THE MODELING OF LAKE RESPONSE TO PHOSPHORUS LOADINGS:
EMPIRICAL, CHEMICAL, AND HYDRODYNAMIC ASPECTS

by

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Accepted by: Chairman, Departmental Committee on Graduate Students of the Department of Civil Engineering

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EMPIRICAL, CHEMICAL, AND HYDRODYNAMIC ASPECTS

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JOSEPH GERARD YEASTED

Submitted to the Department of Civil Engineering
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for the Degree of Doctor of Philosophy

ABSTRACT

Various aspects of the modeling of the response of a lake to phosphorus loadings are studied. Special emphasis is given to models that allow the prediction of lake trophic state for given phosphorus loadings, and to models of individual processes that are known to affect the distribution of phosphorus in natural water systems.

An extensive empirical study utilizing data from 128 phosphorus limited lakes is used to identify basic trends exhibited by a large number of lakes in response to phosphorus loadings. A basic parameter used in the study is the steady-state concentration of a conservative substance in lakes (the average inflow concentration). By isolating this expression for phosphorus, the ability of various morphological parameters (hydraulic residence time, mean depth, surface area) to account for the nonconservative behavior of this nutrient is investigated. The data are first plotted on the phosphorus loading diagrams of Vollenweider and Dillon and then subjected to stepwise discriminant analysis. In each approach the residence time alone is statistically significant in describing the nonconservative behavior of phosphorus. The ability of residence time to replace Dillon's retention coefficient in predictive trophic state models and the advantages thereof are argued. Possible explanations for the significance of residence time are discussed.

The principal findings of the empirical study are incorporated into a phosphorus model for the prediction of lake trophic state. The proposed model is a steady-state version of the phosphorus model formulated by Imboden and Snodgrass and O'Melia, with the settling rate of particulate phosphorus being assigned a functional form that is dependent only on the hydraulic residence time. The data requirements of the model are consistent with those available for most lakes. In a test with 80 lakes, the prediction reliability of the proposed model is shown to be comparable to that of Dillon without the need for an explicit parameter representing phosphorus loss.
The development of an algorithm for the computation of the vertical mixing across the thermocline region of stratified lakes is presented, the primary purpose of which is to test the proposal of Snodgrass and O'Melia, that the rate of such mixing is directly dependent on mean lake depth. The MIT lake temperature model, including the wind-mixing algorithm of Octavio, is supplemented by two routines so as to allow the computation of vertical mixing due to diffusion, advection, and thermocline migration. The mixing so computed represents the effective transport of phosphorus across a fixed thermocline 'barrier' in a two-box lake schematization. As such, it is consistent with that represented by the depth-dependent coefficient in the Snodgrass and O'Melia formulation. An application of the model to various lakes and reservoirs indicates no depth dependency. A critical evaluation of the data base used by Snodgrass and O'Melia to empirically justify their premise is included.

The final phase of the research is the development of a surface complexation model to describe the adsorption of anions onto metal oxide surfaces. All adsorption reactions, including the protonation-deprotonation of the surface groups and the formation of various complexes between surface sites and solution anions, are treated as equivalent coordination reactions at the same surface plane. The model allows both the maximum adsorption density and all stability constants to remain constant with pH. A straightforward method of correcting for coulombic attraction or repulsion is proposed. The model incorporates published data on the acid-base chemistry of aluminum oxide surfaces, and is able to satisfactorily reproduce experimental data describing the adsorption of both arsenate and phosphate using approximately the same set of stability constants. Supplementary model verification is presented, including a good fit to the observed maximum adsorption envelopes.

The thesis concludes with a summary of research and data needs related to the various topics.
ACKNOWLEDGMENTS

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Professor Francois M.M. Morel was the principal supervisor of this work. His technical skill, together with his exceptional ability to diagnose problems and generate new ideas, proved extremely valuable. I consider it my good fortune to have been his student, and I deeply appreciate his guidance, encouragement, and friendship over the past three and one half years.

I would also like to extend my gratitude to the other committee members, Professors Donald R.F. Harleman and Keith Stolzenbach. In particular, Professor Harleman provided many enlightening discussions during the initial phases of this research, while Professor Stolzenbach supervised Chapter 4. A note of thanks also to Profs. Charles O'Melia, William Snodgrass, and Will Rand, Drs. John Westall and Dieter Imboden, and Mr. Marvin Allum for providing any information requested.

I extend my thanks to Ray, Bill, Stan, Andy, and Jean for making my years at M.I.T. memorable ones. The companionship of Dave Ostendorf, especially during my 'live-in' at Parsons Lab, and the friendship of Professor Ole Madsen are especially appreciated.

No thesis could be effectively completed without a competent and good-natured typist. I therefore extend my final thanks to Michele.
The goal of most doctoral candidates is to have all or part of their research accepted for publication. Often, one attempts to extract various publications from a completed thesis. However, because the present research effort addresses several topics that independently represent discrete and well-defined problems, an effort was made to directly prepare the chapter corresponding to each topic in a format suitable for submission to a selected journal. A small degree of repetition is consequently found in the Introduction and Background sections of each chapter. Some variation in format is likewise found, and each chapter is followed by its own list of references.

Among the papers originating in this research are:


A fourth paper not directly incorporated into the thesis, but one which initiated many of the basic ideas and subsequent discussion, is:

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Chapter 1
INTRODUCTION

The need to make engineering and policy decisions in the water quality field creates a great demand for predictive models. An excellent example is the recent appearance of a large volume of literature related to the modeling of phosphorus in lakes. The increased loading of this nutrient to lakes and the resulting potential for accelerated eutrophication has become over the last few decades a central issue of water pollution control. Under the theory that the rate of eutrophication can be retarded if the input of phosphorus to a water body is decreased, administrative agencies have expended large amounts of money to reduce phosphorus influx. The need for a mathematical model able to assess the future trends of a given lake under a changing pattern of nutrient influx became obvious, and many researchers quickly responded.

The reported models are numerous and quite varied, covering a wide spectrum of empiricism versus theory, and simplicity versus complexity. Each has particular advantages and disadvantages. The widespread use of empirical models or simple phosphorus budget models is attributed primarily to their general applicability to a large class of lakes and the small data requirements. The fact that such models often neglect important and critical processes in order to maintain simplicity is their principal drawback. That is, the 'simple' models often do injustice to the present level of related knowledge and available data. The acceptance and use of more complex models is based in their allowance for multi-component analysis and good resolution in time and space. The capacity
to predict algal blooms is a convenient example of the value of 'complex' models. However, such elaborate models are often attractive to use simply because of their 'all-inclusiveness,' and the black-box effect easily occurs with the user not carefully examining the critical assumptions. Errors can be propagated throughout with little chance of detection due to the complexity. The same complexity renders information on critical processes unattainable, thereby limiting the use of complex models as research tools. Many applications of such models become an exercise in curve fitting, with the final outcome being a model that is applicable only to the water body to which it is fit.

The early work of Vollenweider (1) and the widely-used model of Chen and Orlob (2) furnish a suitable example of the extent of variation found in existing models. In the former, the claim is made that the trophic state of a lake can be determined simply by its position on an empirically-based plot of areal phosphorus loading and mean lake depth. On the other extreme, Chen and Orlob treat the temporal and spatial distribution of phosphorus as it is transformed through a complex soluble - particulate cycle. Soluble orthophosphate is incorporated into biomass by algae and subsequently passed in organic form to zooplankton and fish. The cycle is completed by the release of phosphate to the water column through the respiration of living organisms and by the decay of organic matter. The complexity of the model is further evidenced in that each individual constituent of the phosphorus cycle (e.g., algae) is subjected to a mass conservation equation, which includes a series of source and sink terms dependent on the concentration of other constituents.

The primary reason for such a diversity of models is that the
dynamics of phosphorus are governed by many disciplines in which a complete understanding of basic processes and their rates is still lacking. The effects of the flow field on the transport of phosphorus species infers a need for hydrodynamic considerations. Of comparable importance is that the temperature structure of a lake is often governed by hydrodynamics, which in turn modifies the rate of many critical exchange or loss processes involving phosphorus. Processes of a chemical nature are also of concern. The chemistry at the sediment-water interface, and in particular the adsorption of phosphate and the redox conditions, can significantly alter the distribution of phosphorus in lakes. Both the extent of adsorption and the speciation of phosphorus in solution are dependent of pH, which is itself principally buffered by another elemental system (i.e., the carbonate system). The biological sciences are essential to a study of phosphorus due to the uptake and release of this nutrient in the growth and respiration of biota. Not only are the relative concentrations of soluble orthophosphate and particulate phosphorus essential to the rate of many kinetic processes, but the subsequent settling of the particulate form is a principal mechanism for phosphate removal to the sediments. A consideration of the dissolved oxygen budget further supports the need for an interfacing of biological and chemical processes. The chemical response of a lake to phosphorus loadings is highly affected by its capacity to remain aerobic, and often it is the growth-respiration cycle that governs whether an oxygen deficit occurs, especially during the period of stratification. Morel and Yeasted have examined the issues of why and when interfacing of various hydrodynamic, chemical, and biological models should be implemented (3).
The level of detail necessary for a theoretically sound, widely applicable, and verifiable model of phosphorus in lakes remains an unresolved issue among concerned researchers. What cannot be argued is that the functionalities of any model, no matter what its level of treatment, must satisfy any basic trends in response to phosphorus loadings exhibited by a large number of lakes. In Chapter 2, an attempt to identify such trends through an extensive study of published data for 128 phosphorus limited lakes is presented. The empirical analysis consists of two parts, highlighted by an application of the multivariate statistical technique of stepwise discriminant analysis to the data. A basic parameter used in the study is $L_a \tau/Z$, which defines the average concentration of phosphorus in the inflow and would equal the steady-state concentration of total phosphorus in the lake were it not for internal losses. $L_a$ is the average annual loading of phosphorus per unit lake surface area, $\tau$ is the hydraulic residence time, and $Z$ is the mean lake depth. By isolating this expression for phosphorus, the ability of various morphological parameters (hydraulic residence time, mean depth, and surface area) to account for the non-conservative behavior of this nutrient is investigated.

There are many political, economic, and psychological reasons why one chooses whether or not to build large models encompassing all hydrodynamic, chemical, and biological processes relevant to the fate of phosphorus in lakes. Ultimately, however, the decision to interface various submodels into a larger one has to be based on technical arguments. As discussed previously,

"Models which are developed to describe any one aspect (hydrodynamic, chemical, biological) of a field problem are subject to uncertainty due to a lack of knowledge of
the rates and mechanisms employed in the model. While this uncertainty may be acceptable for one aspect of a model, interfacing with other models developed for other aspects of a system can lead to a compounding of uncertainties and a result in which one can have little confidence. Here it is necessary to realize the limit of our ability to build the 'ultimate' predictive model and to recognize the value of a limited model which can be used interactively as a research tool for a reasonably discrete and well-defined problem (3).

Relative to other models investigated, a recent series of models developed by Imboden (4), Snodgrass and O'Melia (5), and Imboden and Gächter (6) represents an effective compromise between current needs and limitations. A good reproduction of observed phosphorus concentrations is achieved by utilizing two phosphorus compartments (soluble orthophosphate and particulate phosphorus) and by defining each critical exchange or loss mechanism in a very simple manner (e.g., as a first-order reaction). As discussed in Chapter 3, the basic approach used in this series of models makes them a valuable asset to subsequent modeling efforts. The principal feature of Chapter 3 is the presentation of a model of lake eutrophication that is based in an Imboden-type phosphorus model and that incorporates the findings of the empirical study described in Chapter 2. In particular, the proposed model is a steady-state version of the Imboden model in which the settling rate of particulate phosphorus is assigned a functional form that is dependent only on the hydraulic residence time. For lakes in which the euphotic zone can be assumed to extend to the lake bottom, the spring concentration of total phosphorus becomes a function of only the inflow concentration of phosphorus and the hydraulic residence time. In a comparison with that of Dillon (7), the model is shown to be just as reliable in predicting lake trophic state without the need for an explicit parameter representing phosphorus loss.
The data required by the model presented in Chapter 3 are consistent with those generally available for a large number of lakes. The extension to more dynamic phosphorus models will require significant progress in both the basic understanding of the governing processes and the obtention of extensive field data for model calibration and testing. In response to the need for basic research, models of two processes that are known to affect the distribution of phosphorus in lakes are addressed in Chapters 4 and 5.

In Chapter 4, the process being modeled is the net mixing across the thermocline region of a lake during the period of stratification. The primary motivation for this study is to test if Snodgrass and O'Melia's proposal, that the rate of mixing is directly dependent on mean lake depth, can be justified by the results of an established temperature model for lakes. Because the extent of mixing computed by the model is defined relative to the 'two-box' lake schematization used by Snodgrass and O'Melia, the direct contribution of this modeling study to a comprehensive model is somewhat limited. Perhaps the proposed routine to locate the position of the thermocline at each time step of interest will find eventual use in a more elaborate model.

Chapter 5 describes a surface complexation model of anion adsorption onto metal oxides, thereby providing insight into the mechanism of phosphate exchange at the sediment-water interface. Using an extensive collection of experimental data describing the adsorption of arsenate and phosphate onto aluminum oxide surfaces, several methods of model verification are presented. The fact that the study is limited to experimental data is noteworthy, for the incorporation of any submodel of phosphate
adsorption into a comprehensive model of phosphorus in lakes is currently inhibited by a lack of field data for both model calibration and verification.

Although the models formulated in Chapters 4 and 5 are not a final solution to the incorporation of mixing and adsorption processes into the 'ultimate' model, they do provide an advancement in the basic understanding of these two essential processes. In Chapter 6, several areas of research to supplement these modeling efforts are summarized. Additional research relative to the other chapters is likewise discussed, as are a number of data needs.


2.1 Introduction

Induced primarily by the activities of man, the cultural eutrophication of lakes has become over the last few decades a central issue of water pollution control. Concerned management agencies, theorizing that the rate of eutrophication can be consequently curbed if the input of nutrients to a water body is decreased, have expended large amounts of money for programs to reduce the flux of nutrients to lakes. Along with this management policy has come the need for a mathematical model able to assess the future trends of a given lake under a changing pattern of nutrient influx.

In this paper, data from a large number of lakes are used to determine the significance of various limnological parameters in simple nutrient budget models. Of primary concern are models that allow the prediction of lake trophic state once nutrient loadings are known. By isolating the expression for the concentration of a conservative substance in these models, the ability of various morphological parameters to describe the non-conservative behavior of nutrients is investigated. Because phosphorus is the limiting nutrient for most lakes in the temperate zone (1) and is of particular importance due to its relationship to man's activities, the study is restricted to this nutrient.

Existing phosphorus budget models and the respective loading diagrams are first examined. Conclusions extracted from this study are then substantiated by the multivariate statistical technique of stepwise
discriminant analysis. Statistically significant parameter relationships pertinent to more complex deterministic phosphorus models are identified, and potential improvements in the analytical scope of predictive models of phosphorus in lakes are proposed. In addition, the resulting statistical functions are recommended as empirical predictive formulas of lake trophic state.

2.2 The Data

The literature was searched for lakes sufficiently studied so as to provide the type of data necessary for the present analysis. A total of 128 lakes were found, including 71 eutrophic, 42 mesotrophic, and 15 oligotrophic lakes. (A complete listing of the data is presented in Appendix II.A.)

The European lakes investigated by Vollenweider (2), a group of Canadian lakes summarized by Dillon (3), the Great Lakes, and various other extensively studied lakes of the United States comprise the first 32 lakes. Additional data for these water bodies were found in Imboden (4) or Dunst (5). All of the remaining lakes are located in the continental United States. Data for these 96 lakes were taken from the results of a National Eutrophication Survey conducted by the U.S. Environmental Protection Agency (6, 7). In order to insure that the data selection remained unbiased, each lake that was phosphorus limited at the times of sampling with a mean depth of greater than four meters was selected. Phosphorus limitation was established either by algal assay results or by the ratio of nitrogen to phosphorus concentrations.

The first 32 lakes have been extensively investigated, and as such
the reliability of the reported data is adequate for models with large time scales of analysis. More caution must be exercised when using data for the other 96 lakes. Many of these lakes were sampled on only three occasions and the estimated annual nutrient loadings were simply extrapolated from a limited number of grab samples. Previous studies of the respective water bodies by local interest groups were frequently used by the National Eutrophication Survey to enhance the reliability of the data.

One problem in the verification of models of trophic state is the subjective, nonstandardized procedures for designating the actual trophic state of a lake. A concise review of the methodologies used to classify the present 128 lakes is called for. In the case of the first 32 lakes, it is not obvious how the reported trophic states were assigned. Apparently, the classifications were based on a qualitative inspection of pertinent data for each lake. More specific guidelines were established for each of four key indicators in order to assign a trophic classification to the lakes of the National Eutrophication Survey (Table II-1). For cases in which all the parameter values did not fall within one trophic classification, a percentile ranking system was used. Details of this classification procedure are found in (1).

2.3 Background

Simple budget models for phosphorus in lakes represent a compromise between generality and reality. They are intended only to describe overall characteristics of phosphorus dynamics and as such their direct use for prediction purposes is limited. On the other hand, because these models incorporate only simple relationships between a few common lake
parameters, they are of value to the present study involving a large and diverse set of lakes.

Phosphorus in lakes is subject to chemical and biological transformations and transfer to (and from) the sediments. In simple mass balance models this 'non-conservative' nature is incorporated into a loss term. Various expressions for the loss term have been proposed, each leading to a unique expression for the steady-state concentration of total phosphorus (Table II-2). Vollenweider (8) considers that phosphorus is removed by a first-order reaction occurring throughout the lake. Imboden (4, 9) and Snodgrass and J'Melia (10) consider sedimentation as the principal removal mechanism and treat the loss as an output of phosphorus across the sediment-water interface only. Another approach is that of Dillon (3), who defines a retention coefficient as the fraction of incoming phosphorus that is lost by internal processes (e.g., sedimentation). Other investigators (Larsen and Mercier (11), Sonzogni, et al. (12)) have formulated similar models, but these will not be considered further since their relationships are basically rearrangements of those of Dillon.

The last column of Table II-2 gives the steady-state phosphorus concentration in a form that separates the conservative term, $L_a \tau/Z$ (the steady-state phosphorus concentration in the absence of internal losses), from the various expressions corresponding to the loss terms. In each expression the loss parameter is combined with parameters of lake morphology in a non-dimensional quantity: $\sigma \tau$, $g \tau/Z$, $R$.

Early empirical studies of lake response to nutrient loadings have indicated that mean depth is the dominant morphological parameter (e.g., Rawson (13), Sakamoto (14)). A similar conclusion can be drawn from the
widely-referenced phosphorus loading-mean depth diagram of Vollenweider (Figure 2-1). That is, for a given degree of eutrophy, deep lakes are capable of assimilating higher areal loadings of phosphorus than shallow ones. An examination of Vollenweider's expression in Table II-2 indicates, however, that for a given concentration of phosphorus in the inflow \((L_a \tau/Z)\), the mean annual phosphorus concentration is unrelated to mean depth if the parameter \(\sigma\) can be taken as a constant. A suitable explanation for the inverse relationship proposed by Vollenweider's diagram is simply the respective presence of areal loading and mean depth in the numerator and denominator of the \(L_a \tau/Z\) term.

Snodgrass and O'Melia argue that the most cogent loss term is that of Imboden. The corresponding equation (second line of Table II-2) implies that the phosphorus concentration is positively related to mean depth for a given inflow concentration if the sedimentation velocity \((g)\) is reasonably constant. The use of the Imboden loss term in a more complex model likewise reversed the observed trend by predicting that deeper lakes will have higher phosphorus concentrations in their euphotic zones than shallow lakes \((4, 9, 10)\). To resolve this discrepancy in their two-box model, Snodgrass and O'Melia have proposed to assign a depth dependence to the coefficient of exchange across the thermocline and to the effective settling velocity of the particulate phosphorus. The second of these functionalities is the most significant in allowing a good fit between observed phosphorus concentrations and those predicted by the two-box model of Snodgrass and O'Melia.

An outcome of Dillon's mass balance model (third line of Table II-2) is a critical phosphorus loading diagram for trophic state prediction.
akin to those of Vollenweider. However, a critical problem in using Dillon's formulation for predictive purposes is an inherent uncertainty when extrapolating a knowledge of present retention coefficients to the study of future loading effects. That is, due to chemical and biological interactions, the retention coefficient is itself dependent on the nutrient loading. Dillon himself notes a decreased phosphorus loading-higher retention coefficient trend (3).

If the mean annual phosphorus concentration [P] is a good indicator of trophic state (somewhat of a tautology in light of Table II-1), then conversely loading diagrams delineating trophic states must contain implicit information regarding the actual phosphorus concentration. In particular, it must be possible by analyzing such diagrams to decide whether the effect of mean depth on [P], and therefore on the trophic state of the lake, is simply that which appears in the conservative term, L_a τ/2, or if an effect of mean depth on the non-conservative behavior of phosphorus must be invoked to explain the data. A reexamination of phosphorus loading diagrams with an extended data base will answer this question.

Given limnological data on a large number of lakes, a more general objective is to decide what parameters are significant in the discrimination of trophic state. Conventional techniques for examining an extensive collection of data to study the significance of various parameters and their relationships are those of multivariate statistics. To date, only a few applications of multivariate techniques to the study of lakes have been reported. Shannon and Brezonik (15, 16) classified the trophic state of 55 Florida lakes by cluster analysis using the trophic state indicators primary production, chlorophyll a, total phosphorus, total organic
nitrogen, Secchi disc, specific conductivity, and Pearsall's cation ratio. In order to rank the lakes on a more quantitative basis, a trophic state index was derived by principal component analysis from the correlation matrices of the trophic indicators. A more recent and intriguing application is Boland's attempt to estimate lacustrine trophic state using multispectral scanner data from the satellite LANDSAT-1 (17). Included in this work is the application of principal component analysis to define a multivariate trophic state index based on indicators similar to those of Shannon and Brezonik.

While these applications of multivariate statistics will promote the standardization and quantification of the definition of trophic state, the present study is concerned with the statistical resolution of critical questions related to trophic state classification. For example, is the classification in three trophic states sufficiently precise to permit a clear identification of relative phosphorus concentrations, at least of the conservative term $L_{a}^{T/Z}$? Can the analysis be pushed further and provide insights into the significant limnological parameters that govern the non-conservative behavior of phosphorus in lakes? In short, can guidelines for the development of cogent deterministic models for trophic state prediction be established?

2.4 A New Look at Phosphorus Loading Diagrams

For purposes of this investigation, a straightforward method of quantifying the results of loading diagram studies is to plot pertinent data onto the diagrams and simply count the number of lakes that are positioned in the correct trophic level relative to the total number of lakes considered.
This is done using data from the 128 lakes available to this study and the loading diagrams of Vollenweider (2, 8) and Dillon (3) (Figures 2-1, 2-2, 2-3). Two sets of lines demarcating the three trophic levels are shown in each figure. The solid lines are those presented in the original model formulations, while the dashed lines represent the set of parallel lines that optimizes the number of correct predictions for the present set of lakes.

Table II-3 includes the results of this procedure, with the number of lakes correctly predicted for each group given as a percentage of the total number of lakes in the group. Also summarized in Table II-3 are the results of a second procedure in which the regions defining each trophic level are simple intervals on a one-dimensional axis corresponding to a pertinent combination of the respective parameters. It must be noted that while the total number of correctly predicted lakes is a reasonable indicator of the discriminating capability of each scheme, a comparable index is the percentage of correctly classified mesotrophic and oligotrophic lakes. This results from the fact that the areal phosphorus loading of eutrophic lakes is unbounded from above and numerous lakes with extremely high loadings are correctly classified no matter what combination of parameters is considered. Mesotrophic and oligotrophic lakes are in a sense bounded, however, and the effects of other parameters on their classification is consequently more significant.

The first section of Table II-3 reports the results based on the original criteria of Vollenweider and Dillon. It is interesting to note how biased the original models are to eutrophic lakes, and to a lesser degree oligotrophic lakes, at the expense of mesotrophic lakes. This is
no doubt due to the small number of mesotrophic and oligotrophic lakes under study at that time. By reformulating the criteria as a 'best fit' to the present set of data, both an increase in the total percentage of correctly predicted lakes and a definite reduction in the biased nature of the predictions are achieved. It is noteworthy that Dillon's diagram required a relatively small revision. Such a result supports the use of total phosphorus concentration as an indicator of trophic state, for the lines originally demarcating the three states in Dillon's diagram represent phosphorus concentrations of 10 and 20 µg/l. These same phosphorus levels, initially recommended as separators of trophic state by Sawyer (18), were used in the National Eutrophication Survey (Table II-1).

The importance of including the hydraulic residence time and the retention coefficient in trophic state classification schemes is indicated by the results of the 'best fit' criteria (second section of Table II-3). The contribution of the hydraulic residence time is most notably reflected in a significant increase in the percentage of correctly classified mesotrophic and oligotrophic lakes, while Dillon's incorporation of a coefficient to account for the non-conservative behavior of phosphorus provides considerable improvement in the prediction reliability for the total set of lakes.

Of more concern to subsequent sections is a comparison of the results based on log-log plots of various parameters and those of a one-dimensional grouping of the same parameters (last two sections of Table II-3). Because of the log-log nature of the plots, the results of the two sections would be identical only if the slope of the demarcation lines is unity. Such is the case with Dillon's scheme (Figure 2-3).
The criteria lines for Vollenweider's original loading diagram have a slope of 0.6 (Figure 2-1). If this diagram is the optimum trophic state classification scheme that uses areal loading and mean depth, then the parameter $L_a/Z^{0.6}$ would provide the optimum separation in a one-dimensional analysis. It is found, however, that the simple ratio $L_a/Z$ (phosphorus loading per unit lake volume) does equally well. In other words, rather than some hidden non-linear effect of mean depth on a lake's assimilative capacity, it is inferred that the apparent significance of mean depth in Vollenweider's treatise is simply a consequence of his use of areal loading rather than volume loading. Shannon and Brezonik (15) express the same notion by excluding both areal loading and mean depth in favor of volume loading in their regression analysis of a trophic state index.

Consider next Vollenweider's second generation phosphorus loading diagram (Figure 2-2), upon which the hydraulic loading rate (mean depth/residence time) replaces the mean depth as the critical morphological parameter. The slope of the demarcation lines is 0.5, indicating that the parameter $L_a(\tau/Z)^{0.5}$ is an excellent one-dimensional discriminator of lake trophic state. A more fundamental, dimensionless quantity formed by the component parameters is $L_a\tau/Z$, the steady-state concentration of a conservative substance in a lake. The discrimination achieved by this concentration term is unsatisfactory, however, due to the low percentage of correctly classified mesotrophic and oligotrophic lakes. That the non-conservative nature of phosphorus must be incorporated into a trophic state classification scheme is a logical conclusion. Of more interest is an indication that the term $(\tau/Z)^{0.5}$ is effective in progressing from a 'poor' to a 'good' classification scheme. In some complex way, this
The term is able to reflect the internal loss of phosphorus. Whereas the use of the hydraulic loading makes it impossible to separate the effects of mean depth and residence time, the previous analysis has disclosed no anomalous effects of mean depth on a lake's response to phosphorus loading. It follows that the hydraulic residence time must be the critical parameter. In the next section, this conclusion is substantiated through the use of multivariate statistics, which enables an isolation of the contributions of mean depth and residence time to trophic state prediction.

2.5 **Stepwise Discriminant Analysis Applied to Predictive Models for Lakes**

Discriminant analysis is a multivariate statistical method that allows the classification of a multi-dimensional observation vector into one of several multivariate normal populations. Because not all of the observed variables are needed to discriminate between the populations in many cases, a modified procedure has been formulated to identify the subset of these variables that furnishes the 'best' discrimination. This is the method of stepwise discriminant analysis. As applied to this study of the degree of eutrophy of lakes, the three trophic states are the 'populations,' and the observed 'variables' include mean depth (Z), hydraulic residence time (T), surface area (A), phosphorus retention coefficient (R), and mean annual phosphorus loading per unit surface area (L_a). The primary goal is to be able to classify a lake into a certain trophic state once its variables are known. A more specific purpose for this application of the stepwise procedure is to clarify the position of various lake parameters in trophic state identification.

The stepwise discriminant analysis program used for this study was
BMD07M (19). The logic of the stepwise procedure is analogous to that of stepwise multiple regression, and is presented in detail by Afifi and Azen (20). For purposes of this study, the procedure can be sufficiently summarized by referring to Table II-4. The first two columns merely identify the case number and the combination of limnological variables selected for analysis. The third column lists these variables in the order in which they have entered the discriminating set. The variable entered at each step is that for which an F statistic based on a one-way analysis of variance test is maximum. This statistic (F' in column 4) is a measure of the 'difference' in the mean values of the conditional distributions of the populations for each variable, given the variables already entered. Column 5 gives the tabulated values of the F-distribution for the 95% significance level. The hypothesis that the entering variable significantly contributes to the discrimination between populations is rejected at a prescribed significance level if F' is less than the value of the F-distribution at that level.

After the last step of each case, the output of the program includes the coefficients of the canonical variables and a scatter diagram of trophic state discrimination based on the first and second canonical variables. Canonical variables are linear combinations of the limnological parameters, and can be used to advantage because the first one or two often explain most of the variance in the multi-dimensional cloud of data points. The value of canonical variables to the present study is discussed below.

For each case, input to the stepwise discriminant analysis program includes the number of lakes in each of the three trophic states and the values of the selected parameters for each lake. In order to satisfy
the assumption of normality, a transformation of the data to the logarithmic scale is required. Numerous combinations of the parameters were tested. Four are considered here (Table II-4).

Case 1 considers the four fundamental independent parameters. It is determined that surface area is not a significant discriminatory variable. This is not surprising since the loading term has already been normalized by the surface area. A second finding is that areal loading and mean depth contributions are not fully realized until the residence time is included, as evidenced by the high $F'$ value for residence time once the other parameters have entered. (A considerable 17 per cent increase in the total number of correctly predicted lakes accompanied the inclusion of residence time.) The presence of $L_a$, $Z$, and $\tau$ in this classification scheme allows a comparison with the results shown in the second line of Table II-2. Of primary interest is the first canonical variable for Case 1:

$$CV(1) = 2.98 \log L_a + 1.88 \log \tau - 2.85 \log Z + 3.19 \quad [2.1]$$

$$CV(1) = 2.98 \log \left\{L_a T/Z\right\} - 1.10 \log \tau + 3.19 \quad [2.2]$$

This canonical variable accounts for over 98 per cent of the total dispersion of the present data, and thus it can serve as a reliable one-dimensional scheme for trophic state classification. The only governing parameter other than the 'conservative' phosphorus concentration ($L_a T/Z$) is the hydraulic residence time, thereby supporting the conclusion that it is highly correlated with in-lake phosphorus losses. For a given value of $L_a T/Z$, lakes with larger residence times cause a lower value of $CV(1)$ indicative of better lake conditions. A higher phosphorus retention also implies more desirable conditions. It follows that the correlation
between residence time and phosphorus retention is positive.

That the residence time is statistically the only morphological parameter effective in describing the non-conservative behavior of phosphorus is even more apparent in Case 2. Not only does the large $F'$ value for residence time indicate its great significance, but the exceptionally low $F'$ values for mean depth and surface area discredit their role in the regulation of phosphorus losses.

Dillon's use of a measured retention coefficient should be sufficient to account for phosphorous losses under current loading conditions. The corresponding parameter for average phosphorus concentration, $L_a \tau (1-R)/Z$, is included in Case 3 to test its discriminating capacity. It is interesting that the residence time ($\tau$) remains significant over and above its inclusion in the concentration term. It is also determined that $(1-R)$ is significant, but the results of Case 4 reveal no such significance when residence time is excluded. The presence of $(1-R)$ in Case 3 reflects a counterbalance to the highly correlated residence time. One possible explanation for the independent appearance of $\tau$ as a significant discriminating factor is that measured phosphorus concentrations are commonly spring or summer values, whereas the concentration defined by Dillon's model is an annual average. The statistical routine discriminates between trophic states defined by the former. Some phenomenon affected by this temporal difference, as for example thermal stratification, may be accounted for by the presence of residence time.

The high correlation between residence time and the retention coefficient is very attractive to simple predictive models of lake trophic state. As discussed earlier, the apparent success of any classification scheme involving $R$ is diminished in that this coefficient, as defined, is
not determinable under changing loading conditions until the new phosphorus budget is known. It is now proposed that two known parameters, \( L_a \tau/Z \) and \( \tau \), are sufficient to predict a priori the trophic state of a lake.

The prediction accuracy of the classification functions of Case 2 is equivalent to that using Dillon's parameter in Case 3. These classification functions, updated in order to exclude the effects of erroneously classified lakes, are given in Table II-5. Given the variables for an 'unknown' lake, its classified trophic state is that for which the classification function is a maximum.

2.6 Discussion of Results

The significance of the term \( L_a \tau/Z \) in the discrimination of lake trophic state is expected in that it is the average concentration of phosphorus in the inflow. A somewhat unforeseen result is that for the morphological parameters considered, the hydraulic residence time alone is statistically significant in describing the non-conservative behavior of phosphorus in simple deterministic trophic state models. Several processes affecting the distribution of phosphorus in lakes entail coefficients that can be non-dimensionalized by the residence time. These include phosphorus settling, first-order reactions, and lake mixing. Data limitations prohibit an investigation of the relative significance of each process through discriminant analysis. Each is now briefly discussed.

Imboden and Snodgrass and O'Melia express the mean annual phosphorus concentration as (Table II-2):

\[
[P] = \frac{(L_a \tau/Z)}{\tau + (g \tau/Z)}
\]  

[2.3]
Assuming that this concentration is a satisfactory indicator of trophic state, it follows that the conspicuous presence of the residence time in the previous analyses must be reflected in the dimensionless settling term, $gT/Z$. A consequence is the repudiation of the use of a constant settling velocity for all lakes in simple models, for if the velocity term ($g$) is constant the significant parameter is the ratio of residence time and depth. Both the loading diagram analysis and the stepwise discriminant analysis have invalidated such a significance. The dominance of a settling process can be maintained, however, if one of two conditions is satisfied. First, if the velocity term is directly dependent on mean depth so that $g/Z$ tends to a scalar, then only residence time remains. Snodgrass and O'Melia have used flocculation arguments to derive such a relationship for hypolimnetic settling (10). A second possibility is to consider the appropriate depth scale ($Z$) to be a parameter that is quasi-constant for all lakes (or at least somewhat uncorrelated to other morphological parameters). An example is the thickness of the epilimnion. However, Snodgrass and O'Melia found that predicted phosphorus concentrations are quite insensitive to the epilimnetic settling rate.

One can also postulate that a first-order reaction (e.g., phosphorus mineralization) is the dominant process governing phosphorus distribution. A term of the form $\sigma T$ would be required in the denominator of equation [2.3], thus justifying to some extent Vollenweider's original conception (Table II-2). From a dimensionless parameter standpoint, the importance of residence time independent of other morphological parameters is explainable only if the rate coefficient ($\sigma$) satisfies this independence. For reactions of a chemical or biological nature this is a credible
assumption. The previously discussed two-box model of Snodgrass and O'Melia considers a reversible chemical-biological reaction between dissolved orthophosphate and 'particulate' phosphorus. If a new phosphorus compartment representing the mineralized form is introduced, such that its reconversion to orthophosphate is prohibited, the associated rate coefficient would impart added significance to the residence time. It is conceivable that the observed relationship between the assimilative capacity of a lake and its mean depth results indirectly from the high correlation between depth and residence time. Snodgrass and O'Melia's use of two depth-dependent processes to moderate their predictions, discredited by the present findings that depth effects are insignificant, may not be necessary.

One final process affecting phosphorus dynamics that can be used to normalize the residence time is vertical mixing. Snodgrass and O'Melia (10) and Stauffer and Lee (21) are among those who have recognized the importance of the exchange of nutrients across the thermocline during the stratification season.

A somewhat unrelated interpretation of the present result, that lakes with longer residence times exhibit better trophic conditions, is that such lakes have not yet 'caught up' with historically increasing concentrations of phosphorus in the inflow \( L_a \tau /Z \). A basic assumption of the present empirical study is that the lakes are at steady-state under the reported phosphorus loadings. This is not entirely satisfied in most cases. To test the hypothesis that the importance of residence time is due to the slow response time of some lakes relative to historical increases in phosphorus loading, Case 2 of the stepwise discriminant analysis
has been repeated excluding all lakes with residence times greater than five years. The F' value for the residence time (entered after $L_a \tau/Z$) remains highly significant even though it is reduced from 29.32 to 9.46, indicating that the equilibration time hypothesis is not sufficient to totally explain the significance of the hydraulic residence time.

2.7 Concluding Remarks

An attempt has been made in this paper to advance the modeling of lake response to nutrient loadings, especially phosphorus. Utilizing data from 128 lakes, existing phosphorus loading diagrams are reexamined and the multivariate technique of stepwise discriminant analysis is applied. Both methods of data analysis produce a 'model' capable of lake trophic state prediction.

The science of limnology has progressed beyond such an 'empirical' modeling stage, however, and modifications that advance the applicability of simple lake models are called for. The interfacing of simple phosphorus models with existing chemical and hydrodynamic models potentially provides a better definition of the speciation of phosphorus and its concurrent transport due to physical processes (22). What is critical is that observed, basic trends must continue to be satisfied as model complexity increases. This study has identified such a trend: that the hydraulic residence time and the assimilative capacity of a lake are positively correlated. Though the empirical approach prohibits the identification of a 'causal' relationship, the statistical significance is clearly demonstrated.


7) Allum, Marvin O., (private communication), Corvallis Environmental Research Laboratory, Corvallis, Oregon (1976).


Figure 2-1

AREAL PHOSPHORUS LOADING VS. MEAN DEPTH DIAGRAM

(after Vollenweider (2))
- ORIGINAl CRITERIA
- 'BEST FIT' CRITERIA

EUTROPHIC

MESOTROPHIC

OLIGOTROPHIC

$LA$ (g/m$^2$-yr)

$Z$ (meters)
Figure 2-2

AREAL PHOSPHORUS LOADING VS. HYDRAULIC LOADING DIAGRAM

(after Vollenweider (8))
Figure 2-3

DILLON'S PARAMETER VS. MEAN DEPTH DIAGRAM

(after Dillon (3))
TABLE II-1

National Eutrophication Survey Guidelines
For Trophic State Determination
(from Gakstatter, et al., (1))

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Oligotrophic</th>
<th>Mesotrophic</th>
<th>Eutrophic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Phosphorus (µg/l)</td>
<td>&lt; 10</td>
<td>10 - 20</td>
<td>&gt; 20</td>
</tr>
<tr>
<td>Chlorophyll a (µg/l)</td>
<td>&lt; 4</td>
<td>4 - 10</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Secchi Depth (m)</td>
<td>&gt; 3.7</td>
<td>2.0 - 3.7</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>Hypolimnetic Dissolved Oxygen (% saturation)</td>
<td>&gt; 80</td>
<td>10 - 80</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>
### Basic Conservation of Mass Equation:

\[ V \frac{d[\bar{P}]}{dt} = L_a A - q_s A[\bar{P}] - \text{Loss Term} \ (= 0) \]

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Loss Term</th>
<th>Steady-State Phosphorus Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vollenweider</td>
<td>( \sigma A [\bar{P}] )</td>
<td>[ [\bar{P}] = \frac{L_a \tau}{Z} \left( \frac{1}{1 + \frac{1}{\sigma \tau}} \right) ]</td>
</tr>
<tr>
<td>Imboden; Snodgrass and O'Melia</td>
<td>( g A [\bar{P}] )</td>
<td>[ [\bar{P}] = \frac{L_a \tau}{Z} \left( \frac{1}{1 + \frac{g \tau}{Z}} \right) ]</td>
</tr>
<tr>
<td>Dillon</td>
<td>( RL_a A )</td>
<td>[ [\bar{P}] = \frac{L_a \tau}{Z} \left( 1 - R \right) ]</td>
</tr>
</tbody>
</table>

**TABLE II-2**

Simple Budget Models for Total Phosphorus
### TABLE II-3

Results of an Analysis of Phosphorus Loading Diagrams

<table>
<thead>
<tr>
<th>Type of Plot</th>
<th>Original Criteria</th>
<th>'Best Fit' Criteria</th>
<th>One-Dimensional Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total E M O</td>
<td>Total E M O</td>
<td>Parameter Total E M O</td>
</tr>
<tr>
<td>$L_a, Z$</td>
<td>69 96 26 60</td>
<td>73 83 64 53</td>
<td>$L_a/Z$ 71 78 64 60</td>
</tr>
<tr>
<td>$L_a, q_s (= Z/\tau)$</td>
<td>70 89 31 93</td>
<td>76 74 76 80</td>
<td>$L_a\tau/Z$ 77 91 65 33</td>
</tr>
<tr>
<td>$[L_a(1-R)\tau], Z$</td>
<td>78 95 55 67</td>
<td>82 92 73 60</td>
<td>$L_a(1-R)\tau Z$ 82 92 73 60</td>
</tr>
</tbody>
</table>

\[ L_a(1-R)\tau Z \]

\[ a \text{ Retention coefficient (R) not available for 6 eutrophic and 2 mesotrophic lakes.} \]
<table>
<thead>
<tr>
<th>Case</th>
<th>Variables Considered</th>
<th>Variable Entered</th>
<th>$F'$</th>
<th>$F_{0.95}(v_1, v_2)$&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$L_a, Z, \tau, A$</td>
<td>$L_a Z^\tau$</td>
<td>46.71</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\tau$</td>
<td>3.65</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A$</td>
<td>19.31</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Z$</td>
<td>0.52</td>
<td>3.08</td>
</tr>
<tr>
<td>2</td>
<td>$L_a^\tau Z, Z, \tau, A$</td>
<td>$L_a^\tau Z$</td>
<td>40.64</td>
<td>3.07</td>
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<td></td>
<td></td>
<td>$A$</td>
<td>29.32</td>
<td>3.08</td>
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<td></td>
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<td>$Z$</td>
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<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>3.08</td>
</tr>
<tr>
<td>3</td>
<td>$L_a(1-R)^\tau Z, Z, \tau, A, (1-R)$</td>
<td>$L_a(1-R)^\tau Z$</td>
<td>78.22</td>
<td>3.07</td>
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<tr>
<td></td>
<td></td>
<td>$\tau$</td>
<td>8.43</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(1-R)$</td>
<td>4.33</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A$</td>
<td>1.36</td>
<td>3.08</td>
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<tr>
<td></td>
<td></td>
<td>$Z$</td>
<td>0.07</td>
<td>3.08</td>
</tr>
<tr>
<td>4</td>
<td>$L_a(1-R)^\tau Z, Z, A, (1-R)$</td>
<td>$L_a(1-R)^\tau Z$</td>
<td>78.22</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$(1-R)$</td>
<td>1.11</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td></td>
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<sup>a</sup> $v_1 = G-1; v_2 = N-G-V; (G = number of groups; N = total number of lakes; V = number of variables entered)

**TABLE II-4**

Summary Table for the Stepwise Discriminant Analysis
### Classification Functions

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<th>Trophic State</th>
<th>Classification Functions</th>
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<td>Eutrophic</td>
<td>$F(E) = -12.542 \log (L \tau / Z) + 1.648 \log (\tau) - 5.889$</td>
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<tr>
<td>Mesotrophic</td>
<td>$F(M) = -25.063 \log (L \tau / Z) + 5.146 \log (\tau) - 18.873$</td>
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<td>$F(0) = -31.475 \log (L \tau / Z) + 9.130 \log (\tau) - 30.009$</td>
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**TABLE II-5**

Classification Functions for a Proposed Trophic State Classification Scheme
APPENDIX II.A

Complete Listing of Lake Data
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<th>Hydraulic Loading Rate (m/yr)</th>
<th>Areal Phosphorus Loading (g/m²-yr)</th>
<th>Retention Coefficient</th>
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<td>Hydraulic Loading Rate (m/yr)</td>
<td>Areal Phosphorus Loading (g/m²-yr)</td>
<td>Retention Coefficient</td>
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<td>Areal Phosphorus Loading (g/m²-yr)</td>
<td>Retention Coefficient</td>
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Chapter 3
AN EMPIRICALLY BASED, STEADY-STATE PHOSPHORUS MODEL FOR THE PREDICTION OF LAKE TROPHIC STATE

3.1 Introduction

The accelerated eutrophication of lakes due to an increased loading of phosphorus provides an excellent example of the detrimental effects of man's activities on the world's water bodies. Engineering and policy decisions directed at this problem are imperative, and under the theory that the rate of eutrophication can be retarded if the input of phosphorus to a water body is decreased, large amounts of money have been expended to reduce phosphorus influx. A great demand for mathematical models able to assess the future trophic state of a given lake under a changing pattern of nutrient influx has become evident.

Reported models dealing with phosphorus in lakes and the related trophic state are numerous and quite varied, covering a wide spectrum of empiricism versus theory, and simplicity versus complexity. The principal reason for such a diversity of models is that the dynamics of phosphorus are governed by many disciplines in which a complete understanding of basic processes and their rates is still lacking. Hydrodynamics, chemistry and biology represent the major sciences involved. At one extreme are those researchers who attempt to incorporate widely accepted kinetic descriptions of simple systems from each discipline into one 'ultimate' predictive model. Others believe that when models from various disciplines are interfaced, a compounding of the uncertainties of each submodel may lead to overall results in which one can have little confidence. An alternative is the empirical approach. That is, to compare the parameters
known to affect trophic state for the lake under consideration with those parameters in lakes of known trophic state.

Relative to other models investigated, a recent series of models developed by Imboden (1), Snodgrass and O'Melia (2) and Imboden and Gächter (3) represents an effective compromise between engineering needs and a treatment of phosphorus dynamics that is consistent with current knowledge of the governing processes. An important objective in the development of these models has been to achieve predictions that are consistent with empirical observations relating areal phosphorus loading and mean lake depth (4, 5, 6).

Following in the same tradition, the model presented in this paper is based on an Imboden-type model and incorporates additional empirical relationships (7). By focusing on spring concentrations of total phosphorus and assuming that a lake reaches a steady-state by the end of the winter circulation period, the model requires few data and can be solved analytically. The resulting explicit formulas are shown to predict spring total phosphorus concentrations as well as the dynamic phosphorus model of Snodgrass and O'Melia (2).

For lakes in which the euphotic zone extends to the lake bottom, the spring phosphorus concentration becomes a function of only two parameters (inflow phosphorus concentration, hydraulic residence time) and a critical loading diagram akin to those of Vollenweider (8) and Dillon (9) can be constructed. Relative to that of Dillon, Vollenweider's diagram requires less data but has been found not to discriminate among trophic states as well (7). In a test with 80 lakes, the prediction reliability of the proposed loading diagram is shown to be comparable to that of Dillon while
retaining the simple data requirements of Vollenweider. This is particularly significant because the measured retention coefficient that limits the use of Dillon's model for prediction purposes is no longer required. In effect, the new model can comparably account for phosphorus retention by imposing various statistical findings relating mean depth, residence time, and the apparent in-lake loss of phosphorus.

3.2 Background

Because most lakes in the temperate zone are phosphorus limited (10), a convenient indicator of lake trophic state is the concentration of total phosphorus in the lake. Sawyer (11) initially recommended total spring phosphorus concentrations of 10 and 20 μg/l as adequate criteria for establishing the trophic state of a given lake. The same guidelines were used in the National Eutrophication Survey (10) as one of four key indicators of lake conditions. Thus, a model of phosphorus in lakes is a logical means for trophic state prediction.

Due to an aggregate of internal processes, including chemical and biological transformations and transfer to and from the sediments, phosphorus in lakes must be treated as a 'non-conservative' substance. The method by which this effective loss of phosphorus is accounted for is commonly the discriminator among reported models. For example, simple mass balance models treat the internal loss either as a first-order reaction occurring throughout the lake (8) or as a sedimentation process across the sediment-water interface only (1, 2, 12). More complex models (e.g., Water Resources Engineers (13)) consider the incorporation of phosphorus into biomass by algae and its subsequent transfer to
zooplankton and fish. The return of phosphorus to the water through respiration and the decay of organic material is also considered. In every modeling effort, however, one or more rate coefficients must be determined. The number of required coefficients generally increases with model complexity, and thus an increase in detail does not always imply an increase in reliability.

Two recent variations in models of phosphorus in lakes are of particular importance to the present investigation. The first is that of Dillon, who is able to eliminate all kinetic processes from his model by defining a loss term of the form $RL_aA$, where $R$ is simply the fraction of incoming phosphorus, $L_aA$ (g/yr), that is lost by the aggregate of internal processes. The resulting expression for the steady-state concentration of total phosphorus, $[P_{TOT}]$, is simply:

$$[P_{TOT}] = \frac{L_a \tau (1 - R)}{Z}$$  \[3.1\]

where $L_a$ is the average rate of phosphorus loading per unit lake surface area (g/m$^2$-yr), $\tau$ is the hydraulic residence time (yr), and $Z$ is the mean lake depth (m). The use of a measured retention coefficient is obviously a reliable method of accounting for phosphorus losses under current loading conditions. However, because the complex relationships between the rates of chemical and biological processes and the available phosphorus supply are generally nonlinear, the retention coefficient is modified by variations in the loading rate. A critical shortcoming in using Dillon's model for predictive purposes is thus an inherent uncertainty when measured retention coefficients are applied to the study of future loading effects.
Under the premise that the reported trophic state of most lakes reflects the 10 and 20 µg/l criteria, Eq. [3.1] should provide an excellent trophic state model when the retention coefficient is estimated for the corresponding phosphorus loadings. As such, the model of Dillon represents a convenient standard to which other models that predict trophic state according to the same criteria can be compared.

A series of models attributable to Imboden (1), Snodgrass and O'Melia (2), and Imboden and Gächter (3) attempts to independently incorporate all principal exchange and removal mechanisms of phosphorus in as elementary a manner as possible. The conceptualization of Imboden's original model is reproduced in Figure 3-1. Two compartments, soluble orthophosphate [OP] and particulate phosphorus [PP], represent all phosphorus species. Two six-month seasons are considered. During the summer stratification, a lake is represented by two well-mixed boxes that are assumed to correspond to the epilimnion and hypolimnion. A single completely-mixed box is assumed to describe the lake system during the winter period, although the euphotic zone may not extend throughout the entire lake depth.

For present purposes, only the winter circulation period is of interest. Table III-1 summarizes the mathematical description of the winter season. The conservation of mass for each phosphorus compartment is described by a linear differential equation. As reported in the original papers, four similar but generally more complex expressions can be derived for the summer stratification period. Note that each term corresponding to an exchange between the two phosphorus compartments can be interpreted as an expression of a simple first-order chemical reaction.

Snodgrass and O'Melia's primary contribution to the Imboden model is the assignment of a depth dependence to both the mixing coefficient
across the thermocline during the stratified season (K) and the effective sedimentation rate of the particulate phosphorus (g). The first modification is based on empirical evidence and has the form $K = 0.00079Z^{1.118}$, while flocculation principles are used to derive a settling rate of the form $g = 0.05(1 + 0.05Z^*)$, where $Z^*$ is the thickness of the hypolimnion in the summer and the difference of the mean depth and euphotic depth in the winter. These depth-dependent processes were thought to be necessary because the model, as formulated by Imboden, predicted that deep lakes will have higher phosphorus concentrations in their euphotic zones than shallow lakes. Such predictions disagree with observations (4,5,6), and the need for some mechanism to increase phosphorus losses in deeper lakes was suggested.

Imboden and Gächter provide a more detailed description of phosphorus in a lake system. First, the concentrations of soluble orthophosphate and particulate phosphorus are described by continuous functions of depth and time. Second, the photosynthetic uptake of phosphorus by algae is no longer limited to a linear expression. Rather, primary production is described by an equation of the Michaelis-Menten type as a function of phosphorus in the algal mass [PP], nutrient concentration [OP], and light intensity. An additional change involves the introduction of two optional terms into the mass balance expressions. The first represents the potential reflux of phosphorus from the sediments, while the other accounts for an irreversible conversion of soluble orthophosphate to the particulate form (e.g., due to chemical precipitation).

The basic notion of the Imboden type model, to incorporate all critical processes with a minimum of complexity, makes it a valuable asset to
subsequent modeling efforts. That is, the user can easily discern the contribution of each term, the modifications that will produce a desired response (recall Snodgrass and O'Melia's revisions), and the relative sensitivity of the results to the various rate coefficients (14).

The adjustment of rate coefficients until a good reproduction of the phosphorus regime for a given lake is secured can indicate the critical processes for that lake. For the model to achieve widespread applicability, however, basic trends satisfied by a large number of lakes must be identified and incorporated into the model. Such was the motivation for an extensive study of published data for 128 phosphorus limited lakes (7). A basic parameter used in the study was the concentration of phosphorus in the inflow, $L_{\alpha}T/Z$, which in the absence of internal losses would be the 'conservative' steady-state concentration of total phosphorus in the lake. By isolating this term, it was possible to decide whether the effect of various morphological parameters (hydraulic residence time, mean depth, surface area) on the inlake concentration of phosphorus is simply that which appears in the 'conservative' term, or if an effect of the various parameters on the non-conservative behavior of phosphorus must be invoked to explain the data. The empirical analysis consisted of two parts. First, the data were plotted onto the loading diagrams of Vollenweider (6, 8) and Dillon (9), and the resulting prediction reliability was compared to that of a second procedure in which the regions defining each trophic level were simple intervals on a one-dimensional axis corresponding to a pertinent combination of the respective parameters. The second procedure was the application of the multivariate statistical technique of stepwise discriminant analysis to the data. A detailed
description of the data, analytical techniques, and results is found in Yeasted and Morel (7).

Among the morphological parameters considered, the residence time alone was found to be statistically significant in describing the non-conservative behavior of phosphorus. Though the empirical approach and data limitations prohibited the identification of a causal relationship, the statistical significance of the finding necessitates its consideration in subsequent models of phosphorus in lakes.

3.3 Model Formulation

The trophic state criteria discussed earlier most appropriately refers to spring concentrations of total phosphorus of 10 and 20 µg/l. A suitable indicator of trophic state according to the Imboden model is therefore the resultant concentration of total phosphorus at the end of the winter circulation period. As formulated, the model yields a repetitive annual cycle of phosphorus in a lake rather than a time-invariant solution. This assumes a constant inflow of water and phosphorus. However, a typical cycle for Lake Ontario reported in Figure 2 of Snodgrass and O'Melia (2) indicates that the variation in total phosphorus concentration with time becomes negligible as the winter period progresses. If this is true for a lake with a relatively long residence time (7.9 years for Lake Ontario), then it is reasonable to assume that most lakes approach steady-state before the onset of stratification according to the Imboden model. For this reason and for the resulting analytical simplifications, the model now being proposed assumes that the spring concentration of total phosphorus can be satisfactorily represented by the
steady-state solution of the equations presented in Table III-1.

Setting the left-hand side of each equation equal to zero and solving for [OP] and [PP], the concentration of total phosphorus at the beginning of spring stratification is expressed as:

$$[P_{TOT}] = [OP] + [PP] \quad [3.2]$$

where

$$[OP] = \frac{L_a T}{365Z} \{f(1+rT+gT/Z) + (1-f)rT \}$$

$$[PP] = \frac{L_a T}{365Z} \{p_{eu}(Z_{eu}/Z) + (1-f)[p_{eu}(Z_{eu}/Z)+R'] \}$$

All parameters are defined in Table III-1, with the hydraulic residence time, $T$, given in years. The solution neglects the sediment reflux term since the present data base is not sufficient for its evaluation.

Recalling that $L_a T/Z$ is the steady-state concentration of a conservative substance in a lake, the expressions given in brackets in Eqs. [3.3] and [3.4] describe the non-conservative behavior of phosphorus under an inflow concentration of $L_a T/Z$. The empirical study summarized earlier gave evidence that these expressions should be functions only of the hydraulic residence time among the morphological parameters. This is satisfied with two exceptions, for both the photosynthetic production term $(p_{eu} T Z_{eu}/Z)$ and the particulate settling term $(gT/Z)$ include the mean lake depth. The next section discusses how the depth dependency can be eliminated from the settling term. On the other hand, the production term is left unchanged in the proposed model. The first reason for this decision is that the nature of the data base used in the empirical investigation
is such that the statistical findings are not in fact being contradicted. To a large extent, the data reflect lake conditions between late spring and early fall (i.e., during the stratified season). According to the Imboden model for the period of stratification, the epilimnion and zone of production are assumed to be identical. In each mass balance equation for the epilimnion, the ratio corresponding to $Z_{eu}/Z$ is $Z_{eu}/Z_{epi}$ and equals unity. The results of the statistical analysis would therefore not be expected to disclose a depth dependency due to photosynthesis. A second reason for retaining the mean depth in the production term is simply that its exclusion cannot be adequately supported. Light limitation obviously prohibits the assumption of identical euphotic and mean depths for all lakes. The only way to eliminate mean depth is then to assume a linear relationship between $Z_{eu}$ and $Z$, and there is no physical basis for such a premise. It should be noted that the appearance of mean depth is limited to lakes in which the assumed thickness of the euphotic zone ($=10$ m) is less than the mean depth. In all other cases, the two are set equal and their ratio becomes unity.

3.3.1 The Settling Rate of Particulate Phosphorus

Snodgrass and O'Melia have determined that the settling rate of particulate phosphorus ranked only behind the input loading rate as the most important parameter affecting total phosphorus concentrations in lakes (14). Among the various exchange or loss parameters, it is therefore most critical for the term $g_t/Z$ to satisfy the findings of the empirical study. To do so, the mean depth must be eliminated from the expression. One way for this to be achieved is to assume that the ratio $g/Z$ tends
to a scalar. The relationship derived by Snodgrass and O'Melia using flocculation arguments, \( g = 0.05[1 + 0.05(Z-Z_{eu})] \), provides initial support for this assumption. The influence of mean depth can also be neglected if the sedimentation process is better represented by a first-order reaction rather than by a settling term. This is discussed later.

No matter which interpretation is adopted, the end result is a settling term of the form \( C \tau \), where \( C \) is independent of all morphological parameters. A second conclusion drawn from the stepwise discriminant analysis indicates, however, that this simple expression may not provide the most effective description of the relationship between phosphorus retention and the hydraulic residence time. The first canonical variable for the case in which \( L_a, \tau, \) and \( Z \) are the primary parameters is

\[
CV(1) = 2.98 \log(L_a/\tau) - \log(\tau^{0.37}) + 1.07 \tag{3.5}
\]

This canonical variable accounts for over 98 per cent of the variance of the multi-dimensional data base, and thus it represents a reliable one-dimensional discriminator of lake trophic state. In effect, the term \( \log(\tau^{0.37}) \) describes the non-conservative behavior of phosphorus.

If particulate settling is indeed the dominant removal mechanism, the overall statistical results indicate that an appropriate representation would be \( g\tau/Z = A\tau^B \), where \( A \) and \( B \) are constants. To investigate the validity of such a relationship, the settling rate, \( g \), necessary to reproduce the measured spring concentration of total phosphorus for each of twenty lakes was determined according to Eqs. [3.2] - [3.4]. The lake data and model coefficients are those reported by Snodgrass and O'Melia (2,14), as listed in Tables III-2 and III-3. The resulting value of \( g \) for each lake was normalized by the mean depth and plotted against the
hydraulic residence time (Figure 3-2). A relationship of the form

\[
\frac{\tau}{Z} = 0.0066\tau^{0.72}
\]  

[3.6]
is shown to reasonably describe the results. The fit is especially convincing when one considers the extensive range of the data:

\[
\tau = 0.05-700.\text{ yr}, Z = 7.-300.\text{ m}, \text{ and } [P_{TOT}] = 2.5-60.\mu g/l.
\]

Many of the European lakes are observed to require settling velocities considerably less than that determined by Eq. [3.6]. The reason is that the contribution of particulate phosphorus from river inflow is negligible relative to the indigenous bioparticles (15). During the winter season, the concentration of biological particulates remains small due to a lack of production, and very little retention of phosphorus is observed. For example, Lake Zurich has an inflow concentration of 39.7 \( \mu g/l \) and a measured spring concentration of 32 \( \mu g/l \). The parameter values assumed in the model result in an overestimation of the amount of particulate phosphorus, which must be counterbalanced by a low settling rate if the measured retention is to be reproduced.

The inconsistency of units in Eq. [3.6] is a result of the empirical nature of its derivation. One possible resolution is to impose units onto the constant coefficient. What is more essential is to realize that the constant 0.0066 corresponds to g in m/day, \( \tau \) in yr, and Z in m. That is, Eq. [3.6] can be directly substituted into Eqs. [3.3] and [3.4] in order to complete the formulation of the proposed model.
3.4 Model Results

Figure 3-3 compares the measured spring concentration of total phosphorus and that computed by the model for the twenty lakes summarized in Table III-2. The model parameters listed in Table III-3 are assumed to apply to all lakes. The fit is very satisfactory, and is in fact comparable to that generated by the more complex, dynamic model of Snodgrass and O'Melia (2,14). Of special note is that Snodgrass and O'Melia's predictions for a group of Canadian lakes with characteristically high hydraulic loadings (Lakes 12-20) are consistently too high, in many cases by more than 25 per cent. The present model provides a more acceptable distribution about the line $[P_{TOT}]_{\text{meas}} = [P_{TOT}]_{\text{pred}}$. The predicted concentrations for the European lakes are generally too low, which reflects the problem of the settling rate described earlier.

A good reproduction of observed phosphorus concentrations for the group of twenty lakes does not provide adequate verification of the model, however, since these same lakes were used for model calibration. A similar testing of the model for an independent set of lakes is prohibited due to a lack of reliable measurements of average spring phosphorus concentrations. A less exact test of model reliability consistent with available data is therefore implemented, this being the capacity of the model to classify a lake in the proper trophic state. The criterion is simply to compare the predicted spring concentration of total phosphorus with the recommended values of 10 and 20 μg/l.

A graphical procedure is implemented to expedite the testing procedure. When the mean depth is less than the assumed thickness of the euphotic zone, it is eliminated from the production term and the
concentration of total phosphorus becomes a function of only two variables: the average inflow concentration, Laτ/Z, and the hydraulic residence time, τ. Under such conditions, a constant value of [P_TOT] defines a curve in the Laτ/Z versus τ plane. The solid lines in Figure 3-4 are the curves for total concentrations of 10 and 20 μg/l. As indicated in the figure, the trophic state of a lake is classified by its position relative to these demarcation lines. Also plotted in Figure 3-4 are data from the lakes used in the previously referenced statistical study. Each lake with a mean depth less than Z_{eu} = 15 m and not used for model calibration (Table III-2) is included. Although the assumed maximum euphotic zone thickness of 15 m is somewhat high, it has been selected so as to increase the number of lakes eligible for the two-dimensional scheme.

The same data are plotted onto Dillon's diagram in Figure 3-5. In both diagrams, the number of correct predictions can be significantly improved by extending the boundaries of the 'mesotrophic' region. The dashed lines correspond to total phosphorus concentrations of 7 and 30 μg/l and represent a 'best fit' to the present set of data.

A comparison of Figures 3-4 and 3-5 reveals that the two models provide relatively the same prediction reliability. Whereas three mesotrophic lakes correctly positioned by Dillon's model are observed to be situated slightly below the demarcation line in the proposed model, the latter more consistently positions oligotrophic lakes in or near the correct zone. Both models are able to describe the capacity of a lake to assimilate higher phosphorus loadings as the abscissa value increases. In the Dillon model, this is primarily a consequence of the choice of axes. According to Eq. [3.1], lake conditions are obviously going to
improve with increasing $Z$ for a constant value of $L_a \tau (1-R)$. On the other hand, the direct effects of morphological parameters on the inflow concentration of phosphorus are already incorporated into the ordinate axis of the proposed model. The tendency of a lake to assume higher inflow concentrations as the residence time increases, as exemplified by the data and effectively described by the model, is totally due to internal mechanisms of phosphorus exchange and removal.

The construction of a generalized form of Figure 3-4 requires the inclusion of mean lake depth as a third dimension. Figure 3-6 presents such a critical phosphorus loading diagram for the parameters listed in Table III-3. As expected, the response of a lake is shown to be independent of mean depth for all values of $L_a \tau /Z$ and $\tau$ when $Z$ is less than $Z_{eu}$. Two additional observations regarding the effect of mean depth can be made. When the residence time of a lake is small, the 'flushing' effect negates any influence of mean depth even for very deep lakes. As the residence time increases, however, the inlake concentration of total phosphorus is observed to increase with increasing mean depth for a given concentration of phosphorus in the inflow. This results from the relative contributions of production and respiration, for the former is limited to a euphotic zone of constant thickness while the latter is assumed to occur throughout the lake. Mathematically, Eqs. [3.3] and [3.4] show that an increasing mean depth decreases the importance of $p_{eu} \tau (Z_{eu} /Z)$ relative to the respiration term $r \tau$. The end effect is that more phosphorus is retained in solution rather than being removed to the sediments.

This finding appears to contradict the early observations of Rawson (4) and Sakamoto (5), that deep lakes are capable of assimilating higher
phosphorus loadings than shallow lakes. The model, however, achieves a very satisfactory 83 per cent prediction reliability for the trophic state of 30 lakes if the 7 and 30 µg/l criteria are used. These lakes (12 eutrophic, 12 mesotrophic, and 6 oligotrophic) have a mean depth greater than 15 meters and exclude those used to establish Eq. [3.6]. What must be realized is that the conclusions of Rawson and Sakamoto are based on areal phosphorus loadings rather than inflow concentrations. The presence of Z in the denominator of the inflow concentration term is undoubtedly the principal source of their observations, and no subsequent effects of mean depth for comparison with the present model can be inferred.

3.5 Discussion of Results

Because the term describing the potential reflux of phosphorus from the sediments has been neglected in Eqs. [3.3] and [3.4], the model should be limited to lakes that maintain oxic conditions throughout the period of interest. The twenty lakes reported by Snodgrass and O'Melia generally satisfy this condition. The same statement cannot be made regarding the lakes plotted in Figure 3-4 due to the unavailability of sufficient data. It is therefore interesting that the trophic state of these lakes is satisfactorily predicted by the model. A reasonable explanation for this is that phosphorus reflux under anoxic conditions is primarily limited to the summer stratification period, when large density gradients inhibit the vertical transfer of oxygen to the extent that its hypolimnion demand due to biological respiration exceeds its regeneration rate from the epilimnion. The extent to which phosphorus regenerated from the sediments during the stratification period affects winter lake conditions is
largely dependent on the hydraulic residence time. The reflux of phosphorus into lakes with low residence times will not significantly modify the results of the present model since any returning phosphorus will be flushed out of the lake system before a steady-state condition is approached for the winter period. In lakes with residence times greater than the seasonal time scale of analysis, a 'memory' of the reflux may be important. Even in this case, because any effects of anoxic conditions are reflected in measured data, it is conceivable that the empirical relationship between $\tau$ and net phosphorus loss to some extent accounts for any recirculation of phosphorus.

A second point of concern is the use of constant rate coefficients for all lakes, as was earlier done by Snodgrass and O'Melia. In particular, the production and respiration rates would be expected to vary relative to the location of the water body. However, not only does the imposition of constant coefficients augment the generality of the model, but some justification for their use is provided by the statistical analysis of lake data. In an attempt to evaluate the significance of lake location, the latitude of each lake was included as a parameter along with areal phosphorus loading, mean depth, hydraulic residence time, and surface area in a stepwise discriminant analysis of the data. The contribution of the latitude to the trophic state discrimination scheme was found to be statistically insignificant.

A major premise of the model is that the sedimentation of particulate phosphorus can be adequately described by a function only of the residence time (Eq. [3.6]). While the principal justification for the relationship is empirical, two possible physical explanations can be advanced. An
examination of Eq. [3.6] reveals that the rate of phosphorus loss decreases with increasing residence time ($\propto \tau^{-0.28}$), while the cumulative loss increases ($\propto \tau^{0.72}$). This dependence can be satisfied if the frequency distribution of settling velocities for the particulate phosphorus monotonically decreases. Admittedly, the internal production of the particulate form and the variation from lake to lake prohibit such a general representation, but the overall concept is intriguing and could provide the basis for a worthwhile field investigation.

A second notion is to consider that the percentage of phosphorus reaching the sediments bound in primary organisms is negligible, a result of a low settling rate and consequent reconversion to the soluble form or uptake by higher organisms. Rather, the dominant removal mechanism is taken to be the incorporation of phosphorus into large, rapidly settling particles, whether they be biological or chemical in nature. The empirical finding that hydraulic residence time rather than mean depth describes the sedimentation process is resolved if the settling process can be approximated as an 'instantaneous' loss to the sediments. The potential significance of mean depth to the sedimentation process is due both to the increased opportunity for respiration as the depth increases and the possibility that a settling particle does not reach the sediments before its release through the outlet. Both are rendered meaningless by the instantaneous loss approximation. Such an approximation is valid if the settling velocity is large enough so that the time of settling is small relative to the other characteristic time scales. The probability of finding such a large particle is no doubt very low, and thus the incorporation of phosphorus into the particle and its subsequent loss can
be effectively described as a 'rare event.' The hydraulic residence time consequently takes on added significance. If the 'rare event' description is indeed reasonable, any related field study will be very difficult.

Although a conclusive interpretation of the hydraulic residence time issue has not been established, the statistical significance of the finding cannot be overlooked. In this paper, a model of lake trophic state based on the statistical study is shown to describe an extensive collection of lake data as effectively as two widely-referenced models that embody additional requirements. For example, the spring phosphorus concentrations predicted by the new model are comparable to those determined by the more complex model of Snodgrass and O'Melia. But while the dynamic nature of the latter necessitates the use of a computer, either an analytical or graphical solution technique is pertinent to the proposed model. A more significant justification of the model is its capacity to classify the trophic state of 80 lakes (independent of those used for model calibration) as well as the model of Dillon, without the need of a separate retention term. Only three parameters (phosphorus loading rate, mean depth, and hydraulic residence time) are necessary, the estimation of which is a standard procedure of any engineering study concerning the construction or modification of a reservoir or lake. A measured retention coefficient required in Dillon's model is eliminated, as are the problems associated with its use for existing water bodies subjected to changes in loading or for new impoundments.

Although an assessment of the eventual trophic state of a lake is sufficient for many engineering needs, it clearly does not provide a detailed description of lake water quality. Such a modeling limitation,
however, is consistent with the type of data available for most lakes: average annual loadings of phosphorus and water, concentrations based on a small number of grab samples, a semi-quantitative determination of trophic state, etc. Current verification and use of more dynamic models of phosphorus in lakes remains limited by available data. Considering that a principal advantage of such a model is its capacity to identify short-term fluctuations, then not until an extensive temporal, and possibly spatial, data base becomes available for a number of lakes will appropriate testing be possible.


Figure 3-1

SCHEMATIC OUTLINE OF THE IMBODEN PHOSPHORUS MODEL

(This particular schematization is that presented by Snodgrass and O'Melia (2), with an exception being an additional first-order reaction \( R'[OP] \) during the winter circulation period. The possible inclusion of such a reaction was suggested by Imboden and Gächter (personal communication, 1977).)
HYDRAULIC RESIDENCE TIME VERSUS PARTICULATE SETTLING RATE
NORMALIZED BY MEAN LAKE DEPTH

(The plotted value of the settling rate, \( g \), is that necessary for the model to reproduce the measured spring concentration of total phosphorus for each of twenty lakes tabulated in Table III-2. The linear relationship shown is:

\[
\log\left(\frac{g}{Z}\right) = -0.28 \log(\tau) - 2.18
\]

or:

\[
\frac{g \tau}{Z} = 0.0066 \tau^{0.72}
\]
\[ \log(g/Z) = -0.28 \log(\tau) - 2.18 \]

\[ \frac{g}{Z} = 0.0066 \tau^{0.72} \]
COMPARISON OF MODEL PREDICTIONS WITH OBSERVED PHOSPHORUS CONCENTRATIONS
(Numbered data points correspond to the lakes listed in Table III-2.)
Figure 3-4

AVERAGE INFLOW CONCENTRATION OF TOTAL PHOSPHORUS VERSUS HYDRAULIC RESIDENCE TIME

(Solid lines designate average spring concentrations of total phosphorus of 10 and 20 μg/l, according to the proposed model. The dashed lines correspond to phosphorus concentrations of 7 and 30 μg/l, and represent the 'best' criteria for discriminating among the trophic states of the present set of lakes. All lakes of Appendix II.A with a mean depth less than 15 meters, with the exception of those included in Table III-2, are shown in the diagram.)
Figure 3-5

DILLON'S PARAMETER VERSUS MEAN LAKE DEPTH

(Solid and dashed lines as defined in Figure 3-4, except that they now represent phosphorus concentrations according to the formulation of Dillon (9). The lakes are the same as those plotted in Figure 3-4.)
Figure 3-6

GENERALIZED PHOSPHORUS LOADING DIAGRAM
ACCORDING TO THE PROPOSED MODEL

(Solid lines correspond to spring concentrations of total phosphorus of 10 and 20 μg/L.)
Mass Balances:

1. \( \frac{d[OP]}{dt} = \frac{fL_a}{Z} - \frac{[OP]}{Z} \left( \frac{qs}{Z} \right) - \frac{[OP]}{Z} \left( \frac{peuZeu}{Z} \right) + \frac{[PP]}{Z} r - \frac{[OP]}{Z} R' \)

2. \( \frac{d[PP]}{dt} = (1-f) \frac{L_a}{Z} - \frac{[PP]}{Z} \left( \frac{qs}{Z} \right) + \frac{[OP]}{Z} \left( \frac{peuZeu}{Z} \right) - \frac{[PP]}{Z} r - \frac{[PP]}{Z} \left( \frac{g}{Z} \right) \)

\[ [OP] = \text{concentration of soluble orthophosphate} \]
\[ [PP] = \text{concentration of particulate phosphorus} \]
\[ L_a = \text{areal phosphorus loading} \]
\[ q_s = \text{hydraulic loading} \ (=Z/\tau) \]
\[ Z = \text{mean depth} \]
\[ f = \text{fraction of incoming phosphorus that is soluble orthophosphate} \]
\[ peu = \text{production rate coefficient in euphotic zone} \]
\[ Z_{eu} = \text{mean depth of the euphotic zone} \]
\[ r = \text{decomposition rate coefficient} \]
\[ R' = \text{first-order decay rate} \]
\[ g = \text{sedimentation rate coefficient} \]

**TABLE III-1**

Winter Circulation Model
<table>
<thead>
<tr>
<th>No.</th>
<th>Lake</th>
<th>Z (m)</th>
<th>$\tau$ (yr)</th>
<th>$L_a$ (gm/m²-yr)</th>
<th>$[\overline{P}_{TOT}]_m$ (µg/ℓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aegerisee</td>
<td>49.0</td>
<td>8.75</td>
<td>0.16</td>
<td>7.6</td>
</tr>
<tr>
<td>2</td>
<td>Zurichsee</td>
<td>50.0</td>
<td>1.50</td>
<td>1.32</td>
<td>32.0</td>
</tr>
<tr>
<td>3</td>
<td>Ontario</td>
<td>89.0</td>
<td>7.00</td>
<td>0.68</td>
<td>23.7</td>
</tr>
<tr>
<td>4</td>
<td>Turlersee</td>
<td>14.0</td>
<td>2.15</td>
<td>0.30</td>
<td>14.5</td>
</tr>
<tr>
<td>5</td>
<td>Bodensee</td>
<td>100.</td>
<td>4.00</td>
<td>1.44</td>
<td>35.0</td>
</tr>
<tr>
<td>6</td>
<td>Sempachersee</td>
<td>46.0</td>
<td>17.0</td>
<td>0.77</td>
<td>35.5</td>
</tr>
<tr>
<td>7</td>
<td>Tahoe</td>
<td>303.</td>
<td>700.</td>
<td>0.04</td>
<td>2.5</td>
</tr>
<tr>
<td>8</td>
<td>Skaha</td>
<td>26.0</td>
<td>1.20</td>
<td>2.20</td>
<td>60.0</td>
</tr>
<tr>
<td>9</td>
<td>Michigan</td>
<td>84.</td>
<td>31.1</td>
<td>0.115</td>
<td>6.1</td>
</tr>
<tr>
<td>10</td>
<td>Huron</td>
<td>59.</td>
<td>49.2</td>
<td>0.07</td>
<td>4.3</td>
</tr>
<tr>
<td>11</td>
<td>Superior</td>
<td>148.</td>
<td>190.</td>
<td>0.05</td>
<td>3.1</td>
</tr>
<tr>
<td>12</td>
<td>Cameron</td>
<td>7.1</td>
<td>0.072</td>
<td>2.20</td>
<td>11.6</td>
</tr>
<tr>
<td>13</td>
<td>Four Mile</td>
<td>9.3</td>
<td>3.88</td>
<td>0.11</td>
<td>8.0</td>
</tr>
<tr>
<td>14</td>
<td>Bob</td>
<td>18.0</td>
<td>2.69</td>
<td>0.16</td>
<td>7.3</td>
</tr>
<tr>
<td>15</td>
<td>Twelve-Mile</td>
<td>18.1</td>
<td>0.42</td>
<td>0.35</td>
<td>5.4</td>
</tr>
<tr>
<td>16</td>
<td>Halls</td>
<td>27.2</td>
<td>1.05</td>
<td>0.22</td>
<td>3.9</td>
</tr>
<tr>
<td>17</td>
<td>Beech</td>
<td>9.8</td>
<td>0.045</td>
<td>1.68</td>
<td>7.0</td>
</tr>
<tr>
<td>18</td>
<td>Maple</td>
<td>11.6</td>
<td>0.13</td>
<td>0.86</td>
<td>7.2</td>
</tr>
<tr>
<td>19</td>
<td>Eagle-Moose</td>
<td>12.8</td>
<td>0.49</td>
<td>0.23</td>
<td>5.8</td>
</tr>
<tr>
<td>20</td>
<td>Oblung-Haliburton</td>
<td>17.7</td>
<td>2.64</td>
<td>0.13</td>
<td>6.0</td>
</tr>
</tbody>
</table>

**TABLE III-2**

Morphometric and Phosphorus Data

For Lakes Shown in Figures 3-2 and 3-3
\[ f = 0.4 \quad ^a \]
\[ p_{eu} = 0.06 \text{ day}^{-1} \]
\[ Z_{eu} = 10 \text{ m} \]
\[ r = 0.03 \text{ day}^{-1} \]
\[ R' = 0.00009 \text{ day}^{-1} \quad ^b \]
\[ g = F(Z, \tau) \quad ^c \]

\(^{a}\) Average value of all lakes in N.E.S. (10)

\(^{b}\) One-fourth of average value recommended by Vollenweider (8), since it is no longer the only removal mechanism.

\(^{c}\) See Eq. [3.6].

**TABLE III-3**

Model Coefficients (from Snodgrass and O'Melia (2))
4.1 Introduction

In an earlier chapter, a somewhat novel approach to modeling the cyclic distribution of phosphorus in lakes, formulated by Imboden (1) and refined by Snodgrass and O'Melia (2), is described. The Snodgrass and O'Melia model has been referenced in various other sections of this research, primarily as a result of two imposed depth-dependent processes and their relationship to subsequent analyses. These processes, required for the reproduction of observed trends, include a settling velocity of particulate phosphorus of the form \( g = g_0 (1 + CZ) \) and a thermocline mixing coefficient \( K = AZ^b \), where \( Z \) is the mean lake depth. The former process and its relationship to the empirical results of Chapter 2 have been carried over to a proposed steady-state version of a modified Snodgrass and O'Melia model in Chapter 3. The depth-dependent mixing coefficient does not enter into the time-invariant model, however, due to the assumption of complete circulation during the time period of analysis (i.e., the winter months). It is now addressed in this chapter.

Vertical transport in the thermocline region of lakes significantly influences the distribution of phosphorus in large water bodies by allowing orthophosphate, generated by the respiration of algal mass in the hypolimnion, to become available to the highly productive epilimnetic zone. A basic cycle is then completed by the subsequent settling of the produced biota through the stratified region.
The two-box lake model of Snodgrass and O'Melia is formulated under the premise that the thermocline, due to its large density gradient, acts as an inhibitor to the vertical transport of passive substances. Any exchange of phosphorus that does occur across the thermocline 'barrier' due to an aggregation of physical processes (except gravitational settling) is accounted for by a simple Fickian equation. Among such processes are molecular and turbulent diffusion, advection, and internal waves. Also necessarily incorporated into the Fickian term by the assumption of a fixed thermocline location is any mixing due to the downward migration of the thermocline itself. The effective transfer of hypolimnic water resulting from an average seasonal migration on the order of 10 meters is obviously a dominant transport mechanism, especially for large, deep lakes with little vertical advection. The highly empirical nature of the rate coefficient of the Fickian equation in the Snodgrass and O'Melia model is therefore not surprising.

In Section 4.2, Snodgrass and O'Melia's basic formulation of a depth-dependent mixing coefficient is critically evaluated. Their use of a two-box, fixed thermocline schematization introduces peculiarities to the mixing processes being accounted for by the Fickian coefficient, and as such a theoretical investigation is infeasible. The study therefore focuses on the data base used to establish a relationship between thermocline mixing and mean lake depth. In particular, the original field studies are shown to have used a variety of techniques which effectively measure different mixing phenomena.

To represent a lake as a simplified system for phosphorus studies is consistent with the limited knowledge of the principles and mechanisms
governing phosphorus dynamics. However, by extending this simplification to the physical (i.e., transport) processes by limiting themselves to a fixed thermocline location and the Fickian approach, Snodgress and O'Melia have introduced unnecessary limitations to their model. Recently (in fact, since the completion of the analysis for this chapter), an improved version of the model has been reported by Imboden and Gächter (3). Although the basic phosphorus dynamics remain essentially unchanged, the revised model uses a time-varying thermocline location. Although the Fickian expression is still used with a 'fitted' or measured rate coefficient, it no longer has to account for the exchange of matter resulting from thermocline movement. That is, any error in estimating the mixing coefficient is much less significant than in the Snodgrass and O'Melia model.

Considering even the improvements introduced by Imboden and Gächter, the progression of such phosphorus models continues to overlook the present knowledge and consequent modeling capacity of the hydrodynamic behavior of lakes. The application of these latter principles to temperature modeling has resulted in an excellent reproduction of the thermal regime of many lakes, and it therefore seems appropriate to interface a detailed lake temperature model with a form of the Imboden-Gächter model. The advantage of such an interfacing is twofold. First, the position of the thermocline can be extracted from the temperature model at each time scale of analysis (the Imboden-Gächter model presently requires measured thermocline locations as input). Second, the residual mixing due to various physical processes can be more effectively evaluated since the Fickian coefficient no longer has to account for either thermocline movement or advection, which are separately evaluated.
This chapter utilizes the lake temperature model developed at M.I.T (4,5), including the wind-mixing algorithm of Octavio, et al. (6), to demonstrate mixing across the boundary of a two-box model. Routines necessary for this application of the lake model are described. In a later section of the chapter, the depth dependency of the thermocline mixing coefficient attributable to Snodgrass and O'Melia is examined in light of results from the temperature model.

4.2 A Critical Look at a Depth-Dependent Mixing Coefficient

Figure 4-1 reproduces Snodgrass and O'Melia's proposed linear relationship between the logarithm of mean depth and that of the vertical exchange coefficient. A primary objective of this chapter is to investigate this relationship using modeling principles associated with the hydrodynamic and temperature regimes of lakes. Prior to this, however, a review of some theoretical and empirical aspects of the issue is in order.

As demonstrated by many investigators (7,8,9), the intensity of turbulent mixing in a stratified fluid is a local phenomenon. The governing parameter is the Richardson number, a dimensionless grouping of variables that expresses the balance between the stabilizing force of the density gradient and the disturbing force of a shear flow. A common form of the Richardson number is:

\[ R_i = \frac{(g/p)(\partial p/\partial z)}{(\partial u/\partial z)^2} \]  

[4.1]

where the differential terms are the local density and velocity gradients.

A first approach to support or reject the Snodgrass and O'Melia relationship between mean depth and mixing appears to be the demonstration or
denunciation of a dependence of the Richardson number on mean depth. However, the basic formulation of a two-box lake model invalidates any such investigation. The use of two discrete, well-mixed boxes implies the need to account for any transport of matter across the thermocline 'barrier' due to a change in its vertical location. In many cases this transfer mechanism is dominant. The Snodgrass and O'Melia formulation of a fixed thermocline location further requires that a single mixing coefficient defining the Fickian equation must additionally account for any mixing due to thermocline migration. It is this coefficient that is presently being examined, and the incompatibility of the turbulent vertical exchange which it represents and that implied by the Richardson number is obvious.

The same basic fallacy is valid when attempts are made to relate field data to the Snodgrass and O'Melia coefficient. The linear trend of the data presented in Figure 4-1 cannot be challenged, but the credibility of an empirical justification for the relationship is dubious. Not only does the need to include thermocline movement generally nullify its use, but an investigation of the original data sources suggests that the coefficients are defined differently in each case. To include coefficients which in fact measure different phenomena on a single plot is to some extent meaningless. A brief review of several of the original investigations will support this claim.

4.2.1 Empirical Considerations: A Review of the Data Sources

The field studies summarized in Figure 4-1 entail a wide range of lakes, mixing mechanisms, and computational procedures. Not all of the original studies were available for review, but the following are
representative of the problems and inconsistencies involved.

Powell and Jassby (10) employed temperature data to estimate the depthwise variation of the mixing coefficient in two ways: McEwen's method and the flux gradient method. What is critical for this study is that the measurements were made only in the clinolimnion, a region below the thermocline in which the water temperature T at depth Z has the property that both the T versus Z and $\partial T/\partial Z$ versus Z curves are exponential with identical rates of falloff. Snodgrass and O'Melia equated the mixing coefficient across the thermocline to the minimum computed value, even though the field of study did not effectively include the entire thermocline region.

Sweers (11) introduced and then argued against the use of a conventional heat transport equation to estimate mixing coefficients because of its neglect of the net advective heat transport term. Rather, a coordinate system fixed with respect to the thermocline was used by Sweers to express the mixing coefficient as a function of the rate of movement of the thermocline. Mixing values for Lake Ontario were computed using each method. The results differ by approximately a factor of two. Reasoning that values calculated for a fixed thermocline would be consistent with their plotted data, Snodgrass and O'Melia chose values from the former method. By doing so they have disregarded the conclusion of the investigator (Sweers).

A heat balance equation was applied by Li (12) to study the vertical variation of the eddy diffusion coefficient. However, in order to smooth out random factors, the temperature measurements were averaged over several years. An important consequence is that significant mixing processes applicable to Snodgrass and O'Melia's mixing coefficient might also have
been smoothed out.

Hesslein and Quay (13) compared the vertical eddy diffusion coefficients resulting from three different measurement techniques: the temperature method of McEwen, a dye method, and a method using radon gas. The values of the three coefficients varied by almost one order of magnitude. The primary causes of this discrepancy were the different time scales of averaging and the possible inhibition of mixing processes due to the use of a device called a limnocorral in the latter two methods. Snodgrass and O'Melia selected the value from the McEwen method.

It is noteworthy that each of the cited studies employ temperature data to estimate the vertical mixing coefficient. The inaccuracies inherent in such studies weakens any empirical analysis of the results. Of primary concern are the various time scales of averaging the data, since the effects of larger-scale mixing processes are reflected in the coefficients as the averaging time increases. Another problem is that heat transfer processes other than those of interest are difficult to eliminate from the data. For example, a common criticism of models that use a heat balance for the determination of mixing coefficients is that the direct contribution of solar heating is often ignored. This heat source can be significant for shallow thermoclines and as such the computed exchange coefficient is often overestimated. The heat exchange coefficient for Lake Tahoe (which is used by Snodgrass and O'Melia) is among those that have been challenged for this reason. Whether such a consideration would modify the empirical findings reported by Snodgrass and O'Melia cannot be inferred.

These qualifications of the data sources provide a basis for rejecting
Snodgrass and O'Melia's empirical evidence for a depth-dependent mixing coefficient. Whether the mixing coefficient is indeed a function of mean lake depth has not been resolved. The MIT lake temperature model, including a thermocline mixing algorithm developed in this research, is now utilized to address this question.

4.3 Use of a Modified MIT Temperature Model to Test For a Depth-Dependent Mixing in Lakes and Reservoirs

The mixing of epilimnetic and hypolimnetic waters has numerous sources. In reservoirs, the dominant mechanism for the vertical transport of heat and matter is advection. By treating in detail the distribution of the inflow and outflow about the points of entry and discharge, the MIT lake temperature model is able to simulate advection quite satisfactorily. Good agreement between measured and predicted temperature profiles has been attained for several reservoirs. In lakes, the dominant transport mechanism is diffusion. Sensitivity studies by Harleman and Hurley (14) indicate that the predicted temperature profiles are very sensitive to the vertical eddy diffusivity, and yet no satisfactory representation of this parameter is available. The most recent version of the MIT model is able to eliminate much of the arbitrariness of the vertical eddy diffusivity, however, by incorporating wind-mixing concepts. Prior to this, the diffusivity coefficient was fitted by a value on the order of 50-100 times the molecular rate. The wind-mixing model retains molecular diffusivity for computational purposes.

Of present concern is the total mixing across a time-varying thermocline in a two-box lake (or reservoir) model. The MIT model is capable
of explicitly treating the physical transport of water due to molecular diffusion and advection. Molecular diffusion is input as a constant value, while advection is available at each time step as a vertical velocity term. The latter is computed by satisfying the continuity equation for each element. Any mass transfer across the thermocline as a consequence of wind mixing is not directly extractable from the model. Rather, wind effects that significantly modify the lakewide temperature structure are accounted for in the routine that evaluates vertical mixing resulting from changes in thermocline location. Mixing due to the migration of the thermocline is required only because the epilimnion is assumed to be a well-mixed discrete system, and any downward movement of the 'boundary' between the epilimnion and hypolimnion results in the transfer of matter from the lower zone to the discrete upper system. Figure 4-2 illustrates this mixing mechanism.

It is noteworthy that the MIT temperature model, being one-dimensional, is best suited to deep lakes and reservoirs that exhibit a stable horizontal thermocline throughout the stratified season. This is not a limitation for the present study, however, since a two-box model is also not appropriate for lakes subject to short-term instabilities due to isolated hydrological events.

4.3.1 An Overview of the Original MIT Temperature Model

The temperature model developed at MIT for lakes and reservoirs is a one-dimensional, time dependent, variable area model. The schematization of the model is shown in Figure 4-3. A horizontal 'slice' of the water body, of thickness $\Delta Z$ and average horizontal area $A(Z)$, is taken
to be the basic control volume. The time-varying heat balance for each internal element is solved by a fundamental heat transport equation of the form:

\[
\frac{dT}{dt} + \frac{1}{A} \frac{\partial}{\partial z}(Q_v T) = \frac{E}{A} \frac{\partial}{\partial z}(A \frac{\partial T}{\partial z}) + \frac{Bu_i T_i}{A} - \frac{Bu_o T}{A} - \frac{1}{\rho c} \frac{\partial \phi_z}{\partial z}
\]  

[4.2]

where \( T \) is the temperature at depth \( z \), \( A \) = area of the element, \( B \) = width of the element, \( u_i \) = horizontal inflow velocity, \( T_i \) = temperature of the inflow, \( u_o \) = horizontal outflow velocity, \( Q_v \) = vertical flow rate, \( \phi_z \) = internal short wave solar radiation flux per unit horizontal area, \( E \) = vertical diffusion coefficient, assumed constant with depth, \( c \) = heat capacity of water, and \( \rho \) = density of water. It is assumed that the heat capacity and density of water are constant. An explicit finite difference scheme is used to solve Equation [4.2] at each time step for each internal element. Modified equations are used for the surface and bottom elements in order to satisfy the respective boundary conditions. A detailed description of the MIT temperature model is found in Ryan and Harleman (4).

In general, the heat flux processes accounted for in the model can be categorized as surface heat transfers and internal heat transfers. Fluxes across the water surface include incident and reflected short wave solar radiation (\( \phi_s, \phi_{sr} \)), incident and reflected long wave atmospheric radiation (\( \phi_a, \phi_{ar} \)), long wave radiation from the water surface (\( \phi_{br} \)), evaporative heat flux (\( \phi_e \)), and sensible heat flux or conduction (\( \phi_c \)). The transfer of heat within the water body is
attributable to the internal absorption of solar radiation, advection resulting from inflows and outflows, wind mixing, convective mixing, and diffusion. Methods by which these heat transfer mechanisms are evaluated and incorporated into the MIT model are found in the above reference.

Horizontal velocities are computed from inflow and outflow rates, assuming Gaussian velocity distributions about the points of entry and discharge. Entrainment can be optionally simulated by mixing the inflowing river water with lake water from the surface elements according to a user-specified ratio. Once the net horizontal velocity into each element is known, the vertical velocity is calculated by satisfying the continuity equation.

A potential fitting parameter of the MIT model is the vertical diffusion coefficient. The early developers of the model attempted to account for all known forms of heat transport (e.g., surface heat fluxes, inflow and outflow velocity distributions) as accurately as possible so as to minimize the significance of the diffusion term. Yet, they still found it necessary to use values orders of magnitude larger than molecular in order to properly simulate lakes in which advection is not dominating. It was not until the model was modified to include wind mixing that a molecular diffusion coefficient was sufficient to obtain agreement between predictions and observations in lakes.

4.3.1.1 The Wind Mixing Algorithm

In order to incorporate the influence of wind mixing into the MIT temperature model, Octavio, et al. (6) propose an iterative numerical approach that sequentially carries out the heating and wind mixing
algorithms in a given time step. The temperature profile in each time step is first determined by incrementing the profile from the previous time step according to Eq. [4.2]. A call to the wind mixing algorithm then defines the depth and temperature of the surface mixed layer resulting from the influx of wind energy. The surface heat flux is recomputed using the mixed layer temperature and then averaged with that computed using the surface temperature of the previous time step. The temperature profile from the previous time step is reincremented based on the revised surface heat flux. The entire procedure is then repeated until the surface heat flux remains the same from one iteration to the next.

Two types of energy change are considered. These include the kinetic energy induced by the wind shear acting on the water surface, and the change in potential energy due to the entrainment of a number of surface elements into a wind-mixed layer. The basic algorithm of the wind mixing routine is to mix progressively deeper elements until an equality is achieved between the wind-induced energy change and that resulting from the mixing process. Additional information is found in Octavio, et al. (6).

Because of the thorough documentation in earlier publications, the original MIT model and the wind mixing scheme have been only briefly summarized. Presented in more detail in the next section is an algorithm of thermocline mixing formulated as part of the present research effort. Once the lake temperature profile at each time step is defined by the aggregate model described in this and the preceding section, the newest algorithm allows the identification of thermocline location and the computation of the net transfer of matter across the thermocline interface.
due to all modeled processes.

4.3.2 An Algorithm for the Computation of Mixing Across the Thermocline in Lakes

The dynamic behavior of the near-surface region of lakes is often much more intense than that of the deeper waters, resulting in a wide diversity of naturally occurring (and modeled) temperature profiles. A conclusively reliable algorithm for identifying the location of the thermocline is thus virtually unattainable. The routine proposed in this section has proven to be reliable for most lakes. Two safeguards found to be necessary are included, while less probable instabilities are easily recognized in the model output and frequently can be readily corrected.

Consider Figure 4-4, which shows a series of discrete elements (as represented in the MIT model) in the neighborhood of the thermocline. By convention, the thermocline is defined as the point at which the temperature gradient is a maximum. The temperature computed by the model for element \( i \) is denoted \( T_i \). The routine first locates the elements across which the temperature change is a maximum. Assume this occurs across elements \( M \) and \( M-1 \). A first approximation would be to simply locate the thermocline at element \( M \), thus implying that the minimum allowable change in thermocline location is \( \Delta Y \). This is not practical for the computation of mixing, however, since \( \Delta Y \) is of the order of a meter and the thermocline is found to remain at one element for several time steps before 'jumping' to the next element. The consequence is a pulse injection of matter across the thermocline every several days (or even weeks). It would be convenient to allow the thermocline to be located at any point within an element, thereby allowing for fractional changes in its location.
The proposed technique is to fit a smooth curve through the known
temperatures in the neighborhood of the thermocline, and then to find the
point of maximum slope. Because of the inflection of the temperature
profile in this region, a suitable representation is a third order Lag-
rangian interpolating polynomial (15). Such a polynomial passes exactly
through the temperature values of four elements (M+1, M, M-1, M-2). The
point at which its second derivative goes to zero defines the thermocline
location, $Y_T$, and has been found to be

$$
Y_T = \frac{(M-1)T_{M+1} - (3M-2)T_M + (3M-1)T_{M-1} - (M)T_{M-2}}{T_{M+1} - 3T_M + 3T_{M-1} - T_{M-2}} \tag{4.3}
$$

Figure 4-5 demonstrates the success of this algorithm.

Two safeguards were found to be necessary when incorporating the al-
gorithm into the MIT model. During periods of high air temperatures and
low wind speeds, extremely high but monotonically decreasing temperature
gradients occur across the first few surface elements. To prevent the
thermocline from being located at the surface under these short-term
conditions, the loop to find element M starts at the uppermost element i
such that the temperature change across elements i and i-1 is greater
than that across elements i+1 and i. On other occasions, an abnormal
temperature profile may erroneously shift the thermocline several ele-
ments only to have it return to near its original position in a few days.
When this occurs, the program sets the thermocline at its position during
the previous time step. A thermocline movement of $DY/2$ meters per time
step is allowed.

Once the exact location of the thermocline is known, the volumes of
the epilimnion and hypolimnion are computed using linear interpolation of the element areas. The mixing due to thermocline movement is simply the rate of change of hypolimnion volume per unit area (average cross-sectional area of the volume being transported). As such, it is treatable as a velocity term.

The modified MIT model is now capable of computing the vertical transport of mass across the thermocline due to molecular diffusion, advection, and thermocline migration. These represent the major transport mechanisms for both lakes and reservoirs.

4.3.2.1 Verification of the Mixing Algorithm

A comparison of field data with results of the mixing algorithm is not a feasible method of model verification. This is due primarily to the different phenomena represented by the respective 'mixing' terms. Recall that the mixing computed by the model represents the cumulative transport of matter across a time-varying thermocline 'barrier' in a two-box lake scheme. On the other hand, field studies often measure mixing across a specified depth, as for example in the measurement of dye migration from a point source. Field studies do not account for mixing due to thermocline movement commensurate with the model.

A first method of substantiating the adequacy of the model is to compare the resultant mixing value with that predicted by the empirical relationship used by Snodgrass and O'Melia in their two-box lake model. Consider Lake Anna, which most closely approximates the type of water body examined by Snodgrass and O'Melia. An application of the modified MIT model to Lake Anna results in an average mixing from the hypolimnion
to the epilimnion of 0.105 m/day, while the average mixing in the opposite direction is 0.012 m/day (see next section, Table IV-2). Using the equation of Snodgrass and O'Melia, the rate coefficient (K) for their Fickian-type expression is 0.096 m²/day. The incompatibility of the dimensions prohibits a direct comparison of the mixing values, but this can be somewhat resolved by normalizing K to the distance (Z') across which the concentration gradient in the Fickian term is calculated (i.e., \( \frac{dC}{dz} = \frac{C_2 - C_1}{Z'} \)). Snodgrass and O'Melia arbitrarily define Z' to be a 5-meter thermocline thickness, in which case K/Z' = 0.019 m/day. A second appropriate choice for Z' is the 1.22 meter thickness of the vertical elements used in the Lake Anna model, with K/Z' = 0.079 m/day. In each case the resulting mixing value is reasonably close to one of the directional values generated by the mixing algorithm.

Recognizing that the computation of thermocline mixing is straightforward once the thermal regime of a lake is known, the critical reliability criterion for the cumulative model is its ability to reproduce observed temperature profiles. A review of the completed applications of the MIT temperature model to a wide variety of lakes and reservoirs is called for. These include Flaming Gorge Reservoir, Fontana Reservoir, Cayuga Lake, and Lake Anna. Table IV-1 summarizes these applications.

Also reported in Table IV-1 is the value of the parameter AE/QD for each water body. This dimensionless quantity, arrived at by Harleman and Hurley (14) by non-dimensionalizing the basic heat transport equation, expresses the relative influence of heat transport by diffusion compared to heat transport by advection. The scaling parameters are A, the horizontal cross-sectional area at the depth of the outlet, E, the vertical
diffusivity, $Q$, the discharge rate, and $D$, the depth at which the outlet is located. When $AE/QD << 1$ advection dominates diffusion, while $AE/QD >> 1$ implies the dominance of diffusion. The transport mechanisms are competitive when $AE/QD$ is close to one. Although the $AE/QD$ values listed in Table IV-1 are approximations, it is evident that advection is the dominant heat transport mechanism for Flaming Gorge and Fontana Reservoirs, while vertical diffusion is of primary importance for Cayuga Lake. The two are competitive transport mechanisms for Lake Anna.

This series of applications thus represents a wide spectrum of lakes and reservoirs. Also represented by the respective investigations are the various versions of the MIT temperature model used to date. The Flaming Gorge and Fontana Reservoirs were best-suited to the 'original' model formulation since the domination of advection allowed the use of a molecular value for the vertical diffusion coefficient. For Lake Cayuga, investigated prior to the introduction of the wind mixing algorithm, a diffusion coefficient approximately 200 times larger than molecular had to be employed in the original model. This was required in order to properly simulate observed temperature changes below the surface elements in the relative absence of advection. Lake Anna represents the most recent approach of utilizing a wind mixing algorithm. A molecular diffusion coefficient is found to be sufficient for such a modeling scheme.

In each of the four cases a good fit between observed and predicted temperature profiles was attained, thus indicating the wide applicability of the MIT model. (It is also noteworthy that the model proved capable of describing the temperature regime of a laboratory reservoir in which
turbulence was generally absent (5). These same applications are used in the next section of this chapter to examine Snodgrass and O'Melia's relationship between mean lake depth and the effective mixing across the thermocline. Because of each model's case-dependent prediction reliability, the actual one used for each original study is retained. An increased confidence in the mixing results consequently follows.

4.3.3 Use of the Thermocline Mixing Algorithm to Test for a Depth-Dependent Mixing in Lakes and Reservoirs

This study is based on the investigations summarized in Table IV-1 for Fontana Reservoir and Lake Anna. Flaming Gorge Reservoir is not considered due to a high degree of similarity between it and Fontana Reservoir, while Cayuga Lake has been eliminated due to the infeasibility of testing for a depth dependent mixing when an externally imposed constant diffusion value (200 times molecular) represents the primary mixing mechanism. In order to retain a water body in which diffusion is dominant, a hypothetical lake that is identical to Fontana Reservoir except that all inflow and outflow rates are reduced by a factor of $10^4$ has been added.

The data base used in the present study is unchanged from the original investigations, with the following exceptions. First, the outlet is arbitrarily located two elements (Fontana Reservoir, 4 meters; Lake Anna, 2.44 meters) below the surface in order to prevent extremely small withdrawal layers. Second, the surface elevation is kept constant with time as a safeguard against its falling below the outlet during periods of low inflow. This in turn requires a third qualification, that the rate of
withdrawal be equated to the inflow rate in order to satisfy the conservation of mass. The use of a near-surface discharge is consistent with a two-box phosphorus model, since a deep outlet would deepen the thermocline to a point where light limitation prohibits the epilimnion from being a uniform zone of production. Further, the lakes used in the Snodgrass and O'Melia study all have surface discharges.

Table IV-2 reports the average directional mixing across the thermocline due to a combination of advection, diffusion, and thermocline migration. In order to correct for units in the vertical diffusion term, a thermocline thickness of 5 meters is assumed. Also listed in Table IV-2 are the values of \( \frac{AE}{QD} \) revised to account for the imposed changes in outlet depth. Note that the dominant transport mechanism for each lake is unchanged from that discussed earlier, and that the hypothetical lake is governed by vertical diffusion. The wind-mixing algorithm with molecular diffusivity is employed for the hypothetical lake.

Three cases are reported for each water body. The first represents field conditions including the various changes just described. For cases 2 and 3, the lake dimensions are symmetrically reduced to simulate progressively shallower lakes. The only other data revised for these latter cases are the inflow and outflow rates, which are reduced in the same ratio as the lake surface area in order to retain equal hydraulic loading rates (i.e., discharge per unit surface area) among the cases. The overall effect is to decrease mean depth (see Table IV-2) while retaining an equivalency of the vertical advection term for each case.

No interrelation between mean depth and thermocline mixing is indi-
cated, a result in direct contrast to the relationship proposed by Snodgrass and O'Melia. For example, Snodgrass and O'Melia would predict that mixing in case 1 for Lake Anna is 1.65 times greater than in case 3. The model computes an equivalent mixing. Small differences in the values reported in Table IV-2 are explainable in terms of the externally imposed period of stratification. If the thermocline is in a period of high transition at the beginning or end of the stratification cycle for one case but fairly stable in the next, the average mixing values are somewhat affected. An attempt has been made to choose the stratification period so as to minimize this discrepancy. The greater variance observed for Fontana Reservoir is due to the dominance of advection. The correction of the inflow and outflow rates results in an equivalence of the advection term only if the mixing is occurring across the same elements in each case (i.e., only if the thermocline is located at the same element at a given time step). This is not always the case. Additionally, small variations in the temperature profile among cases could force the inflow to be centered at different elements. The resulting advection field would consequently be affected.

A consideration of the physical processes governing the MIT model explains the lack of a depth dependence. Under stratified conditions, the only effective transport mechanism in the lower elements of a lake is molecular diffusion across an extremely small temperature gradient. To make a lake deeper or shallower would therefore not affect vertical mixing in the thermocline region. It is conceivable that advection due to a deep outlet or an unusually cold inflow would reach the lake bottom, but even then the positive correlation between mean depth and mixing reported
by Snodgrass and O'Melia would not be expected.

It is also noteworthy that the wind mixing algorithm relates wind speed and surface shear using Wu's (18) wind stress coefficient, which is independent of lake surface area. This suppresses any correlation between the mixing imparted by the wind and lake surface area, and therefore between wind mixing and mean depth that would follow from the high correlation between surface area and mean depth.

4.3.4 Concluding Remarks Regarding the Proposed Mixing Algorithm

The inadequacy of the Snodgrass and O'Melia relationship is particularly evident in the comparative results for Fontana Reservoir and the hypothetical lake (Table IV-2). By design each has the same mean depth, and as such the relationship predicts equal mixing for the water bodies. The contribution from advection for Fontana Reservoir nullifies this equality. The capability of the mixing algorithm in the MIT model to differentiate between mixing in reservoirs dominated by advection and that in lakes with negligible advection is but one of its advantages.

The fact that the mixing algorithm is able to compute directional values is itself an advancement in two-box lake models. Due mostly to the overall downward migration of the thermocline, the mixing of hypolimnetic water into the epilimnion is considerably larger than the mixing in the opposite direction. An obvious restriction in the two-box model of Snodgrass and O'Melia is their use of the same rate coefficient for both directions.

Another advantage of using a temperature model is that the user has
an internal control for determining the endpoints of the stratification season. Assume that the user arbitrarily defines a temperature gradient across which mixing is sufficiently retarded to be representative of a 'barrier' in a two-box scheme. The beginning and end of the stratification season (and thus the applicability of a two-box model) can then be determined by computing the maximum gradient of the known temperature profile at each time step and comparing it to the critical value. In contrast, the Snodgrass and O'Melia model uses an externally fixed thermocline period of 180 days.

Throughout this chapter, the method used by Snodgrass and O'Melia to model mixing across the boundary of their two-box model has been criticized relative to the newly-formulated mixing algorithm. Excluding the repudiation of their assigned depth-dependence, the criticism reduces to the wider applicability of the proposed scheme (an expected result considering its detailed treatment of the physical processes governing heat transport). What must be additionally recognized is that the criticism of Snodgrass and O'Melia's model applies only to their treatment of the pertinent hydrodynamics. Their simple approach to the chemical and biological aspects of phosphorus dynamics is not being judged. In fact, a similar approach has been adopted in the proposed model described in Chapter 3 of this research.
LITERATURE CITED


Figure 4-1

CORRELATION BETWEEN VERTICAL MIXING COEFFICIENT AND MEAN LAKE DEPTH

(From Snodgrass and O'Melia (2). Linear relationship shown is:
\[ K_{th} = 0.00079 \times 1.118 \])
FIGURE 4-1

LOG K_{th} (cm^2/sec) vs LOG Z (meters)
Figure 4-2

VERTICAL MIXING DUE TO THERMOCLINE MIGRATION
IN A TWO-BOX LAKE MODEL

(In time \( \Delta t \), the thermocline drops a distance
\( Z_{tb}(t + \Delta t) - Z_{th}(t) \). The volume of water
transferred from the hypolimnion to the
epilimnion is \( V_H(t + \Delta t) - V_H(t) \). The rate
of mixing due to thermocline migration is
thus \( \frac{V_H(t + \Delta t) - V_H(t)}{A_{ave} \Delta t} \).)
FIGURE 4-2
Figure 4-3

SCHEMATIZATION AND CONTROL VOLUME
FOR THE MIT TEMPERATURE MODEL
(From Octavio, et. al. (6))
CONTROL VOLUME SLICE

SIDE ELEVATION

FIGURE 4-3
Figure 4-4

DISCRETIZED TEMPERATURE PROFILE IN THE NEIGHBORHOOD OF THE THERMOCLINE

(Such a temperature profile represents the output of the MIT temperature model at any given time step for the elements shown.)
NUMBER OF VERTICAL ELEMENT

M+1
M
M-1
M-2

TEMPERATURE (°C)

FIGURE 4-4
Figure 4-5

EXACT THERMOCLINE LOCATION USING EQUATION [4.3]

- Discretized temperature profile
- Third-order Lagrangian polynomial
- Thermocline location (Equation [4.3])
FIGURE 4-5
<table>
<thead>
<tr>
<th>Impoundment</th>
<th>Location</th>
<th>Reference</th>
<th>Vertical Coefficient</th>
<th>AE/QD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fontana Reservoir</td>
<td>North Carolina</td>
<td>Ryan and Harleman (4)</td>
<td>Molecular</td>
<td>0.0007</td>
</tr>
<tr>
<td>Flaming Gorge Reservoir</td>
<td>Utah-Wyoming</td>
<td>Adams (16)</td>
<td>Molecular</td>
<td>0.0002</td>
</tr>
<tr>
<td>Cayuga Lake</td>
<td>New York</td>
<td>Adams, Freudberg, Stolzenbach (17)</td>
<td>~200 x Molecular</td>
<td>20.</td>
</tr>
<tr>
<td>Lake Anna</td>
<td>Virginia</td>
<td>Octavio, et al. (6)</td>
<td>Molecular, with Wind-Mixing Algorithm</td>
<td>0.15</td>
</tr>
</tbody>
</table>

TABLE IV-1

Summary of the Applications of the MIT Temperature Model
<table>
<thead>
<tr>
<th>Water Body</th>
<th>Case</th>
<th>Mean Depth (m)</th>
<th>AE/QD</th>
<th>Average Mixing: Epilimnion to Hypolimnion (m/day)</th>
<th>Average Mixing: Hypolimnion to Epilimnion (m/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fontana Reservoir</td>
<td>1</td>
<td>37.8</td>
<td>0.010</td>
<td>0.320</td>
<td>0.178</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30.2</td>
<td>0.013</td>
<td>0.324</td>
<td>0.120</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>24.2</td>
<td>0.016</td>
<td>0.301</td>
<td>0.125</td>
</tr>
<tr>
<td>Lake Anna</td>
<td>1</td>
<td>10.6</td>
<td>0.12</td>
<td>0.105</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.5</td>
<td>0.15</td>
<td>0.107</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.8</td>
<td>0.19</td>
<td>0.118</td>
<td>0.014</td>
</tr>
<tr>
<td>Hypothetical Lake</td>
<td>1</td>
<td>37.8</td>
<td>100.</td>
<td>0.090</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>30.2</td>
<td>125.</td>
<td>0.086</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>24.2</td>
<td>156.</td>
<td>0.087</td>
<td>0.011</td>
</tr>
</tbody>
</table>

**TABLE IV-2**

Average Directional Mixing, as Computed by the MIT Model: Thermocline Mixing Algorithm.
Chapter 5

A SURFACE COMPLEXATION MODEL FOR ANION ADSORPTION
ONTO METAL OXIDES

5.1 Introduction

The adsorption of anions onto oxide surfaces is of interest to many scientific disciplines. Limnologists involved with nutrient loadings to natural water bodies and the subsequent potential for accelerated eutrophication are concerned with phosphate removal to the sediments due to its adsorption onto colloidal metal oxides. Of similar interest to sanitary engineers is the enhancement of phosphate removal in water treatment processes as a result of its adsorption onto hydrous metal oxides. Soil scientists, on the other hand, are concerned with the retention of the phosphate nutrient by its adsorption onto oxides present in soil systems.

To date, most presentations of experimental data of anion adsorption have taken the form of a Langmuir isotherm for which both the maximum monolayer adsorption density and the energetic Langmuir constant necessarily vary with pH (1,2,3,4). From a physicochemical standpoint, however, the number of potential adsorption sites for a given oxide surface is an intrinsic property of that surface. Basic mass law considerations at the surface therefore require that the maximum adsorption envelope should not be pH-dependent in the limit of anion saturation. As regards the energetic constant, its variation with pH is likewise not amenable to fundamental mass law expressions for chemical systems.

In this paper, a surface complexation model is presented to
describe the adsorption of arsenate and phosphate onto aluminum oxide surfaces. Such a model treats various protonated-deprotonated surface groups as being capable of forming complexes with solution ions. The original conceptualization of the surface complexation model to describe the adsorption of metal ions is attributable primarily to Stumm and Schindler and co-workers (6,7,8). The issue of a pH-dependent maximum adsorption density was not critical in the metal adsorption studies because the available surface was always in large excess relative to the metal in solution. Such is not the case for the experimental studies of anion adsorption now under consideration, for the data imply an eventual saturation of the surface by the solution anions. The surface complexation model allows the use of a maximum adsorption density that is constant for all pH values. All intrinsic stability (energetic) constants are likewise kept constant. The observed pH dependence of anion adsorption is accounted for by the acid-base properties of the surface groups, the acid-base equilibria of the anion in solution, and the number of surface groups reacting with each adsorbate anion. All reactions are assumed to take place at the surface plane itself, and thus the differentiation of adjacent planes of varying potential present in other models is not required.

Although the surface complexation model has been successfully applied to several systems of metal adsorption onto metal oxides (6,7,8), no previous attempt to utilize this modeling approach for anion adsorption has been reported. The present study, while requiring some changes in the original model formulation, provides a good fit of experimental data describing the adsorption of arsenate and phosphate onto aluminum
sclids over a wide range of pH and total anion concentrations. Other
tests of the validity of the model are also presented. The model incor-
porates published data on both the acid-base chemistry of aluminum oxide
surfaces and the necessary corrections resulting from coulombic attrac-
tion or repulsion.

5.2 Background

Experimental data of the adsorption of various anions onto metal
oxide surfaces have been successfully described by a Langmuir isotherm
of the form

\[
\Gamma = \Gamma_{\text{max}} \frac{K_L(C)}{1 + K_L(C)}
\]  

[5.1]

where \( \Gamma \) is the measured adsorption (moles-g\(^{-1}\)), \( \Gamma_{\text{max}} \) is the maximum ad-
sorption density (moles-g\(^{-1}\)), \( C \) is the total concentration of all
forms of the anion in solution (moles-l\(^{-1}\)), and \( K_L \) is the energetic
Langmuir constant (1-mole\(^{-1}\)). The single reciprocal form of this equa-
tion can be written as

\[
(C) = \frac{\Gamma_{\text{max}}(C)/\Gamma}{1} - K_L^{-1}
\]  

[5.2]

Hence, at a given pH, a plot of \( (C) \) vs. \( (C)/\Gamma \) yields \( \Gamma_{\text{max}} \) and \( K_L^{-1} \) as
the slope and intercept of the straight line generated. The resulting
values have been found to be pH-dependent.

The reported variation of the Langmuir energetic constant with pH
usually approximates a 'step' function. For example, the \( K_L \) values de-
termined by Huang (2) remain nearly constant for pH \( \sim 4-7 \) and then assume
a different constant value when pH \( \sim 7-10 \). Considering that \( (C) \) in the
Langmuir equation is taken to be the total concentration of anion remaining in solution, the observed variation with pH represents a change in both the dominant anionic specie in solution and the affinity of the surface for that specie. One must then consider the acid-base equilibria of the solution anion and allow for more than one adsorbing specie if an adsorption model with pH independent energetic constants is to be formulated.

The experimentally derived maximum adsorption density for anions of weak polyprotic acids (e.g., phosphate, arsenate) monotonically decreases with pH. The reported shape of the $\Gamma_{\text{max}}$ versus pH curve varies, however. In a series of papers by Hingston and his co-workers (3,4,9), the maximum adsorption density is shown to decrease linearly with breaks in the slope occurring near the $pK_a$ values of the adsorbate acids. Huang (2) reports that similar results were found by Zobrist and Stumm (unpublished data, 1970). In contrast, the data of Anderson (1) and Huang (2) fail to establish a relationship between a break in the curves and the $pK_a$ values for arsenate and phosphate.

Based on their observations, the Hingston group theorized that the anionic species must include both proton donors and proton acceptors before adsorption can take place. An expression relating maximum adsorption and pH is derived based on the probability of finding both types of specie in solution. In a more recent modeling effort to explain the discontinuities at the $pK_a$ values, Hingston et al. (10) assume the existence of a maximum free energy of adsorption of the anion ($\Delta G \text{cal-g}^{-1}$ of solid) that is constant and independent of pH. The maximum adsorption at any pH is then defined as the product of this
free energy and the number of protons that can be abstracted by surface OH\(^{-}\) groups from the undissociated acid per unit free energy change. The resulting expression relating \(\Gamma_{\text{max}}\) and \(\text{pH}\) is very similar to that of their earlier approach:

\[
\Gamma_{\text{max}} = (\Delta G/RT)\alpha(1 - \alpha)
\]

where \(\alpha\) is the degree of dissociation of the adsorbate acid.

From a chemical standpoint, the meaning of the \(\Delta G\) term and its assumed constancy, independent of \(\text{pH}\) and total anion concentration, is difficult to resolve. Cabrera et al. (11) recognize the shortcomings of such a term. They proceed to modify the model through the use of chemical potentials of the anions in solution. A weakness of this model is that it requires a 'comprehensive' experimentally determined constant that reportedly incorporates the influences of surface charge, chemical affinity of the surface for the anion, specific surface area, etc. The constant is obtained by plotting observed maximum adsorption densities against \(\log [\alpha(1-\alpha)]\).

Each of the above models supposes that the undissociated acid is the only specie able to provide protons to the surface OH\(^{-}\) groups. A more general approach is that of Bowden et al. (12), who view the adsorption process as encompassing three distinct regions. The protonation-deprotonation reactions of the surface groups are assumed to occur at a surface plane of potential \(\psi_s\) (relative to the bulk solution). A \(\text{pH}\)-dependent charge \(\sigma_s\) is developed by the reactions. The specific adsorption of any solution ions takes place in a second plane of potential \(\psi_i\), contributing a net charge \(\sigma_i\). The model for this plane is that of
Stern (13) for specific adsorption at an electrified interface. A diffuse layer of 'indifferent' counterions then extends from the second plane to the bulk solution. The charge of the diffuse layer, \( \sigma_d \), is computed using the Gouy-Chapman theory. By demanding electroneutrality in the neighborhood of the surface (\( \sigma_s + \sigma_i + \sigma_d = 0 \)), and assuming a linear drop in potential between the first and second planes, a model of the maximum adsorption envelope is developed. The model allows the use of a constant \( \Gamma_{\text{max}} \) for all pH values.

Malotky and Anderson (14) have directly revised the Langmuir expression such that \( \Gamma_{\text{max}} \) and an intrinsic \( K_L \) remain constant with pH. They propose an equation of the form

\[
\Gamma = \Gamma_{\text{max}} \frac{(C) \exp \left[-(\psi Z e + \phi)/kT\right]}{1 + (C) \exp \left[-(\psi Z e + \phi)/kT\right]}
\]

where \( K_L = \exp(-\phi/kT) \). From data at the isoelectric point (pH_{iep}, at which \( \psi = 0 \)), \( \Gamma_{\text{max}} \) and \( K_L \) are determined to be 1522 \( \mu \)mole-g\(^{-1}\) and 0.186 l-\( \mu \)mole\(^{-1}\) respectively. \( (C) \) is still taken to be the sum of the arsenate species in solution. Experimental data is then used to find \( \psi \) as a function of pH_{iep} - pH, where the isoelectric point is computed from an experimentally derived plot. The resulting expression relating \( \psi \) and pH_{iep} - pH is then used along with Eq. [5.4] in an iterative scheme to model \( \Gamma \) as a function of pH and total arsenate in solution.

A notable shortcoming in Malotky and Anderson's model is that the so-called Stern potential (\( \psi \)) must account not only for coulombic effects, but also for the pH-dependent acid-base chemistry of both the surface and the adsorbing arsenate. As such, \( \psi \) must be fitted to a particular data base. The subsequent use of the model for predictive purposes is consequently limited.
5.3 The Surface Complexation Model

The adaptation of the original surface complexation model to anion adsorption is technically straightforward, the interpretation being a series of reactions between positively charged surface groups and solution anions. A complication arises due to the acid-base equilibria of the anions in solution, requiring in effect the identification of additional adsorbed species. As will be subsequently discussed, the selection of the species is primarily mediated by experimental observations.

Using the adsorption of arsenate onto an aluminum oxide surface for illustrative purposes, a mathematical description of the anion adsorption model is presented in Table V-1. The system is basically defined by a series of mole balance and mass law expressions. The mole balance equations represent the conservation of total surface and total anion (as expressed by the component species $\equiv\text{AlOH}_2^+$ and $\text{AsO}_4^{3-}$). Note that in the surface complexation model, the total concentration of surface species (moles-l$^{-1}$) is the product of the total concentration of solid in the system (g-l$^{-1}$) and the maximum adsorption density (moles-g$^{-1}$).

The form of the reactions in Table V-1 corresponds to that used in the present investigation, using $\equiv\text{Al}^+$, $\text{H}^+$, and $\text{AsO}_4^{3-}$ as component species. Reactions $[R_1]$ and $[R_2]$ characterize the potential for proton transfer at the oxide surface, while reactions $[R_3]$-$[R_7]$ describe surface coordination reactions between protonated surface groups and the anionic species. The hydrolysis of the adsorbate acid is represented by $[R_8]$ - $[R_{10}]$. The pH-dependent fractionation of the component anionic specie (e.g., $\text{AsO}_4^{3-}$), as defined by the three hydrolysis reactions, intrinsically accounts for the acid-base chemistry of the solution anions.
The inclusion of a bidentate specie in which one arsenate ion binds with two surface sites is consistent with the early model formulation of Stumm. Through the use of infrared spectroscopy, Parfitt and Russell (15) provide experimental evidence of complexes where two surface groups are replaced by two oxygen atoms of one ligand. The use of a tridentate specie, on the other hand, has no basis in earlier investigations. As is discussed in a later section, the need for such a specie is primarily dictated by the arsenate data. The possible occurrence of a tridentate complex is arguable from a physicochemical standpoint due to the tetrahedral configuration of the arsenate ion. That is, the coexistence of three negatively charged oxygen molecules in a planar region allows for their binding to three protonated surface groups. The formation of bidentate and tridentate species can be effectively interpreted as an exchange of a proton for an $\text{AlOH}_2^+$ group, as exemplified by subtracting reactions $[R_3]$ and $[R_5]$.

It is noteworthy that the equilibrium mass law expressions corresponding to reactions $[R_5] - [R_7]$ deviate from the standard form in that the exponent of the component $\equiv \text{Al}^+$ ($\equiv \text{AlOH}_2^+$) in the bidentate and tridentate species remains 1. In a highly simplified representation, the standard use of an exponent of 2 for X in the mass law for specie $X_2Y$ infers that the probability of contacting two X molecules in a dilute solution is the square of the probability of contacting one molecule. When an anion comes in contact with a surface, however, the probability of finding two available sites in close proximity is much greater than the square of the probability of finding one available site due to their 'concentrated' and 'immobile' position on the surface. Of greater significance in the decision to use an exponent of unity is the excellent fit of the experimental
data with the modified model, and the fact that the data cannot be reproduced over the entire range of pH and total anion concentration without the change. This is demonstrated in a later section.

5.3.1 The Coulombic Correction

The stability constants relating products and reactants in the mass law expressions are only 'apparent' due to coulombic effects on the intrinsic free energy of surface complex formation. The 'apparent' constants can be related to the 'intrinsic' constants (i.e., the stability constants in the absence of electrostatic attraction or repulsion) by (6)

\[ (K_{\text{app}})_i = (K_{\text{int}})_i \cdot \exp(Z_i F \psi_s / RT) \]  \[5.5\]

where \( Z_i \) is the change in surface charge corresponding to reaction \( i \) and \( \psi_s \) is the potential of the surface plane with respect to the bulk solution. \( F, R, \) and \( T \) have their standard thermodynamic meaning. In general, \( \psi_s \) cannot be directly measured and the incorporation of Eq [5.5] into adsorption models is infeasible. To account for this, most models employ simplified expressions relating the potential difference to experimentally derivable quantities. A common approach is to define neighboring adsorption layers (e.g., inner Helmholtz plane, outer Helmholtz plane, diffuse layer) of differing potential, with the assumption of a linear drop in potential between them (12, 16, 17). Necessary parameters, such as the slope of the potential drop, are reportedly obtained from titration curves of the adsorbents in a solution of indifferent electrolyte.

In the surface complexation model, a more straightforward approach is taken in which both the protonation-deprotonation reactions of the surface
and the formation of complexes between surface sites and solution ions are treated identically as coordination reactions at the same surface plane. It is then assumed that each surface specie is subject to the same coulombic correction. A reasonable approximation to the correction can be derived from experimental data describing the acid-base properties of an adsorbing surface.

Hohl and Stumm (7) report an extensive collection of data relating the 'apparent' acidity constants \( K_{a1}, K_{a2} \) for \( \gamma \)-Al\(_2\)O\(_3\) to the concentration of the charged surface species \( \equiv\text{AlOH}_2^+, \equiv\text{AlO}^- \) in the absence of an adsorbing metal or ligand. The data is reproduced in Figure 5-1. By extrapolating the data to zero-charge conditions, the intrinsic first and second acidity constants are determined to be \( 10^{-7.0} \) and \( 10^{-9.5} \), respectively. (Using linear extrapolation, Hohl and Stumm found \( pK_{a1}^{\text{int}} = 7.2 \), but the trend of the data indicates that 7.0 is more appropriate. Figure 5-1 is based on \( pK_{a1}^{\text{int}} = 7.0 \).) The corresponding point of zero charge \( pH_{ZPC} \) is 8.25. At pH values below \( pH_{ZPC} \), \( \equiv\text{AlOH}_2^+ > \equiv\text{AlO}^- \) and the net surface charge can be approximated by \( \equiv\text{AlOH}_2^+ \). A similar argument can be made for the net negative charge and \( \equiv\text{AlO}^- \) at pH values above 8.25. In other words, the abscissa of Figure 5-1 effectively represents the net charge on the surface. Under the assumption that the same charge correction applies regardless of what species are charge determining, then the relationship exhibited in Figure 5-1 can be used to correct the 'intrinsic' constant of any specie adsorbing onto \( \gamma \)-Al\(_2\)O\(_3\)(s) once the net surface charge is known.

The general shape exhibited by the data in Figure 5-1 is that of a hyperbolic sine, which is analogous to the functional relationship of
the Gouy-Chapman theory. However, no single hyperbolic sine function is capable of describing the data over the entire range of surface charge (note particularly the asymmetry of the data relative to the point of zero charge). Due to the scatter of the data field and the lack of a better approximation, the present modeling effort assumes linear approximations. In addition, a bounded coulombic correction is proposed as a result of the observed asymptotic behavior of the data.

The resulting expressions relating net surface charge and the coulombic correction are presented in Table V-1. The net charge \( Q \) has the form of a concentration relative to the amount of solid present (moles kg\(^{-1}\)):

\[
Q = \frac{\sum Z_i C_i}{S} \tag{5.6}
\]

where \( Z_i \) is the charge of the surface specie \( i \) of concentration \( C_i \) (moles kg\(^{-1}\)). \( S \) is the amount of solid in solution (kg m\(^{-3}\)). In general, the coulombic correction imposed on the stability constant is

\[
(pK_i^S)_{\text{app}} = (pK_i^S)_{\text{int}} + Z_i^* \cdot pK_{\text{coul}} \tag{5.7}
\]

where \( Z_i^* \) is the change in surface charge resulting from the formation of one mole of surface specie \( i \). It should be pointed out that the stability constant of every surface specie is corrected, whereas in the original applications of the model to metal ion adsorption only the two surface acidity constants were modified (6,7,8).

5.3.2 The Solution Scheme

For a given pH, total surface concentration, and total arsenate concentration, the chemical system defined in Table V-1 can be solved to obtain the equilibrium concentrations of all species. As a consequence of
the coulombic correction, however, an iterative solution scheme is required. That is, the equilibrium concentration of all surface species is dependent on the charge correction, which in turn is dependent on the equilibrium concentrations.

A guess of the net surface charge is made. All surface stability constants are corrected according to [5.7], and the system is solved. The resulting concentrations are used to compute $Q$ according to [5.6], which is compared to the assumed value. When a violation of charge equality occurs for a given iteration, the assumed charge is corrected by an 'interval halving' technique so as to properly modify the stability constants toward convergence. In general, larger stability constants imply increased adsorption, which results in a decrease in the computed net surface charge. The modeled adsorption is taken to be the sum of the concentrations of all adsorbing species when the assumed and computed charges are equal (i.e., when the computed charge is that for which the coulombic correction was made).

The use of an exponent of 1 for $\equiv\text{AlO}_\text{H}_2^+$ in the mass law expressions permits an analytical solution of the equations governing the chemical system. Due to the complexity of the various terms (primarily of exponential form), however, the use of a computer is expedient.

5.4 The Maximum Adsorption Envelope

The primary data base for the present work is that of Anderson and his co-workers (1,14), in which arsenate adsorption onto aluminum hydroxide is reported over a pH range of 4.5 - 8.5 for total arsenate concentrations of $6.67 \times 10^{-5}$ M - $1.0 \times 10^{-3}$ M. A superposition of the data for total arsenate above $4.0 \times 10^{-4}$ M (refer to Figure 5-3) indicates
that the respective experimental adsorption envelopes can be well-approximated by a single adsorption versus pH curve. That is, the maximum adsorption envelope is a function only of pH and not of the amount of arsenate in the system. The current observation can be resolved only by considering that the arsenate completely covers the surface sites once a saturation value of total arsenate is exceeded. The decrease in maximum adsorption with increasing pH is explainable in terms of the adsorbing anions exchanging bound hydrogen ions for additional surface sites as the pH increases (i.e., each adsorbing anion becomes bound to two, or even three, surface sites).

As saturation of the surface is approached, the concentration of adsorbate-free surface species (\( \equiv \text{AlOH}^+ \), \( \equiv \text{AlOH} \), \( \equiv \text{AlO}^- \)) becomes negligible and the acid-base equilibria of the surface no longer affects the adsorption process. An approximate expression for the number of bound anions at saturation (\( \mu \text{moles-g}^{-1} \)), relative to the total number of surface sites (\( \mu \text{moles-g}^{-1} \)), is thus:

\[
\frac{\Gamma_{\text{sat}}}{\Gamma_{\text{max}}} = \frac{(\equiv \text{AlH}_2\text{AsO}_4^0) + (\equiv \text{AlHAsO}_4^-) + (\equiv \text{Al}_2\text{HAsO}_4^0) + (\equiv \text{Al}_2\text{AsO}_4^-)}{(\equiv \text{AlH}_2\text{AsO}_4^0) + (\equiv \text{AlHAsO}_4^-) + 2(\equiv \text{Al}_2\text{HAsO}_4^0) + 2(\equiv \text{Al}_2\text{AsO}_4^-)}
\]

\[
+ \color{red}{(\equiv \text{Al}_3\text{AsO}_4^0)}
\]

\[
+ \color{red}{3(\equiv \text{Al}_3\text{AsO}_4^0)}.
\] [5.8]

The substitution of the mass law expression for each specie allows a simplification to

\[
\frac{\Gamma_{\text{sat}}}{\Gamma_{\text{max}}} = \frac{k_1^S(H^+)^2 + k_2^S(H^+) + k_3^S(H^+) + k_4^S + k_5^S}{k_1^S(H^+)^2 + k_2^S(H^+) + 2k_3^S(H^+) + 2k_4^S + 3k_5^S}
\] [5.9]
Accordingly, $\Gamma_{\text{sat}}$ is a function only of pH. Note that the stability constants $K_1 - K_5$ assume different values at each pH due to changes in the coulombic correction.

Using the 'intrinsic' stability constants established for the arsenate data and appropriately correcting them for coulombic effects, a plot of $\Gamma_{\text{sat}}$ versus pH is constructed according to [5.9] (Figure 5-2). $\Gamma_{\text{max}}$ is taken to be 1600 μmoles-g$^{-1}$. Also plotted in Figure 5-2 are the pH-dependent maximum adsorption values reported by Anderson when the data is fitted to a Langmuir equation at each pH. The fit is very satisfactory.

A second set of independent data reported by Huang (2) for phosphate adsorption onto $\gamma$-Al$_2$O$_3$ is likewise subjected to [5.9], using the corrected stability constants for phosphate and $\Gamma_{\text{max}} = 345$ μmole-g$^{-1}$. The modeled saturation values are again very close to the values that effectively describe the data through pH-dependent Langmuir isotherms (Figure 5-2), thereby further establishing the validity of the proposed representation of anion adsorption under saturation conditions. A problem in the Langmuirian description is evident at high pH, where the plateau value of the isotherm is less than the observed adsorption value. The surface complexation model predicts a value close to that observed.

5.5 Overall Model Results

Anderson et al. (1) report a pH$_{\text{ZPC}}$ of 8.4 for amorphous Al(OH)$_3$, essentially the same as that extrapolated for $\gamma$-Al$_2$O$_3$. It is then reasonable to assume that the acid-base chemistry of the two surfaces is similar and that both the intrinsic acidity constants of $\gamma$-Al$_2$O$_3$ and the charge correction also apply to the hydroxide surface. Five stability constants
(K_1 - K_5) thus remained to be determined for the arsenate system. As a consequence of the known saturation adsorption at various pH values, the relative magnitude of the stability constants can be estimated according to Eq. [5.9]. In addition, an educated guess of the stability constant for $\equiv \text{AlH}_2\text{AsO}_4^-$ is possible since only this specie is significant at low pH values. A first approximation to all stability constants follows. The 'best fit' set of constants is then obtained by trial and error, with emphasis being placed on high pH conditions at which the model is most sensitive.

Figure 5-3 reports the results of the surface complexation model for the arsenate system. The corresponding set of intrinsic stability constants is listed in Table V-1. Whereas the low saturation values at high pH required the inclusion of a tridentate specie, the only bidentate specie needed is $\equiv \text{Al}_2\text{HAsO}_4^-$, the transition specie between $\equiv \text{AlH}_2\text{AsO}_4^-$ and the tridentate $\equiv \text{Al}_3\text{AsO}_4^-$. Figure 5-3 also presents the results of Malotky and Anderson's model described earlier. Not only does the surface complexation model significantly improve the prediction reliability relative to the earlier modeling effort, but a very satisfactory fit is exhibited over the entire range of pH and total arsenate values. Several experimental points not well-satisfied by the model appear to be erroneous in that they represent discontinuities in otherwise smooth experimental adsorption curves as pH increases for a given total arsenate concentration.

A relatively consistent 5 per cent over-prediction is observed at low values of total arsenate. These conditions correspond to an excess of surface and the subsequent adsorption of nearly all the arsenate in solution. Total concentrations of arsenate remaining in solution are on the
order of micromolar. A possible explanation for this discrepancy is that the data represent 48-hour equilibration times, while the model reflects complete equilibrium. An adsorption versus time curve reported by Anderson et al. (1) indicates that a 5 per cent increase in adsorption after 48 hours is not unreasonable. This is especially true when the concentration of the anion in solution is small, since the kinetics of adsorption are then greatly diminished. The discrepancy is not sensitive to order of magnitude changes in the intrinsic stability constants.

A somewhat independent test of model reliability is its capacity to reproduce the experimental curve relating pH_{iep} and the adsorption at that pH (Figure 5-4). The model points were determined by iterating on pH until the \equiv AlO^- and \equiv AlHASO_{4}^- species balanced the protonated \equiv AlOH_2^+ surface sites. Being at the pH_{iep}, no correction was made to the intrinsic stability constants. Especially critical to this test of the model is that the results of the iteration are very sensitive to the relative values of the stability constants since only one adsorbing specie (\equiv AlHASO_{4}^-) is charged and it is not dominant below pH = 6.3. It is noteworthy that the experimental values were extrapolated from electrophoretic mobility experiments, and thus the model results are within the bounds of experimental error. A final comment is that the model deviates from a linear relationship at low pH, but this is not surprising since a strictly linear plot on semi-logarithmic axes is not a valid description of a chemical phenomenon.

Further testing of the model is provided by Huang's data of phosphate adsorption onto \gamma-Al_2O_3. The chemistry of the aqueous phosphate group is very similar to that of arsenate. Most notable is the near equality of their acidity constants, indicative of an equivalent affinity for the
hydrogen ion over a wide pH range. A logical consequence is that the adsorption characteristics of the two anions onto protonated $\equiv \text{AlOH}_2^+$ surface groups are also equivalent. As such, the phosphate data would be expected to satisfy the surface complexation model using nearly the same set of stability constants as those established for arsenate. A lengthy series of trial and error model runs showed this to in fact be the case, with one significant variation. Both the saturation adsorption values and the overall model reliability indicated the need for a solely dominant bidentate specie at the high pH values under consideration. Due to the equivalency of their mass law expressions when each exponent is 1, the incorporation of $\equiv \text{Al}_2\text{AsO}_4^-$ and the exclusion of $\equiv \text{Al}_3\text{AsO}_4^-$ was suggested. In order to both effect this change and somewhat retain the concept of an equivalency between phosphate and arsenate in the model, the intrinsic stability constants of the two species in question were simply interchanged. The physical explanation for the specie change is most likely based in the surface configuration of $\gamma$-Al$_2$O$_3$ relative to that of Al(OH)$_3$(s). The fact that the hydroxide solid has a maximum adsorption density nearly five times as large as that of the oxide is indicative of the surface variations involved.

A correction in the intrinsic constants was also required due to a difference in the ionic strengths of the systems (arsenate: 0.01 M, phosphate: 0.1 M). Table V-1 presents the stability constants for the phosphate surface species that result by correcting the arsenate values according to the Davies approximation (18). The possible limitations of applying a standard ionic strength correction to species adsorbing onto a charged surface is recognized, but a more appropriate correction is not available.

Figure 5-5 reports the complexation model results for phosphate.
The fit is again very good. Although only three total phosphate concentrations are reported in Figure 5-5, these span the reported experimental range and are representative of the fit for other cases. The model is observed to under-predict adsorption under high pH and high phosphate conditions. But as shown in the figure, Huang had the same difficulty when he modeled his data using the James and Healy approach, which considers coulombic, solvation, and specific chemical energy interactions as the anion approaches the surface (19). Reasons for this discrepancy are being investigated, but at high pH values the chemistry of the system becomes complicated due, for example, to the possible dissolution of the aluminum solid as Al(OH)₄⁻ (1,18).

Huang reports the results of his model only for a total phosphate concentration of 10⁻³ M. A detailed comparison of the prediction reliability of the surface complexation model with Huang's is therefore not possible. However, it seems that to obtain a fit of the maximum adsorption envelope using the James and Healy approach might be problematical. Since in this approach the maximum adsorption density is defined as a monolayer coverage of the surface by partially hydrated adsorbate ions, it would appear to be a pH independent process.

5.6 Discussion of Results

Figures 5-2 through 5-5 exhibit the capability of the proposed surface complexation model to describe two extensive sets of experimental data. Required for obtaining such a good fit are two changes relative to a similar model developed for metal ion adsorption: the introduction of a tridentate adsorption specie and the use of an exponent of 1 for the
surface component $\equiv AlOH^+_2$ in the mass law expressions. Though each modification has a reasonable physical basis as discussed earlier, their incorporation into the model is primarily due to the nature of the data itself.

An initial attempt to model the anion adsorption data employed the 'standard' surface complexation model that retains the exponent of 2 for the bidentate specie. After an exhaustive search for a 'good' set of stability constants, including also the introduction and subsequent deletion of other adsorbate species (e.g., $\equiv AlAsO_4^{2-}$), it was concluded that such a model is unable to reproduce the data for the entire range of pH and arsenate concentrations. Table V-2 presents representative trials for a subset of the arsenate data. As is evident, either the high or low arsenate conditions could be reproduced, but not both. A simplistic demonstration of the problem is that the concentration of component $\equiv AlOH^+_2$, which is squared (cubed) in the mass law expression for the bidentate (tridentate), decreases exponentially with increasing pH above the first acidity constant of the surface. It is therefore difficult to maintain the dominance of the bidentate at high pH (as the data suggests) without affecting the model results at lower pH values. Other investigators are currently justifying the suitability of an exponent of 1 by defining reactions between dimeric surface species (e.g., $\equiv Al_2^{2+}$) and solution ions (J. Westall, J. Davis, personal communication, 1977).

A primary advantage of the surface complexation model is the straightforward method of correcting for coulombic effects relative to other adsorption models that treat the chemical system in the same detail. This correction technique is consistent with the simplified representation of
adsorption phenomena as a series of equivalent coordination reactions at the same plane. Considering the limited knowledge of the electrostatic forces generated at solid-solution interfaces and the inability to directly measure their effects, the simpler scheme seems justified until a more dependable method can be demonstrated. The satisfactory results of the surface complexation model support the use of the less complex approach. Recall also that the necessary data is obtained from a fundamental acid-base titration of a suspension of the adsorbing solid.

A second advantage of the surface complexation model is that the mass law and mole balance equations defining the system are directly adaptable to the metal-ligand approach used to solve large chemical systems. As such, the adsorption model is easily incorporated into generalized computer programs for the determination of the equilibrium composition of aqueous chemical systems (e.g., MINEQL (20)).

Critical to the applicability of any model are the kind and quantity of data required for the determination of its parameters. The acid-base properties of the adsorbing surface have previously been noted as necessary data for the surface complexation model. Both the intrinsic acidity constants of the surface groups and the information necessary for the derivation of the coulombic correction are so provided. Other necessary data include adsorption isotherms as a function of pH for a series of total adsorbate concentrations. The primary use of these measurements is model calibration and verification. However, if the same data are plotted as Langmuir isotherms for given values of pH, the maximum adsorption envelope can be approximated. The relative magnitude of the stability constants can then be estimated according to Eq. [5.9]. Electrophoretic
mobility measurements provide additional useful data allowing the construction of a \( \Gamma_{\text{IEP}} \) versus \( \text{pH}_{\text{IEP}} \) curve similar to that of Anderson et al. (1) (Figure 5-4). While this information is not required, it is useful both for the initial guess of surface charge and as additional verification of the intrinsic stability constants. Recall that the capability of the model to reproduce such a curve is relatively sensitive to the chosen set of stability constants. In summary, the data commonly produced in experimental adsorption studies are sufficient for determining the parameters of the surface complexation model.


Figure 5-1

COULOMBIC CORRECTION AS A FUNCTION OF THE NET SURFACE CHARGE

(To plot the data, the assumption is made that the net charge is equal to the concentration of the dominant charged specie. Data is from Hohl and Stumm (7).)
\[ \alpha-Al_2O_3 \text{ Conc. (g-}^{-1}) \]

- 17.40
- 11.73
- 3.75
- 3.28
- 3.16

\[ Q \approx - \{\equiv AlO^-\} \text{ (moles-Kg}^{-1}) \]

\[ Q \approx \{\equiv AlOH_2^+\} \text{ (moles-Kg}^{-1}) \]
Figure 5-2

MAXIMUM ADSORPTION CURVE ACCORDING TO EQUATION [5.11]

(Maximum values determined from reciprocal Langmuir plots of the data are shown for comparison.)
SURFACE COMPLEXATION MODEL (EQ [II])

- Plateau value of Langmuir isotherm: Anderson (1)
- Plateau value of Langmuir isotherm: Huang (2)
- Observed adsorption for TCT(PO₄) = 1.00 x 10⁻³ M
Figure 5-3 (a-c)

ADSORPTION OF ARSENATE ON AMORPHOUS Al(OH)₃
AS DETERMINED BY THE SURFACE COMPLEXATION MODEL

(The experimental data of Anderson, et. al. (1) and the results of the Malotky and Anderson model (14) are shown for comparison.)
SURFACE COMPLEXATION MODEL

- EXPERIMENTAL DATA
- MALOTKY AND ANDERSON MODEL

\[ \text{TOT(AsO}_4\text{)} = 8.00 \times 10^{-4} \text{M} \]
\[ \text{TOT(AsO}_4\text{)} = 1.33 \times 10^{-4} \text{M} \]
\[ \text{TOT(AsO}_4\text{)} = 6.67 \times 10^{-5} \text{M} \]
SURFACE COMPLEXATION MODEL

EXPERIMENTAL DATA

MALOTKY AND ANDERSON MODEL

\[ \text{TOT(AsO}_4\text{)} = 1.60 \times 10^3 \text{M} \]

\[ \text{TOT(AsO}_4\text{)} = 2.67 \times 10^4 \text{M} \]

\[ \text{TOT(AsO}_4\text{)} = 1.00 \times 10^4 \text{M} \]
SURFACE COMPLEXATION MODEL

EXPERIMENTAL DATA

MALOTKY AND ANDERSON MODEL

\[ \text{TOT(AsO}_4\text{)} = 4.00 \times 10^4 \text{M} \]

\[ \text{TOT(AsO}_4\text{)} = 1.33 \times 10^4 \text{M} \]

(0.15 g⁻¹ Al(OH)₃(s))

[Graph showing the relationship between pH and \( \Gamma \) (µmol-g⁻¹) with different total arsenate concentrations and solid phase concentration.]
Figure 5-4

ADSORPTION VALUES AT THE ISOELECTRIC POINT COMPUTED USING THE SURFACE COMPLEXATION MODEL

(Experimental adsorption values at the point of zero surface charge, as extrapolated from electrophoretic mobility measurements by Anderson, et. al. (1), are shown for comparison.)
ANDERSON: PROPOSED LINEAR RELATIONSHIP

O ANDERSON: EXPERIMENTAL DATA
Δ SURFACE COMPLEXATION MODEL
Figure 5-5

ADSORPTION OF PHOSPHATE ON $\gamma$-Al$_2$O$_3$
AS DETERMINED BY THE SURFACE COMPLEXATION MODEL

(The experimental data of Huang (2) are shown for comparison. Also shown are the results of Huang's model for TOT($P0_4$) = 1.00E-3 M.)
SURFACE COMPLEXATION MODEL

O, △, □ EXPERIMENTAL DATA
□ HUANG MODEL.

\[ \text{TOT(PO}_4\text{)} = 1.00 \times 10^{-3} \text{M} \]

\[ \text{TOT(PO}_4\text{)} = 6.00 \times 10^{-4} \text{M} \]

\[ \text{TOT(PO}_4\text{)} = 2.00 \times 10^{-4} \text{M} \]
**COMPONENT SPECIES:** \( H^+ \), \( \equiv AlOH^2_2 \) \( \equiv Al^+ \), \( AsO_3^{3-} \)

**MOLE BALANCE EQUATIONS:**

\[
\begin{align*}
\text{TOT}(\equiv Al^+) &= (\equiv Al^+) + (\equiv AlOH^\ast) + (\equiv AlO\,2\equiv) + (\equiv Al\,2\equiv AsO_4^\ast) + 2(\equiv Al_2\equiv AsO_4^\ast) + 2(\equiv Al_2\equiv AsO_4^\ast) + 3(\equiv Al_3\equiv AsO_4^\ast) \\
\text{TOT}(AsO_4^{3-}) &= (R_2\equiv AsO_4^\ast) + (R_2\equiv AsO_4^\ast) + (R_2\equiv AsO_4^\ast) + (R_2\equiv AsO_4^\ast) + (R_2\equiv AsO_4^\ast) + (R_2\equiv AsO_4^\ast) + (R_2\equiv AsO_4^\ast)
\end{align*}
\]

**REACTIONS:**

\[
\begin{align*}
[R_1] &= Al^+ + 2H^+ + AsO_4^{3-} \\
[R_2] &= Al^+ + 2H^+ + AsO_4^{3-} \\
[R_3] &= Al^+ + 2H^+ + AsO_4^{3-} \\
[R_4] &= Al^+ + 2H^+ + AsO_4^{3-} \\
[R_5] &= 2Al^+ + 2H^+ + AsO_4^{3-} \\
[R_6] &= 2Al^+ + 2H^+ + AsO_4^{3-} \\
[R_7] &= 3Al^+ + 3AsO_4^{3-} \\
[R_8] &= 3Al^+ + 3AsO_4^{3-} \\
[R_9] &= 2H^+ + 2AsO_4^{3-} \\
[R_{10}] &= H^+ + AsO_4^{3-}
\end{align*}
\]

**MASS LAW EXPRESSIONS:**

\[
\begin{align*}
K^a_{1} &= (\equiv AlOH^\ast)(H^+)/\equiv Al^+ \\
K^a_{2} &= (\equiv AlO\,2\equiv)(H^+)/\equiv Al^+ \\
K^a_{3} &= (\equiv Al\,2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{4} &= (\equiv Al_2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{5} &= (\equiv Al_2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{6} &= (R_2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{7} &= (R_2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{8} &= (R_2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{9} &= (R_2\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{10} &= (H_3\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{11} &= (H_3\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{12} &= (H_3\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{13} &= (H_3\equiv AsO_4^\ast)(H^+)/\equiv Al^+ \\
K^a_{14} &= (H_3\equiv AsO_4^\ast)(H^+)/\equiv Al^+
\end{align*}
\]

**ARSENATE**

\[-(p^a_{K_{1}})_{\text{int}} = 7.0 \quad -\frac{(p^a_{K_{1}})_{\text{int}}}{10} = 7.0\]

**PHOSPHATE**

\[-(p^a_{K_{1}})_{\text{int}} = 7.0 \quad -\frac{(p^a_{K_{1}})_{\text{int}}}{10} = 7.0\]
COULOMBIC CORRECTION (Refer to Figure 5-1):

\[
(pK)_{\text{coul}} = \begin{cases} 
2.2 & \text{if } Q > 0.18 \\
12.2 \cdot Q & \text{if } 0. < Q < 0.18 \\
5.0 - Q & \text{if } -0.14 < Q < 0. \\
-0.7 & \text{if } Q < -0.14 
\end{cases}
\]

TABLE V-1

MATHEMATICAL DESCRIPTION OF THE SURFACE COMPLEXATION MODEL
<table>
<thead>
<tr>
<th>(\text{TOT}(\text{AsO}_4^3^-)) (M)</th>
<th>pH</th>
<th>(\Gamma_{\text{observed}}) ((\mu\text{mole-g}^{-1}))</th>
<th>(\Gamma_{\text{predicted}}) ((\mu\text{mole-g}^{-1}))</th>
<th>(\Gamma_{\text{predicted}}) ((\mu\text{mole-g}^{-1})): Exponent of 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.67 (10^{-3})</td>
<td>8.49</td>
<td>362</td>
<td>382</td>
<td>228** b</td>
</tr>
<tr>
<td>1.6 (10^{-4})</td>
<td>7.66</td>
<td>6.50</td>
<td>613</td>
<td>568*</td>
</tr>
<tr>
<td>1.00 (10^{-4})</td>
<td>8.41</td>
<td>481</td>
<td>500</td>
<td>333**</td>
</tr>
<tr>
<td>1.33 (10^{-4})</td>
<td>8.81</td>
<td>645</td>
<td>653</td>
<td>447*</td>
</tr>
<tr>
<td>1.33 (10^{-4})</td>
<td>8.28</td>
<td>537</td>
<td>556</td>
<td>447*</td>
</tr>
<tr>
<td>1.33 (10^{-4})</td>
<td>7.99</td>
<td>678</td>
<td>622</td>
<td>550*</td>
</tr>
<tr>
<td>1.33 (10^{-4})</td>
<td>8.21</td>
<td>542</td>
<td>575</td>
<td>482*</td>
</tr>
<tr>
<td>4.00 (10^{-4})</td>
<td>7.49</td>
<td>1030</td>
<td>1008</td>
<td>942*</td>
</tr>
<tr>
<td>4.00 (10^{-4})</td>
<td>7.77</td>
<td>931</td>
<td>909</td>
<td>839</td>
</tr>
<tr>
<td>4.00 (10^{-4})</td>
<td>8.35</td>
<td>545</td>
<td>693*</td>
<td>663*</td>
</tr>
<tr>
<td>8.00 (10^{-4})</td>
<td>7.93</td>
<td>999</td>
<td>925</td>
<td>908</td>
</tr>
<tr>
<td>8.00 (10^{-4})</td>
<td>8.45</td>
<td>681</td>
<td>693</td>
<td>705</td>
</tr>
<tr>
<td>1.60 (10^{-3})</td>
<td>8.20</td>
<td>759</td>
<td>796</td>
<td>925*</td>
</tr>
</tbody>
</table>

---

*a* Intrinsic Stability Constants, \(-pK_i (i=1,5)\)

*b* * > 10% Error; ** > 25% Error (Relative to the measured adsorption value)

**TABLE V-2**

RESULTS OF A SERIES OF MODEL RUNS USING AN EXPONENT OF 2 FOR THE BIDENTATE SPECIE
Chapter 6
EPILOGUE

The original goal of this research was to interface various sub-models into a modified Imboden-type model, thereby extending its capacity to effectively describe the prototype. In addition to the thermocline mixing and adsorption submodels described in Chapters 4 and 5, an existing chemical equilibrium model (1) was to be implemented to provide the necessary information on the soluble carbonate and phosphate systems. However, it was soon evident that even if such submodels could be formulated, their interfacing into a comprehensive model of phosphorus in lakes would be infeasible due to a lack of sufficient field data for model calibration and verification. The obtention of reliable, representative field data may prove to be necessary for pursuing several aspects of this research further.

The stepwise discriminant analysis reported in Chapter 2 proved valuable in establishing a statistical significance of the hydraulic residence time relative to other morphological parameters in describing the non-conservative behavior of phosphorus. The interrelationship between the amount of information gained from such a study and the extent of available data is obvious. Any additional variable known for each of the lakes used in the study, whether it be physical, chemical, or biological, would contribute to the knowledge generated. For example, the degree of stratification achieved by a lake during the summer period would prove useful in establishing the importance of the mixing
process modeled in Chapter 4. It is noteworthy, however, that such a parameter, while proving useful for developing and calibrating a model, may not directly contribute to the reliability of the prediction of phosphorus concentration in lakes since its value is not known \textit{a priori}. That is, it represents a potential output of a predictive model rather than an input parameter.

A lake parameter that would enhance the applicability of Chapter 5 is the concentration of suspended metal oxides, especially iron. The general importance of the adsorption process for phosphorus removal could be analyzed by including the metal oxide concentration in a discriminant analysis. A knowledge of the pH and ionic strength would augment any such analysis.

Any data that promote a resolution of the statistically derived importance of hydraulic residence time are of value to Chapters 2 and 3. As discussed, the term representing phosphorus loss to the sediments is a prime area of concern. Two potential explanations of the imposed relationship between the rate of phosphorus sedimentation and the residence time have been presented in Chapter 3. A field study to determine if the size or settling velocity distribution of particulate phosphorus is responsible for the empirical findings appears to be feasible. On the other hand, testing the idea concerning the incorporation of phosphorus into large, rapidly settling particles would presumably encounter design problems. Foremost are the temporal and spatial scales involved in detecting such a 'rare event' phenomenon.

Other data and research needs relative to Chapter 3 have been
discussed by Snodgrass and O'Melia (2). They conclude that a reliable estimation of phosphorus loadings should be emphasized and that high research priority should be given to studies related to processes by which nutrients are removed from lakes. Production in the euphotic zone during the summer stratification period, which has received considerable attention in the past, appears to be of secondary importance.

A general problem in modeling the extent of mixing in the thermocline region of lakes is the large number of physical processes contributing to the overall effect. It is not within the scope of present knowledge to treat each process individually, and commonly a Fickian-type equation is utilized to describe the aggregate effect of those processes not otherwise treated in the model. As exemplified in Chapter 4 by the discussion of Snodgrass and O'Melia's data base, the field techniques used to evaluate the rate coefficient of the Fickian equation are quite varied and effectively measure different mixing phenomena. Recall the study of Hesslein and Quay (3), in which the coefficients derived from three measurement techniques differed by almost an order of magnitude. A major point made in Chapter 4 is that the use of a detailed hydrodynamic-temperature model of a lake somewhat minimizes the need for a Fickian dispersion term. However, phosphorus models that describe mixing by a Fickian term continue to be developed, with most emphasis being placed on the extension of chemical and biological details. Recall, for example, that the principal contributions of Imboden and Gächter's most recent version of the Imboden model dealt with the growth function and the reflux of phosphorus from the sediments. Some
attention should be directed to the treatment of the vertical mixing process in such models. In particular, the establishment of a relationship between the various field techniques and the physical mechanisms being measured by each would be worthwhile. It is also critical that the model developers recognize the mixing processes being described by their respective rate coefficients. The fact that Snodgrass and O'Melia gave no explicit indication that their use of a fixed thermocline location required the coefficient to account for any mixing due to thermocline migration illustrates the potential for erroneous formulations.

A consideration of the mixing model described in Chapter 4 suggests two areas of possible improvement. First, the computed temperature profile often exhibits two regions of high density gradient and the resulting thermocline location is sometimes found to 'jump' from one region to the other. The most frequent cause of this anomaly is the presence of large temperature variations near the surface. As discussed earlier, the model includes two externally imposed safeguards to minimize the occurrence of this instability. Under the current procedure, a maximum thermocline movement of one-half the element thickness per time step is allowed, and if a violation occurs the thermocline location is assigned its value at the preceding time step. In some instances, the thermocline does actually change from one region to another. The model computes a sudden movement that violates the criterion, but as the number of time steps since the last movement increases, the average movement per time step eventually satisfies the criterion and a 'jump' of several elements is properly allowed. This technique is suitable when one is
concerned only with a mixing value averaged over the period of stratification. However, if the mixing model is incorporated into a phosphorus model, the response to such a stepwise mixing would differ from that associated with a continuous, average movement since all exchange and loss processes are dependent on the temporal variation of the constituent concentrations. One possible solution would be to modify the storage requirements and logic of the model so as to provide a record of the temporal history of the thermocline location. When a jump takes place, the resultant mixing can be averaged over the time periods in which a violation occurred. The average value is then reassigned to each time period involved. Note that this procedure likewise requires that the values of the phosphorus model be stored, since no computations can be made during time periods in which the maximum movement criterion is violated.

A second shortcoming of the present mixing model is that the length of the stratification period is controlled by the user. What would be more attractive is some internal test to determine its onset and termination. The most logical approach would be to establish a minimum density gradient that is representative of stratified conditions across which transport is inhibited. At each time step, the maximum computed density gradient would be compared to the assumed value as a test for the presence of a thermocline. Problems, of course, could arise due to abnormal short-term meteorological conditions. For example, the critical gradient may be exceeded for a short time period very early in the year, and to isolate the epilimnion and hypolimnion for the few time steps
involved would no doubt give rise to a misrepresentation of the prototype response.

The chemistry of phosphorus at the sediment-water interface is largely dependent on the redox potential. For example, phosphate bound to ferric iron solids under oxic conditions can be returned to the water column upon the reduction of the ferric form when anoxic conditions set in. Consequently, the full potential of the adsorption model presented in Chapter 5 cannot be realized without a knowledge of the oxygen regime. However, no model of dissolved oxygen in lakes presently exists that would provide sufficiently accurate predictions, and none can be expected in the near future even though the formulation of such a model remains a prime area of research. The large number of physical, chemical, and biological factors governing the distribution of oxygen represent the principal sources of modeling difficulty. This is essentially a Catch-22 situation since dissolved oxygen is governed to a large extent by the biological activity in lakes which, in turn, depends on the phosphorus cycle. This is the basic rationale for the integrated approach exhibited by 'complex' models, which represents a drastic qualitative change of the modeling approach. However, if such models are to be valuable predictive tools, significant progress in the understanding of the basic processes and the obtention of intensive field data must be forthcoming.

During conversations relative to this research, the opinion has been expressed that the modeling of phosphate adsorption at the sediment-water interface is somewhat futile given the limited modeling
capacity of the oxygen regime. Such would be the case if the adsorption model were expected to be finalized in a relatively short time period. However, the modeling of the adsorption process is still in its infancy -- recall that the model formulated in Chapter 5 is the first reported attempt to describe anion adsorption as a series of surface complexation reactions. As described in Chapter 5, the surface complexation model is able to satisfactorily reproduce two extensive sets of data of anion adsorption onto aluminum surfaces. Extension of the model to other surfaces and adsorbing ions is called for. As regards the modeling of phosphate adsorption in lakes, the most logical next step is to test the capacity of the model to describe the adsorption of phosphate onto iron oxides. Some pertinent data are found in references (4)-(6).

Another useful project is further testing of two proposed modifications in the surface complexation model. These include a scheme to correct for coulombic effects based on net surface charge, and the use of an exponent of unity in the mass law expressions for bidentate and tridentate species. A suitable test would be to compare the results of the present model for systems of metal adsorption with those generated by Hohl and Stumm (7), and Schindler, et al. (8), using the earlier version of the surface complexation model. Note that for surfaces other than aluminum oxides, additional information on the acid-base chemistry of the surface is required so that a coulombic correction versus net surface charge plot can be generated.

Assuming that all subsequent testing of the surface complexation model proves it to be a reliable predictive tool, its general use will
then be limited only by the availability of intrinsic stability constants for each combination of surface and adsorbate. The large number of constants that must be determined for each system proves a difficult task. What is needed is some systematic and computationally consistent technique by which the 'best fit' constants can be found. A general scheme to determine stability constants utilizing the mass law and mole balance expressions of a general equilibrium program has been formulated by Westall, et al. (9), but the available data in most adsorption studies are not sufficient for its use. Other schemes that would circumvent these data limitations are presently under consideration.

The final outcome of a modeling scheme that generates stability constants for surface species will hopefully be an extensive listing of surfaces, adsorbates, and the respective stability constants. At this time, such a collection appears to be an essential need of the adsorption modeling field. Perhaps one of the most significant contributions of this thesis is that it may provide the impetus to undertake this formidable task.
LITERATURE CITED


