Z_s$  is equal to  $S_p q/H$ , where  $S_p$  is a sorption coefficient and  $q$  is the sorbent's density. This is derived by assuming that for hydrophobic compounds at concentrations well below their solubilities, the linear sorption equilibrium equation (Karickhoff et al.<sup>129</sup>)

$$X = S_p C \quad (70)$$

is applicable.  $X$  is the sorbed concentration (mol solute/10<sup>6</sup> g sorbent) and  $C$  is in units of g/m<sup>3</sup>. The concentration of sorbed material ( $C_s$ ), expressed as mol/m<sup>3</sup> sorbent, is thus  $Xq$  mol/m<sup>3</sup>. At equilibrium, the fugacities of the sorbed and dissolved material must be equal and hence if  $Z_s$  is the sorbed-phase fugacity capacity:

$$f = HC = C/Z_s \quad (71)$$

then  $Z_s = C/HC = Xq/H(X/S_p) = S_p q/H$ .

$S_p$  is strongly correlated to the organic carbon content of a soil or sediment. If  $S_p$  is normalized on an organic carbon basis, a new partition coefficient,  $K_{oc}$  can be defined:

$$K_{oc} = S_p / f_{oc} \quad (72)$$

where "foc" is the fractional mass of organic carbon in the soil or sediment. Karickhoff et al.<sup>129</sup> found the following relationship between the  $K_{oc}$  of hydrophobic compounds and octanol-water coefficients ( $K_{ow}$ ):

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad (73)$$

This is the correlation used to estimate  $K_{oc}$  and hence  $S_p$  when experimental values are not available.

### *Biota*

A bioconcentration factor,  $K_B$ , is used instead of the partition coefficient for biota. However, if it is expressed as a ratio of the concentration in the biota on a wet weight basis, it is identical to  $S_p$ . If it is expressed on a wet volume basis, it is analogous to  $S_p,q$ . Consequently, the fugacity capacity for the biota,  $Z_B$ , is defined as:

$$Z_B = K_B q_B / H \quad (74)$$

The above relationships for fugacity capacities can be used in mass balance equations to determine the amount of a compound in each model compartment. The same results would be obtained if partition coefficients were used in the mass balance equations for steady-state equilibrium models. The advantage of the fugacity approach is that the behaviour of each phase is treated separately but in the same units so that pseudopartition coefficients between phases which are not in contact do not need to be developed. This simplicity results in identical mathematical expressions of mass balance which becomes most advantageous for more complex systems where a large set of equations need to be solved. However, the fugacity approach is not applicable when pollutant transport occurs by processes which are not dominated by equilibrium driving forces. The fugacity approach also becomes inappropriate when spatial transport equations are needed.

## 5. Conclusions

Nutrient water quality models are, in general, more advanced than toxic chemical models. This is due largely to the limited amount of *a posteriori* testing of these models. This is a consequence of the much greater amount of high quality, long-term field data which has been and continues to be available for nutrients than for toxic chemicals. As the spectrum of toxic chemicals being produced continues to expand, this lack of field data for testing toxic chemical models will continue to hamper their development, calibration and verification.

Many of the concepts presented in this chapter are equally applicable to marine models. For example, the partition coefficient concept can be used equally well in marine models for the distribution of metals or for slowly decaying radionuclides. As in freshwaters, if the decay process is greater than the adsorption-desorption rates, then a kinetic approach will be required rather than assuming pseudo-equilibrium. The fact that some models use different mathematical expressions to describe similar ecological processes is due mainly to the model developer's attempt to match the complexity of a particular application scenario. Ideally, *a posteriori* sensitivity analyses should reveal which model processes and parameters are essential and which can be ignored.

Although a general water quality model cannot be developed for all contaminants, the increasing use of hierarchical models and expert systems will probably expand the capabilities of modelling a wide range of ecosystems and contaminants by allowing a model user to choose appropriate sub-models from a computer library of compatible programs. However, simultaneous efforts must continue to be made into the research of the individual processes.

An area of water quality modelling that needs to be developed is at the land-water interface. This includes such processes as fine-particle transport, particularly at the land-river<sup>130</sup> or land-ocean interface. Nonpoint source models or submodels are needed to increase the accuracy of loading predictions to be used in the current nutrient and toxic chemical models which typically use forcing functions to simulate linkages to terrestrial processes.

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TABLE 1 WATER QUALITY MODELS (Nutrients)

Model and Principal Investigator(s)	Time Domain	Spatial Domain	Chemical	Input Data	Output Data	Application	Assumptions /Features
Lake Erie Model LEMB (14) D.K. Saisbury J.V. DePinto T.C. Young	Dyn Daily	2-D 10 box 2 sed	P	Morphometry, hydraulics, nutrient loads, biochemical kinetics, SRP, PP and ERP forms of P, wind and solar radiation	Phytoplankton, algal-available P, autochthonus P, available and unavailable allochthonus P	Modified P dynamics are used for the evaluation of nonpoint source P management scenarios	Offers separate representation of allochthonus and autochthonus particulate P kinetics and transport
Lake Michigan (MICH) Model (15) P.W. Rodgers D.K. Saisbury	Dyn Daily	2-D 4 box	P	Morphometry, hydraulics, nutrient loads and concentrations biochemical kinetics, solar radiation and temperature	Phytoplankton zooplankton, SRP, and TP	1977 data, analysis of the effect of ice cover on P transport and assessment of IJC loading recommendations	Phosphorus recycling resulting from phytoplankton decomposition and zooplankton feeding
Lake Ontario Phosphorus Model (16) R.H. Montgomery V.D. Lee K.H. Reckhow	S-S	W/L	P	Phosphorus loadings, apparent P settling velocity, hydraulics and morphometry	Total phosphorus concentrations	First-order error analysis and Monte Carlo simulation analysis applied to a mass-balance for Lake Ontario	Assumes that, for the results presented, supplemental error is negligible
Water Analysis Simulation Program WASP (17) D.M. DiToro J.J. Fitzpatrick R.V. Thomann	Dyn Var	1-D 2-D 3-D	Organics Metals Phyto	Loads, boundary conditions, mass transfer rates, kinetic rates, segment parameters	State variable concentrations	Applicable to a wide variety of water quality problems	Generalized model structure to allow site-specific applications

## Booty and Lam

Lake Erie P and DO Model (18,19) D.C.L. Lam W.M. Schwertzer A.S. Fraser	Dyn Daily	9 box 3 basin 3 layer	P	P loads, dynamic thermocline positions, water levels, morphometry of basins, wind, solar radiation and temperature and extinction coefficient	Concentrations of TP, SRP and DO in compartments	Calibrated using 1978 CCIW data, verified using 1967-77 CCIW data, 1979-82 CCIW and CLEAR data for varying water levels, nutrient loadings and weather	Includes unique moveable vertical interfaces so that physical diffusion and entrainment are simulated separately to account for weather influences
Lake Erie Statistical Dissolved Oxygen Model (20) A.H. El-Shaarawi	Dyn Var	1-D	DO P	Time series data of DO, P, temperature, and water levels	DO concentrations	Time series stochastic model correlating DO with temperature, SRP, and water levels for 1965-80	Probability curves show possible DO values for given temperatures, SRP concentrations and water levels
Lake Superior Primary Production Model (21) D.C.L. Lam E. Halfon	Dyn Daily	3-D 235 Hor 4 water	P	Phosphorus loads, transports, temperatures, solar radiation	Primary production rates, SRP, TP concentrations	Calibrated using 1973 data	Nearshore effects investigated as a function of lake circulation and P loading sources
Simon's 3-Dimensional Water Quality Model (22) T.J. Simons	Dyn Daily	3-D 21 Hor 4 water	Nutr	Nutrient loads, lake hydro-dynamics and transports, solar radiation, mixing coefficients	Nutrient concentrations, phytoplankton, zooplankton	Calibrated using 1972 IFYGL data	3-D approach is only better than a 1 box model if the nearshore effects are to be examined
Lake Huron Cladophora Model (23,24) R.P. Canale M.T. Auer	Dyn Daily	2-D 28 Hor	Clad	Morphometry, hydraulics, nutrient loadings, bio-kinetics, wind, temperature and light	Cladophora biomass	Calibrated using 1979 data from Harbor Beach, Mich. verification using 1980 data after 85% loading reduction	Designed to predict nearshore zone near point source nutrient discharge

Great Lakes Chloride Model (25) W.C. Sonzogni et al.	S-S Dyn	WL	Cl	In-lake chloride concentrations, lake volume, loads and flows	Chloride concentrations for each Great Lake basin	Prediction of chloride concentrations for stable loadings	P-C version useful for modeling conservative substances
Maumee River Dissolved Oxygen Model (26) P.L. Freedman J.D. Sherrill	Dyn Var	1-D	DO	Morphometry, hydraulics, BOD loadings, temperature and biochemical kinetics	Dissolved oxygen and biochemical oxygen demand	Used with two other interactive models to evaluate numerous CSO control alternatives	Based on Thomann (1972) model, and is appropriate for simulating CSO impacts on back-ground conditions
Maumee River Fecal Coliform Model (26) P.L. Freedman J.D. Sherrill	Dyn Var	1-D	NH4 P Metal Col B	Morphometry, hydraulics, loads, biochemical kinetics and temperature	Fecal coliform and ammonia, phosphorus, and heavy metal concentrations	Used with two other interactive models to evaluate numerous CSO control alternatives	Applicable only to zero- and first-order reaction kinetics in intermixed overflow and upstream sources
Rochester Embayment and Saginaw Bay Phytoplankton Model (27) J.T. Kuo R.V. Thomann	S-S	2-D	Nutr	Morphometry, hydraulics, wind, nutrient loads, biochemical kinetics, light and temperature	Chlorophyll, zooplankton and nutrients concentrations	Applied to embayment during non-stratified season and to Saginaw Bay for whole year	Incorporates lake circulation to improve eutrophication analysis
Steady-State Lakes in Series Model for the Great Lakes (SLIS) (28) B. Guerra et al.	S-S	WL	Var	Loads of chemicals of interest	Concentrations of chemicals of interest	Applied to chloride and sodium	First-order reaction rates for non-conservative substances
Saginaw Bay-5 Phytoplankton Class Model (29) V.J. Biermann, Jr. D.M. Dolan	Dyn	2-D	Phyt	Nutrient loads, initial and boundary conditions, morphometry, transport parameters, temperature and kinetic rates	Biomass for 5 classes of phytoplankton and zooplankton, nutrient concentrations	Calibrated to 1974-76 data and verified on 1980 data	Average concentrations in homogeneous segments for 5 groups

Schmoor and O'Connor Phosphorus Loading Model (30) J.L. Schmoor D.J. O'Connor	S-S Dyn Daily	WL	TP	TP loads, lake mean depth, volume, flushing rate, algal growth coefficients, and rates of photosynthesis, mineralization and settling	Concentrations of TP, algal P, dissolved P, and chlorophyll	Applied to Lake Ontario, Lake Lyndon B. Johnson, Texas	Intermediate in complexity, between nutrient loading models and multi-variable models
Modified Chapra P Loading Model (31) S.C. Chapra	LTA	WL	TP	TP loads, lake mean depth, flushing rate	Concentrations of TP	Applied to 3 basins of Lake Erie	Accounts for the fraction of P loads which do not affect lake water quality
Nurnberg P Retention Models (32) G.K. Nurnberg	AA	WL	P	Areal water loading rate	Phosphorus retention, internal P loading rate	Developed from North American and European lakes	Empirical model which can be used to predict release of P from anaerobic sediments
Smith Photosynthesis Model (33) V.H. Smith	SA Daily	WL	P N	TP loads, lake mean depth, flushing rate, epilimnetic TP and TN	Epilimnetic volumetric rates of photosynthesis	Developed from data on 58 north temperate lakes	Empirical model, only used if summer TN:TP ratio > 13 by weight
Smith Nitrogen-Phosphorus Chlorophyll Model (34) V.H. Smith	SA	WL	P N	Epilimnetic TP and TN	Epilimnetic chlorophyll	Based on data from 228 northern lakes	Multivariate empirical model
Kalff and Knoechel Phosphorus-Algal Biomass Model (35) J. Kalff R. Knoechel	SA	WL	P	Epilimnetic TP	Epilimnetic total algal cell volume	Developed from data from 28 northern lakes	Empirical model

U.S. OECD P Loading Model (36) R.A. Jones G.F. Lee W. Rast	LTA	WL	P	TP loads, lake mean depth, hydraulic residence time	Concentrations of TP, chlorophyll, Secchi depth, hypolimnetic oxygen deficit	Developed from U.S. lakes, applied to the Great Lakes and also Lake Mjosa, Norway	Empirical model
Canfield and Bachmann Loading Model for Natural Lakes (37) D.E. Canfield, Jr. R.W. Bachmann	LTA	WL	P	TP loads, lake mean depth, flushing rate	TP concentrations	Developed using data from 704 lakes in National Eutrophication Survey	Empirical model
Hanson and Peters Zooplankton and Profundal Macrobenenthos Biomass Models (38) J.M. Hanson R.H. Peters	AA	WL	P	TP concentrations, lake surface area, maximum depth	Zooplankton and profundal macrobenenthos biomass	Developed from 80 lakes worldwide	Empirical model for lakes with pH > 5.5
Cornett and Rigler Hypolimnetic Oxygen Deficit Model (39) R.J. Cornett F.H. Rigler	SA	WL	O	Annual P retention rate, hypolimnion thickness and temperature	Areal hypolimnetic oxygen deficit	Developed on data from north latitude lakes	Empirical model
Modified Cornett and Rigler Hypolimnetic Oxygen Deficit Model (40) R.J. Cornett F.H. Rigler	SA	WL	O	TP concentrations, annual pelagic primary production, hypolimnion thickness and temperature	Areal hypolimnetic oxygen deficit	Developed from north latitude lakes	Empirical model
Bird and Kalff Bacterial Abundance Model (41) D.F. Bird J. Kalff	SA	WL	P	Chlorophyll concentrations, TP concentrations	Acridine orange direct count estimate of bacterial numbers	Developed from north latitude lake data	Empirical model

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Welch and Perkins Hypolimnetic-Oxygen Deficit Model (42)	SA	W/L	P	TP loading, mean lake depth, flushing rate	Areal hypolimnetic oxygen demand	Developed from north latitude lake data	Empirical model
E.B. Welch M.A. Perkins							
Charlton Hypo- limnetic Oxygen Deficit Model (43)	SA	W/L	O	Epilimnetic chlorophyll concentrations, hypolimnetic thickness and temperature	Areal hypolimnetic oxygen deficit	Developed from 6 Great Lakes and 19 other North American lakes	Empirical model
M. N. Charlton							
Vollenweider and Janus Hypolimnetic Oxygen Depletion Model (44)	SA	W/L	O	Annual average chlorophyll, annual primary pro- duction, mean lake depth, euphotic depth, maximum depth, volumes, vertical extinction coefficients	Volumetric rates of hypolimnetic oxygen depletion	Developed from OECD study lakes, including 6 Great Lakes	Empirical models
R.A. Vollenweider L.L. Janus							
Reckow and Simpson Blue-Green Algal Model (45)	SA	W/L	P N	TP concentrations of influent, median summer total inorganic N concentrations, flushing rate	Probability of blue-green algal dominance	Developed from lakes in the National Eutrophication Survey	Uses discriminant analysis to determine the probability of blue-green algal dominance in high alkalinity lakes ( $> 56 \text{ mg/L CaCO}_3$ )
K.H. Reckow J.T. Simpson							
Smith Blue-Green Algal Model (46,47)	SA	W/L	P N	Epilimnetic TN, TP	Proportion of blue-green algae in total summer algal biomass	Developed from 17 lakes worldwide	Threshold model, predicts that blue- green algae will be rare when summer TN:TP ratio $> 29$ by weight
V.H. Smith							

Complex Sediment Phosphorus Model (48) S.E. Jorgensen L. Kamp-Nielsen H.F. Mejer	Dyn	WL	P N C	Lake morphometry, biochemical kinetics, sediment depth, settling rates, light intensity, concentrations of inorganic C, NO <sub>3</sub> , NH <sub>4</sub> , P and O	P and oxygen concentrations in the water column and sediment, phytoplankton biomass	Applied to Lake Esrom, Denmark	Comparison of results with earlier version indicate the newer model is only more useful if grazing at the sediment interface is incorporated
Nyholm Model for Phytoplankton in Shallow Lakes (49) N. Nyholm	Dyn Var	WL	P N	Nutrient loads, growth and nutrient uptake kinetics, lake morphometry, decay and settling rates, temperature and light, hydraulics	Phytoplankton biomass, TP, TN and PP concentrations	Applied to 12 eutrophic lakes with no thermocline, in Denmark	Designed for management application; assumes system in equilibrium with inputs of nutrients over one year
Simulation by means of an Analytical Lake Model SALMO (50) J. Benndorf F. Recknagel	Dyn	2 water	P	Phosphorus loads, lake morphometry, settling rates, biochemical kinetics	Phytoplankton and zooplankton biomass, dissolved orthophosphate	Applied to pelagic zones of 4 lakes and reservoirs in Germany	Priority given to internal ecological control mechanisms
Dynamic Lake Model for Trophic State Prediction (51) D.M. Imboden R. Gachter	Dyn Daily	2-D 2 water 1 sed	OP PP	Morphometry, hydraulic loading, depth of thermocline, rates of respiration and sediment-water column exchange rate, and light	Trophic state as defined by the sum of the phosphorus, expressed as primary production per unit lake area	Applied to 2 Swiss lakes and 1 U.S. lake (Lake Washington)	Nutrient and biomass concentrations described by continuous functions of depth and time
Ecological Model of Lake Ontario (52) D. Scavia	Dyn Daily	2-D 2 water 1 sed	C N P Si	Morphometry, biochemical kinetics, light, sedimentation rates, and temperature	Carbon cycle flow diagram, concentrations of the various forms of C, N, P and Si in	Applied to 1972 IFYGL data for Lake Ontario	Comprehensive nutrient- food chain model



the 3 layers

Long-Term Model of the Vertical Distribution of Mass in Large Lakes (DYSREM 5) (53,54)	Dyn Daily	1-D	Salinity	Meteorological input data, lake morphometry, river inflows	Dissolved and suspended solids concentrations, temperature, and salinity distributions	Applied to Lake Constance, Central Europe for the period Feb, 1979-Mar., 1980.	Extended version of the model, DYRESM
Hollan, E. Hamblin, P.F. Letn, H.							

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S-S = Steady State, Dyn = Dynamic, Var = Variable, LTA = long term average, AA = annual average, SA = summer average  
 WL = Whole Lake, sed = sediment layer, water = water column layer, 1-D = 1 dimensional, 2-D = 2 dimensional  
 3-D = 3 dimensional, Hor = horizontal segments, P = phosphorus, DO = dissolved oxygen, BOD = biological oxygen demand  
 SRP = soluble reactive phosphorus, PP = non-available particulate phosphorus, ERP = external refractory phosphorus  
 Nutr = nutrients, Clad = cladophora biomass, Col B = fecal coliform bacteria, Phyt = phytoplankton biomass  
 \*Note: Table includes only post-1977 models or model versions

TABLE 2 WATER QUALITY MODELS (TOXIC SUBSTANCES)

Model and Principal Investigator(s)	Time Domain	Spatial Domain	Chemical	Input Data	Output Data	Application	Assumptions /Features
QWASI (55) D. MacKay	S-S Dyn	WL 1 sed	Organic	Loads of solids and chemical, physical-chemical properties and rate coefficients	Concentrations and masses in system compartments and persistence	Partial validation with laboratory microcosms	Based on physical /chemical principles
Physico-Chemical Model of Toxic Substances in the Great Lakes (56) R.V. Thomann D.M. DiToro	Dyn Annual	WL 5 water	Organic Metal	Loads of solids and chemical, rate coefficients of particulate sorption-desorption and chemical transformation	Toxic substance concentrations, time of response following loading	Calibrated with Pu-239 data, applied to PCB, cadmium, and benzo (a)pyrene equilibrium with external loads	Instantaneous sorption-desorption equilibrium reactions
Saginaw Bay Metals Model (SBM) (57) D.M Dolan V J Bierman, Jr.	Dyn Var	5 water 5 sed	Metal	Loads of solids and metals, partition coefficients	Concentrations of metals in model compartments	Applied to Zn, Cu, Pb and solids in Saginaw Bay	Equilibrium kinetics for metals-solids
EXAMS-II (58) R.R. Burns D.M Cline	S-S Dyn	3-D	Organic	Loads of solids and chemical, physical-chemical properties and rate coefficients	Compartment concentrations and overall persistence	Validated for numerous stream eco-systems	equilibrium sorption-desorption, 2nd order transformation rate kinetics
Mirex Dynamics in Lake Ontario (59) E. Halfon	Dyn	4 water 4 sed	Organic	Chemical loads, flow volumes, physical-chemical properties and rate coefficients, sediment re-suspension	Concentrations in biota, fish, sediments	Calibrated with mirex concentrations in bottom sediments of Lake Ontario	Same as EXAMS

MICHRIV (60) W.L. Richardson	S-S	1-D	Organic Metal	Physical-chemical properties, rate coefficients for chemical reactions, partition coefficients	Compartment concentrations	Equilibrium sorption- desorption, 1st order transformation kinetics
Persistence (61) J.R. Roberts M.S. Mitchell	Dyn	1-D	Organic	Physical-chemical properties and rate constants	Compartment concentrations, system persistence	Unvalidated
TOXIWASP (62) R. B. Ambrose	Dyn Var	3-D	Organic Metal	Loadings of solids and chemicals, chemical transfer rates and coefficients	Exposure concentrations in each compartment	Completely mixed, time and space averaged
Partitioning of Synthetic Organic Chemicals (63) B.J. Eadie	S-S	1-D	Organic	Physical-chemical properties and system parameters	Compartment concentrations and masses	Global application
WASTOX Part I (64) J.P. Connolly R.P. Winfield	S-S Dyn Var	3-D	Organic Metal	Initial and boundary conditions, loads, partition coefficients and transformation rates	Toxicant concentrations in selected segments	Equilibrium kinetics
WASTOX Part II (65) J.P. Connolly	Dyn Var	3-D	Organic Metal	Exposure concentra- tions, food chain structure and biomass	Toxicant concentrations in biota	Sub-model of WASTOX
DDT Dynamics in Lakes Michigan and Superior (66) V.J. Bierman, Jr.	Dyn Annual	1-D	Organic Metal	Inputs of DDT, sediment process rates	Annual average concentrations	Developed from simple mass balance models used for phosphorus

WASP4 (67) R.B. Ambrose	S-S Dyn	3-D	Organic Metal	Loadings of solids and chemicals, reaction rates, physical-chemical properties, sorption desorption rates, initial and boundary conditions.	Contaminant concentrations in water column, sediment, pore water, and biota	Applied extensively to lakes, estuaries, and rivers	Generalized modeling framework, based on the flexible compartment modeling approach.
Toxic Substances Model for the Great Lakes (68) G.A. Lang S.C. Chapra	S-S Dyn Annual	2-D	Organic	Various lake, contaminant and solids parameters	Contaminant concentrations in water column, sediment, pore water	Analysis of Lake Michigan response to a range of PCB loads	Coefficients calibrated to scientific literature data
HSPF (69) R.C. Johanson	Dyn	1-D	Organic Metal	Watershed-stream physical parameters, chemical transform- ation rates, initial conditions, adsorption rates	Time history of flows, sediment loads, downstream concentrations at any point in a watershed	Applied extensively	Sorption is modeled as a 1st order process, values for three solids required
Lake Michigan PCB Model (70) P.W. Rodgers	S-S Dyn	W L	Organic	Mean depth, volume of water column and sediments, flows, PCB loads, solids concentrations, partition coeffic- -ients, transform- -ation rates	Concentrations of PCB in water column and sediments	Historical mass loading trend analysis and forecast of water and fish PCB concentrations in Lake Michigan	Assumes historical fish concentrations are proportional to concurrent water column concentrations of PCB
Lake Michigan PCB Model (71) P.W. Rodgers W.R. Swain	Dyn Annual	W L	Organic	Mean depth, volume, flow, past PCB levels in fish and biota, suspended solids concentrations, PCB water:fish distrib- -ution coefficient, net solids loss rate	Historic and predicted simulations of PCB in fish and water column	Comparisons with measured Lake Michigan data averages	Assumes historical fish concentrations are proportional to concurrent water column concentrations of PCB

PCB Fate Model for Saginaw River and Bay (72) Limno-Tech, Inc.	Dyn Annual	2-D	Organic	Volume of water column and sediments, flow, PCB loads, suspended solids concentrations, reaction rates, PCB fish:water distribution coefficients and hydraulic retention time	Total PCB concentrations in water, sediment, and fish	Calibrated to 1965-1981 observed sediment, water, and fish PCB data. Forecasts impacts of mitigative options such as dredging in Saginaw River	Mechanistic biological processes are not represented
PBB Fate Model for Pine River and St. Louis Reservoir (73) Limno-Tech, Inc.	Dyn Annual	2-D	Organic	Volume of water column and sediments, flow, PBB loads, suspended solids concentrations, reaction rates, PBB fish:water distribution coefficients, flushing rate	Total PBB in water column and sediment	Forecasts water column and sediments response to load elimination	Mechanistic biological processes are not presented
Saginaw Bay PCB Model (74) M.L. Anderson R.P. Canale	Dyn Var	2-D	Organic	Morphometry, hydraulics, PCB loads and PCB biological degradation kinetics	Concentrations of PCB in the water column and the sediments	Analysis of the biological degradation of PCB's	PCB decay rates based on in-situ studies of two species of sediment bacteria
Age-Dependent Model of PCB in Lake Michigan Food Chain (75) R.V. Thomann J.P. Connolly	Dyn Annual	W L	Organic	Species bioenergetics information	Concentrations of PCB in levels of food chain	Assess the effect of reduced PCB concentrations on lake trout	Phytoplankton assumed to be in dynamic equilibrium with water column dissolved PCB
Model of PCB Mixtures in Saginaw Bay (76) W.L. Richardson	Dyn Var	2-D	Organic	Initial and boundary conditions, Aroclor 1242 and 1260 loads, system morphology partition coefficient, deposition and	Total PCB, Aroclor 1242 and 1260, chloride, solids concentrations in each of 19	Calibrated to 1979 PCB, solids, and chloride data	Equilibrium kinetics

			volatilization rates, wind speed	water and sediment layers			
LTI Toxics Model Application: PCB's in Lake Ontario (77) P.W. Rodgers T. Slawicki J.V. DePinto W.G. Booty	S-S Dyn Annual	2-D	Lake morphometry, transport and transformation coefficients, physico-chemical parameters, loadings and flow regimes	Steady-state and dynamic water, fish and sediment PCB concentrations	Calibrated to measured water column and sediment PCB levels for lake Ontario	Completely mixed water column, biotic and abiotic suspended solids are assumed to be at steady state	
Tritium Spill Model (78) D.C.L. Lam	Dyn Hourly	2-D	Spill amount, current regime, half-life decay constant	Tritium concentration	Calibrated to Lake Ontario data from Pickering Station	Current field generated by objective analysis method	
TOXFATE (79) E. Halfon	Dyn Var	4 water 4 sed	Physical-chemical properties, rate constants, loadings, sediment resuspension, flow, suspended solids	Concentrations in biota, fish, and sediment	Calibrated with Niagara River data	Ignores within year variations	
TODAM (80) Battelle Northwest	Dyn	1-D	Loadings of solids and chemical, flow, transformation rates, physical-chemical parameters, partition coefficients	Downstream concentrations of contaminant with time	General application for rivers and waste streams	Second order reaction kinetics, kinetic sorption processes	
FETRA (81) Battelle Northwest	Dyn	2-D	Loadings of solids and chemical, flow, transformation rates, physical-chemical parameters, partition coefficients	Concentrations of contaminant in estuary compartments as a function of time	General application for estuaries	Second order reaction kinetics, kinetic sorption processes	

SERATRA (82) Y. Onishi S.F. Wise	Dyn	2-D	Organic Metal	Loadings of solids and chemical, flow, reaction rates, physical-chemical parameters, partit -ion coefficients	Downstream concentrations of contaminant in water and sediments with time	General application for rivers and waste streams	Second order reaction kinetics, kinetic adsorption processes
UTM-TOX (83) M.G. Browman	Dyn	1-D	Organic Metal	Loadings of solids and chemical, flow, transformation rates, physical-chemical parameters, partit -ion coefficients	Downstream concentrations of contaminants as a function of time	General application for rivers and waste streams	First and second order reaction kinetics, equil -ibrium sorption processes
SLSA (84) D.M. DiToro	S-S	1-D	Organic	Chemical load, flows, physical- chemical parameters	Compartment concentration of contaminant	General application for lake or river	
SARAH (85) R.B. Ambrose	S-S	2-D	Organic	Flows, reaction kinetics, initial waste-stream chemical concentration, diffusion coeffic -ients, transform -ation rates	Downstream concentration of pollutant in water and fish	Applied to land disposal and wastewater treatment facilities	Treatment loss is handled empirically
DYNTOX (86) Limno-Tech, Inc.	Dyn	1-D	Organic Metal	Flows and loads, net loss rate	Concentration of contaminant in water	Applied to toxic waste discharge streams	Probalistic dilution technique
MINTEQ (87) D.S. Brown et al.	S-S	--	Metal	Transport and transformation data from another model	Concentrations of selected metal species		Equilibrium speciation, adsorption, precipitation -dissolution

E4CHEM (88,89)	S-S Dyn	1-D 2-D	Organic Metal	Chemical loads, single species toxicity data, chemical usage	Concentrations, masses in system compartments, fluxes, regional distributions, and toxicity ranks	Partial validation on River Main	Based on physical /chemical principles trophic levels as descriptors for populations
Organic Chemical Pathway and Fate Model (90,91)	Dyn Var	1-D 2-D	Organic	Loadings of particulate and dissolved organic chemicals, river flows and tides	Particulate / dissolved concentrations of contaminants in estuary, river segments as a function of time	Calibrated and verified with chlorobenzene data from the Niagara River and chloro- phenol data from the Fraser River	Based on partition coefficient, biodegradation, photodegradation settling, flows and tidal cycles
D.C.L. Lam J.H. Carey C.R. Murthy R.C. McCrimmon							

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S-S = Steady State, Dyn = Dynamic, Var = Variable, W L = Whole Lake, sed = sediment layer, water = water column layer  
 1-D = 1 dimensional, 2-D = 2 dimensional, 3-D = 3 dimensional



TABLE 3 Equations for the nine-box three-variable model.

A) Mass Balance Equations

$$d/dt (V_i \text{SRP}_i) = F_i(\text{SRP}_i) - U_i + R_i + r_p(\text{AB}_{i+1} - \text{AB}_i) \quad (20)$$

$$d/dt (V_i \text{OP}_i) = F_i(\text{OP}_i) + U_i - R_i + r_w(\text{AB}_{i+1} - \text{AB}_i) - \sigma_{i+1} A_{i+1} (\text{OP}_i - 0.005) + \sigma_{i+1} \text{AB}_{i+1} (\text{OP}_{i+1} - 0.005) \quad (21)$$

$$d/dt (V_i \text{DO}_i) = F_i(\text{DO}_i) + [f_{po} U_i - f_{po} R_i - k_s(\text{AB}_{i+1} - \text{AB}_i)] \text{DO}_i / (\text{DO}_i + K_o) + r_{A_i} \text{AB}_{i+1} (\text{DO}_i - \text{DO}_s) \quad (22)$$

B) Rate Formulations and Calibrated Constants

$U_i = B_i \rho_i (1.07)^{T_i} (\text{OP}_i - 0.005) V_i (\text{SRP}_i / (\text{SRP}_i + 0.0005))$  where  $B_1 = 0.43$ ,  $B_2 = 0.60$ ,  $B_3 = 0.60$  (day<sup>-1</sup>) and  $\rho_i =$  light factor

$R_i = Y_i (1.07)^{T_i} (\text{OP}_i - 0.005) V_i$  where  $Y_1 = 0.02$ ,  $Y_2 = 0.00$ ,  $Y_3 = 0.001$  (day<sup>-1</sup>)

$\sigma$  (settling velocities in m/day);  $\sigma_0 = 0$ ,  $\sigma_1 = 0.2$ ,  $\sigma_2 = 0.4$ ,  $\sigma_3 = 0.4$

$F_i$  (source term due to loading advection, diffusion, entrainment, and mixing; see Figure 3).

$f_{po}$  (phosphorus to oxygen ratio in photosynthetic product on of chlorophyll):  $f_{po} = 140.0$

$r_w$  (phosphorus resuspended by wind waves, in g/m<sup>2</sup>/day) = .001 w/w<sub>s</sub> where w is wind speed in m/day and w<sub>s</sub> = 500,000 m/day

$r_p$  (phosphorus return per area, in g/m<sup>2</sup>/day):  $r_p = 0.0001$  or  $r_p = L(\text{TP}) \times 3 \times 10^{-7}$  if  $\text{DO}_i < 1.5$  mg/L

$R_{A_i}$  (reparation coefficient, in m/day):  $r_{A1} = 2$ ,  $r_{A2} = 0$ ,  $r_{A3} = 0$

$\text{DO}_s$  (saturated oxygen concentration, in mg/L)

$K_o$  (half-saturated coefficient for oxygen):  $K_o = 1.4$  mg/L

$k_s$  (sediment oxygen demand, in gO<sub>2</sub>/m<sup>2</sup>/d:  $k_s = L(\text{TP}) \times 10^{-5}$ ,  $L(\text{TP}) =$  lakewide total phosphorus load in MT

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Note: The subscript "i" denotes the location of the parameter value, with  $i = 0$  denoting the surface value and  $i = 1, 2, 3$  denoting the value in the first, second, and third lake model layers. SRP, OP, and DO are concentrations (mg/L) of soluble reactive phosphorus, organic phosphorus, and oxygen, respectively. AB and V are area ( $m^2$ ) and volume ( $m^3$ ), U and R are the algal uptake and release rates (g/day). T is temperature ( $^{\circ}C$ ).

Figure Captions

- 1) Kinetics and transport of nutrient-phytoplankton system
- 2) Schematic of physical processes incorporated in the nine-box model
- 3) Schematic of biological and chemical processes incorporated for a water column in the nine-box model. The subscripts 1,2,3 denote first, second, and third layers (SRP = soluble reactive phosphorus, OP = organic phosphorus, DO = dissolved oxygen).
- 4) Schematic of a freshwater system
- 5) Schematic diagram of a coupled metals mass balance model

Figure 1

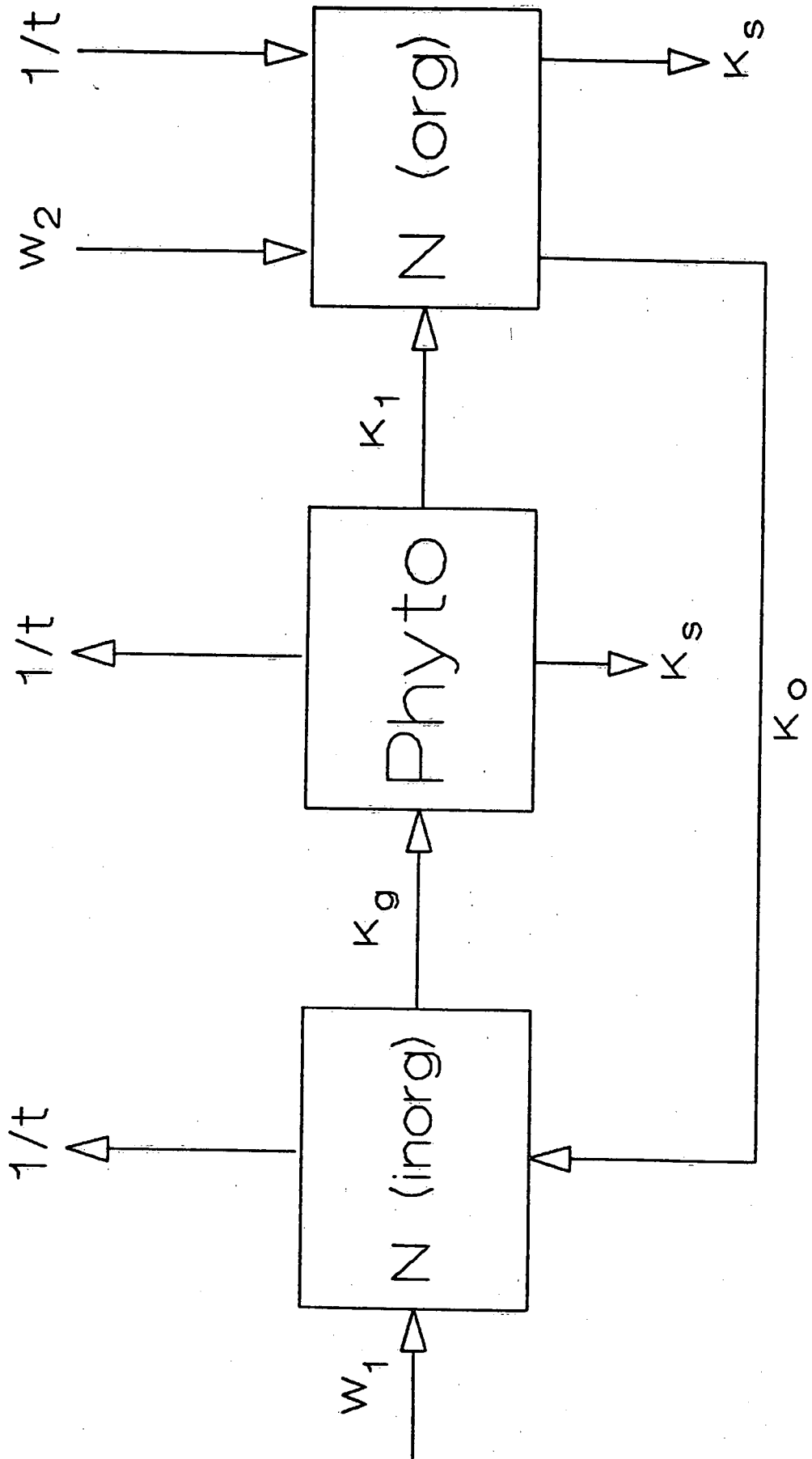


Figure 2

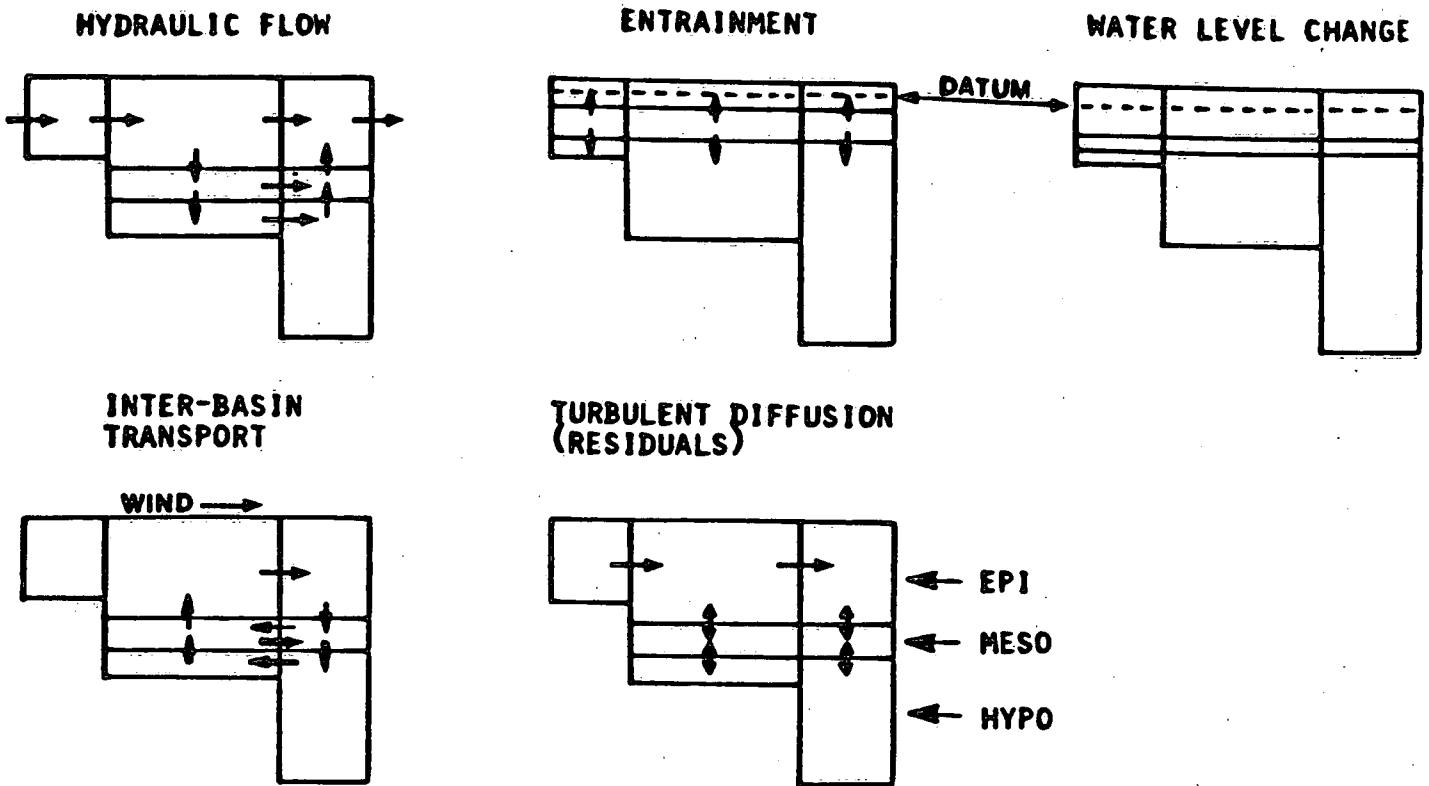


Figure 3

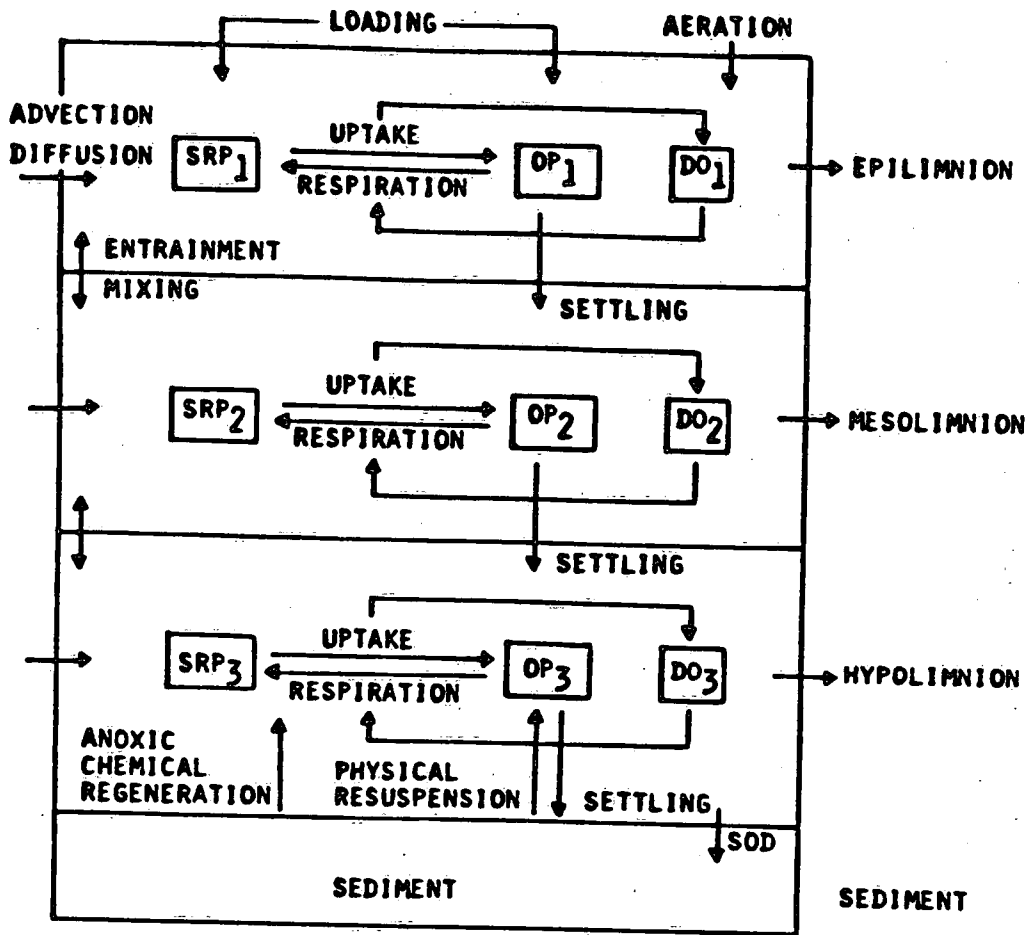


Figure 4

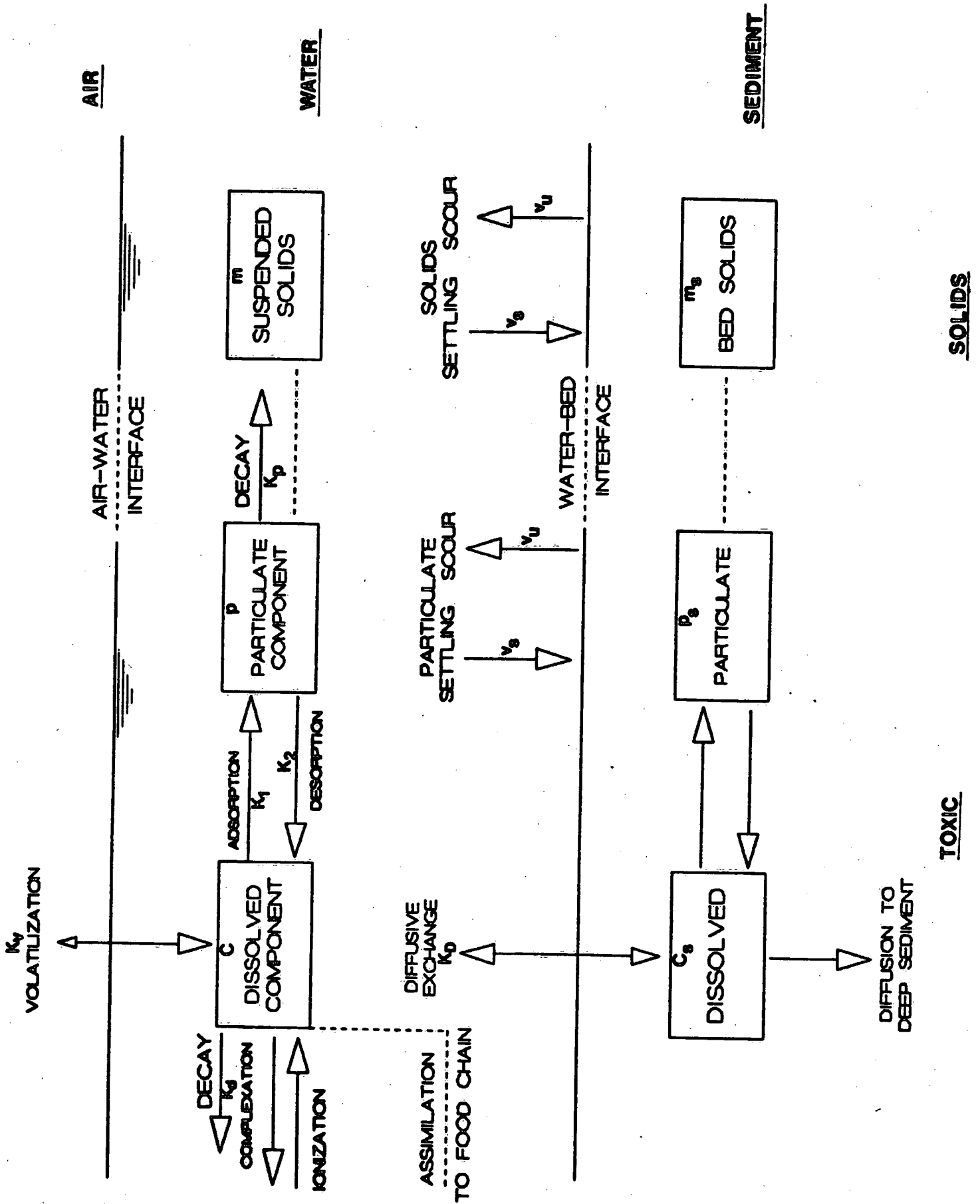
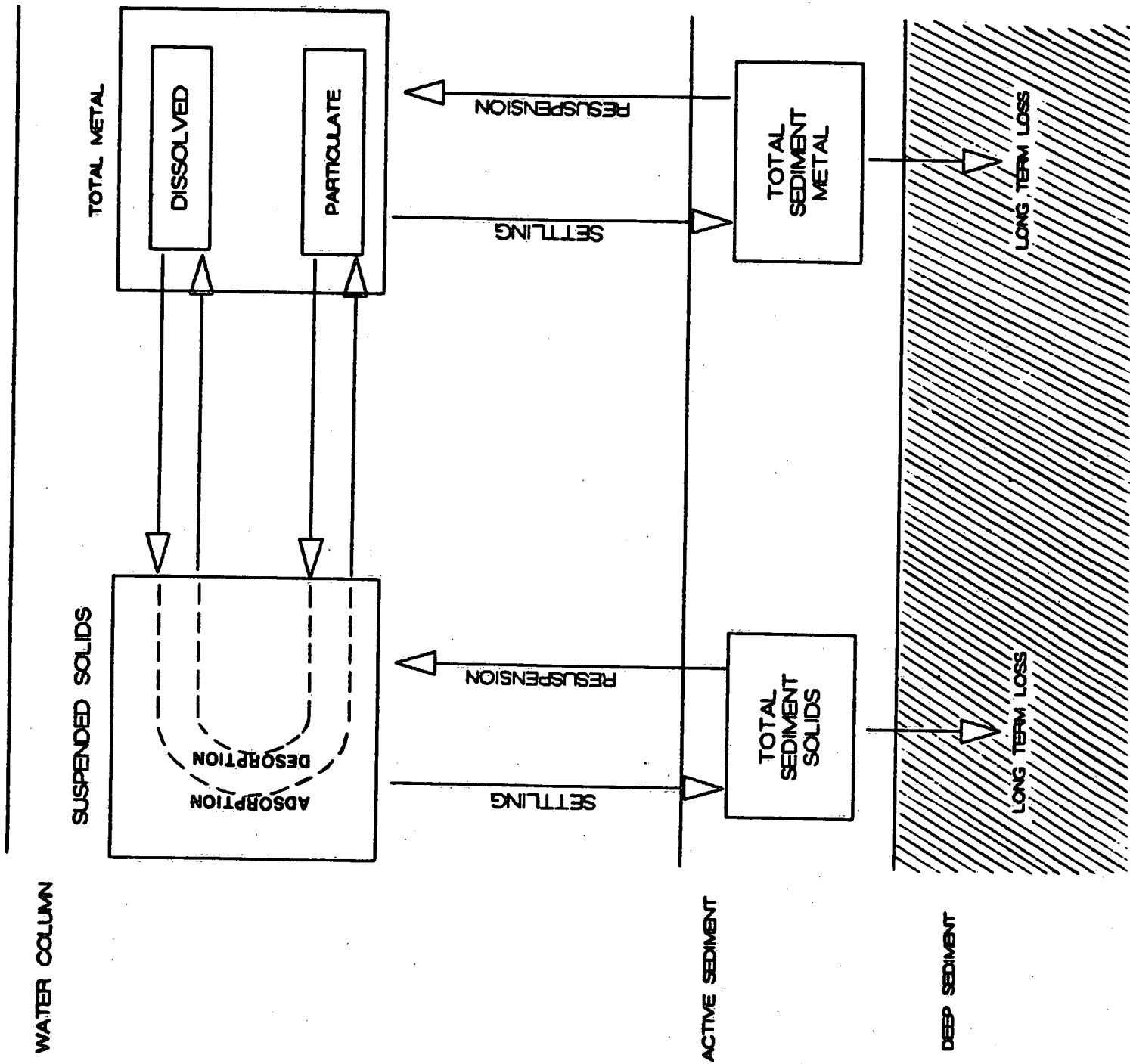


Figure 5





## Appendix. Notation

The following symbols are used in this chapter:

$a$  = empirical coefficient;

$A$  = interfacial area ( $L^2$ );

$A_s$  = area of the sediment ( $L^2$ );

$AB_i$  = lake layer areas ( $L^3$ );

$b$  = empirical coefficient;

$B_i$  = algal uptake rate coefficients ( $T^{-1}$ );

$C$  = dissolved concentration of chemical ( $M/L^3$ );

$C_a$  = concentration of chemical in atmosphere ( $M/L^3$ );

$C_d$  = concentration of chemical in dissolved phase ( $M/L^3$ );

$C_p$  = concentration of chemical in particulate phase ( $M/L^3$ );

$C_s$  = concentration of chemical in the sediment ( $M/L^3$ );

$C_T$  = total concentration of chemical ( $M/L^3$ );

$C_s$  = total concentration of chemical in the sediment ( $M/L^3$ );

$D$  = depth of water segment ( $L$ );

$D_s$  = mean lake depth ( $L$ );

$D_s$  = depth of sediment segment ( $L$ );

$DO$  = dissolved oxygen concentration ( $M/L^3$ );

$DO_s$  = saturated dissolved oxygen concentration ( $M/L^3$ );

$E_i$  = dispersion at the  $i$ th interface ( $L^3/T$ );

$f$  = fugacity (atm);

$f_o$  = fraction of incoming phosphorus going to open lake;

$f_d$  = dissolved fraction in water;

$f_p$  = particulate fraction in water;

$f_{ds}$  = dissolved fraction in sediments;

$f_{po}$  = phosphorus to oxygen ratio in photosynthetic chlorophyll production;

$f_p$  = particulate fraction in sediments;

$F_i$  = source term due to loading advection, diffusion, entrainment, and mixing (M/T);

$G$  = empirical unitless constant;

$h$  = hydraulic flushing rate (1/T);

$H$  = Henry's Law constant (atm m<sup>3</sup>/mol);

$j_b$  = scour flux of sediments (M/L<sup>2</sup>T);

$J_o$  = oxygen flux into the sediment (M O<sub>2</sub>/L<sup>2</sup>T);

$kb$  = sediment burial rate (L/T);

$k_1$  = volatilization transfer rate (L/T);

$k_o$  = Michaelis constant for oxygen (M/L<sup>3</sup>);

$ks$  = normalized settling velocity (L/T);

$K$  = overall loss rate of toxicant (1/T);

$K_D$  = sediment-water diffusion coefficient (L/T);

$K_d$  = decay rate of dissolved fraction (1/T);

$K_f$  = transfer coefficient of dissolved component (1/T);

$K_L$  = surface volatilization coefficient (1/T);

$K_p$  = decay rate of particulate fraction (1/T);

$K_{oc}$  = organic carbon normalized partition coefficient (L/kg);

$K_{ow}$  = octanol-water partition coefficient (L/kg);

$K_o$  = adsorption coefficient (1/T);

$K_1$  = adsorption coefficient (1/T);

$K_2$  = desorption coefficient (1/T);

$K_s$  = settling coefficient (1/T);

$K_s'$  = porosity corrected settling coefficient (1/T);

$K_T$  = sum of adsorption, desorption and volatilization rates (1/T);

$K_s$  = scour coefficient (1/T);

$K_v$  = volumetric volatilization coefficient (1/T);

$L$  = annual phosphorus loading per lake area (M/L<sup>2</sup>T);

$L(TP)$  = lakewide total phosphorus load (M);

$m$  = concentration of solids in water (M/L<sup>3</sup>);

$m_s$  = concentration of solids in sediment (M/L<sup>3</sup>);

$m_i$  = concentration of solids in layer  $i$  (M/L<sup>3</sup>);

$m_o$  = equilibrium concentration of suspended solids (M/L<sup>3</sup>);

$n$  = number of moles of gas;

$N$  = number of lake segments;

$N_i$  = inorganic nutrient concentration (M/L<sup>3</sup>);

$N_o$  = organic nutrient concentration (M/L<sup>3</sup>);

$N_p$  = phytoplankton nutrient concentration (M/L<sup>3</sup>);

$OP$  = organic phosphorus concentration (M/L<sup>3</sup>);

$P$  = partition coefficient (L/kg);

$P_p$  = partial pressure (atm);

$P_s$  = sediment partition coefficient (L/kg);

$p$  = particulate component concentration (M/L<sup>3</sup>);

$p_i$  = light factor;

$p'$  = porosity corrected partition coefficient (L/M);

$q$  = density of sorbent (M/L<sup>3</sup>);

$q_b$  = density of biota (M/L<sup>3</sup>);

$Q$  = advective flow (L<sup>3</sup>/T);

$Q_i$  = advective flow across the  $i$ th interface (L<sup>3</sup>/T);

$r$  = concentration of toxicant per unit solids (M/M<sub>T</sub>);

- $r_s$  = maximum adsorption capacity of solid (M/M);  
 $r_p$  = phosphorus return per area (M/L<sup>2</sup>T);  
 $r_w$  = resuspended phosphorus (M/L<sub>2</sub>T);  
 $R$  = Ideal Gas Law constant (atm m<sup>3</sup>/mol °K);  
 $R_{Ai}$  = reparation coefficient, (L/T);  
 $R_i$  = algal release rate (M/T);  
 $R_r$  = phosphorus retention coefficient;  
 $s_o$  = sediment oxygen demand coefficient (M O<sub>2</sub>/L<sup>2</sup>T);  
 $S_p$  = sorption coefficient (M<sup>3</sup> water/10<sup>6</sup>g sorbent);  
 $SRP$  = soluble reactive phosphorus concentration (M/L<sup>3</sup>);  
 $t$  = time (T);  
 $t_o$  = detention time (T);  
 $T$  = temperature;  
 $TP$  = total phosphorus concentration (M/L<sup>3</sup>);  
 $U_i$  = algal uptake rates (M/T);  
 $v$  = apparent settling velocity (L/T);  
 $v_s$  = variable settling velocity (L/T);  
 $v_n$  = net sedimentation velocity (L/T);  
 $v_r$  = settling velocity (L/T);  
 $v_{rs}$  = resuspension velocity (L/T);  
 $v_s$  = scour coefficient of sediment solids (L/T);  
 $V$  = volume of water (L<sup>3</sup>);  
 $V_g$  = volume of gas (L<sup>3</sup>);  
 $V_s$  = bulk volume of sediment layer (L );  
 $w_n$  = net loss of sediments from water column (L/T);  
 $w$  = wind speed (m/day);

$w_s$  = areal water loading (L/T);

$W$  = loading rate of chemical (M/T);

$W_i$  = input rate of inorganic nutrient (M/T);

$W_o$  = input rate of organic nutrient (M/T);

$W_m$  = loading rate of suspended solids (M/T);

$x_f$  = fugacity coefficient (mol/m<sup>3</sup> atm);

$X$  = sorbed chemical concentration (M/M);

$Y_i$  = algal release coefficients (1/T);

$Z$  = fugacity capacity (mol m<sup>3</sup>/atm);

$Z_b$  = fugacity capacity of biota (mol M<sup>3</sup>/atm);

$Z_s$  = sorbed phase fugacity capacity (mol m<sup>3</sup>/atm);

$Z_w$  = fugacity capacity in water (mol m<sup>3</sup>/atm);

$\Theta$  = sediment porosity (L<sup>3</sup>/L<sup>3</sup>);

$\phi_o$  = dimensionless entrainment coefficient;

$\sigma_i$  = settling velocities (m/day).