

### Benthic Phosphorus Cycling in Lake Champlain: Results of an Integrated Field Sampling/Water Quality Modeling Study

Part A: Water Quality Modeling

By
Jeffrey C. Cornwell and Michael Owens,
University of Maryland Center for Environmental Sciences
Horn Point Laboratory
for HydroQual, Inc.

for Lake Champlain Basin Program

June 1999

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This technical report is the thirty-fourth in a series of reports prepared under the Lake Champlain Basin Program. Those in print are listed below.

#### Lake Champlain Basin Program Technical Reports

- 1. A Research and Monitoring Agenda for Lake Champlain. Proceedings of a Workshop, December 17-19, 1991, Burlington, VT. Lake Champlain Research Consortium. May, 1992.
- 2. Design and Initial Implementation of a Comprehensive Agricultural Monitoring and Evaluation Network for the Lake Champlain Basin. NY-VT Strategic Core Group. February, 1993.
- 3. (A) GIS Management Plan for the Lake Champlain Basin Program. Vermont Center for Geographic Information, Inc., and Associates in Rural Development. March, 1993.
  - (B) Handbook of GIS Standards and Procedures for the Lake Champlain Basin Program. Vermont Center for Geographic Information, Inc. March, 1993.
  - (C) GIS Data Inventory for the Lake Champlain Basin Program. Vermont Center for Geographic Information, Inc. March, 1993.
- 4. (A) Lake Champlain Economic Database Project. Executive Summary. Holmes & Associates. March 1993.
  - (B) Socio-Economic Profile, Database, and Description of the Tourism Economy for the Lake Champlain Basin. Holmes & Associates. March 1993
  - B) Socio-Economic Profile, Database, and Description of the Tourism Economy for the Lake Champlain Basin. Appendices. Holmes & Associates. March 1993
  - (C) Potential Applications of Economic Instruments for Environmental Protection in the Lake Champlain Basin. Anthony Artuso. March 1993.
  - (D) Conceptual Framework for Evaluation of Pollution Control Strategies and Water Quality Standards for Lake Champlain. Anthony Artuso. March 1993.
- 5. Lake Champlain Sediment Toxics Assessment Program. An Assessment of Sediment Associated Contaminants in Lake Champlain Phase 1. Alan McIntosh, Editor, UVM School of Natural Resources. February 1994.
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- 6. (A) Lake Champlain Nonpoint Source Pollution Assessment. Lenore Budd, Associates in Rural Development Inc. and Donald Meals, UVM School of Natural Resources. February 1994.
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- 7. Internal Phosphorus Loading Studies of St. Albans Bay. Executive Summary. VT Dept of Environmental Conservation. March 1994.
  - (A) Dynamic Mass Balance Model of Internal Phosphorus Loading in St. Albans Bay, Lake Champlain. Eric Smeltzer, Neil Kamman, Karen Hyde and John C. Drake. March 1994.
  - (B) History of Phosphorus Loading to St. Albans Bay, 1850 1990. Karen Hyde, Neil Kamman and Eric Smeltzer. March 1994.
  - (C) Assessment of Sediment Phosphorus Distribution and Long-Term Recycling in St. Albans Bay, Lake Champlain. Scott Martin, Youngstown State University. March 1994.
- 8. Lake Champlain Wetlands Acquisition Study. Jon Binhammer, VT Nature Conservancy. June 1994.
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  Deborah A. Moreau and Donna L. Parrish, VT Cooperative Fish & Wildlife Research Unit, University of Vermont. June 1994.
- 10. Population Biology and Management of Lake Champlain Walleye. Kathleen L. Newbrough, Donna L. Parrish, and Matthew G. Mitro, Fish & Wildlife Research Unit, University of Vermont. June 1994.
- 11. (A) Report on Institutional Arrangements for Watershed Management of the Lake Champlain Basin. Executive Summary. Yellow Wood Associates, Inc. January 1995.
  - (B) Report on Institutional Arrangements for Watershed Management of the Lake Champlain Basin. Yellow Wood Associates, Inc. January 1995.
  - (C) Report on Institutional Arrangements for Watershed Management of the Lake Champlain Basin. Appendices. Yellow Wood Associates, Inc. January 1995.
- 12. (A) Preliminary Economic Analysis of the Draft Plan for the Lake Champlain Basin Program. Executive Summary. Holmes & Associates and Anthony Artuso. March 1995
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- 18. Catalog of Digital Spatial Data for the Lake Champlain Basin . Vermont Center for Geographic Information, Inc. September 1996.
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- 25. Urban Nonpoint Pollution Source Assessment of the Greater Burlington Area. Urban Stormwater Characterization Project. James Pease, VT Dept. of Environmental Conservation. December 1997
- 26. Long-Term Water Quality and Biological Monitoring project for Lake Champlain. Cumulative Report for Project Years 1992- 1996. VT Dept of Environmental Conservation and NYS Dept of Environmental Conservation. March 1998.
- 27. Cumberland Bay PCB Study. Clifford W Callinan, NY State Dept. of Environmental Conservation; Lyn McIlroy, Ph.D., SUNY Plattsburgh; and Robert D. Fuller, PhD., SUNY Plattsburgh. October 1998.

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- 31. Estimation of Lake Champlain Basinwide Nonpoint Source Phosphorus Export, William Hegman, Associates in Rural Development, Inc., Deane Wang and Catherine Borer, UVM Water Resources & Lake Study Center, September 1999.
- 32. The Freshwater Mussels of the Lower Missisquoi Rivers: Current Status and the Potential for a Refugium from Zebra Mussel Impacts. Paul Marangelo, VT Agency of Natural Resources, Dept of Environmental Conservation. August 1999.
- 33. Ecological Effects of Sediment-Associated Contaminants in Inner Burlington Harbor, Lake Champlain. Tetra Tech, Inc. September 1999.
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This report was funded and prepared under the authority of the Lake Champlain Special Designation Act of 1990, P.L. 101-596, through the U.S. Environmental Protection Agency (EPA grant #EPA X 001840-01). Publication of this report does not signify that the contents necessarily reflect the views of the States of New York and Vermont, the Lake Champlain Basin Program, or the U.S. Environmental Protection Agency.

Lake Champlain Management Conference
U.S. EPA Region I
New England Interstate Water
Pollution Control Commission

# BENTHIC PHOSPHORUS CYCLING IN LAKE CHAMPLAIN: RESULTS OF AN INTEGRATED FIELD SAMPLING/WATER QUALITY MODELING STUDY

June 9, 1999

Project No: NENGO050

HydroQual, Inc.
Environmental Engineers and Scientists

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#### **EXECUTIVE SUMMARY**

Eutrophication caused by phosphorus enrichment is a major water quality management issue for Lake Champlain. Over the past fifteen years efforts have been made to reduce the magnitude of phosphorus discharged to the lake. These efforts include the continuation of phosphorus detergent bans in Vermont, New York and the Province of Quebec; the construction of phosphorus removal facilities at a number of Vermont municipal wastewater treatment plants; and the implementation of nonpoint source controls in various agriculturally-dominated watersheds that drain to Lake Champlain. Despite the implementation of these control measures, it appears that current phosphorus levels are too high in some areas (Smeltzer, 1992) and that further reductions are necessary.

The magnitude by which phosphorus inputs must be further reduced is complicated by the fact that the sediments within the lake may be acting as a source of phosphorus. The importance of these internal phosphorus loads was recognized during the development of a whole-lake phosphorus budget and total phosphorus water quality model of the lake (VTDEC, 1997). Included among the recommendations of that study was a call for additional research on internal phosphorus processes in the lake with particular emphasis on St. Albans Bay and Missisquoi Bay. The goal of the proposed research effort was to provide information which would confirm or modify mass balance terms representing internal phosphorus processes in the water quality model developed for the lake. The Lake Champlain Management Conference acting upon this recommendation issued an RFP calling for field and laboratory studies that could be used to better understand and quantify the internal phosphorus processes in Lake Champlain.

HydroQual, Inc., together with the Horn Point Environmental Laboratory (HPEL) of the University of Maryland, proposed a joint field/laboratory and water quality modeling study. Awarded a contract by Management Conference, HPEL conducted field studies which consisted of six field surveys conducted between July 1994 and November 1996, while HydroQual developed and calibrated a coupled water quality/sediment model of the lake. The field surveys, conducted by HPEL, included measurements of pore water and solid phase phosphorus, as well as measurements of sediment phosphorus flux. These sediment data provide a global look at the sediment phosphorus cycle in Lake Champlain. The results of the field investigation are detailed in a separate (but companion) report (Cornwell and Owens, 1998).

In addition to the field and laboratory investigations, this study has also led to the development of a new phosphorus-based eutrophication model of the lake. The new water quality model includes a coupled sediment nutrient flux submodel. The kinetic framework for the coupled eutrophication/sediment nutrient flux model draws from modeling efforts on the Chesapeake Bay system (Cerco and Cole, 1993, Di Toro and Fitzpatrick, 1993). The model segmentation used in this study was based on the BATHTUB model segmentation developed by the Vermont Department of Environmental Conservation (VTDEC). However, the model segmentation was expanded to include vertical segmentation for the deeper basins within the lake and the subdivision of the Northeast Arm into two horizontal segments. The model calibration presented in this report is the result of over 60 model runs which were made to obtain a set of model coefficients that are reasonable and reproduce the observed data.

The calibrated model reproduces many of the features of the phosphorus cycle in Lake Champlain. For the majority of the lake, the model computes the magnitude of the observed total phosphorus and properly distributes the phosphorus between the dissolved inorganic, dissolved organic and particulate organic fractions in both the sediment and the water column. The model also reproduces, for many regions of the lake, the temporal variation in the phosphorus cycle, including the timing and magnitude of algal blooms and the subsequent phosphorus limitation in the surface waters.

However, the model has difficulty reproducing the observed water column phosphorus concentrations in areas of the lake where low concentrations of dissolved oxygen are observed. These areas include St. Albans Bay, Missisquoi Bay and portions of the south lake. It is well known that dissolved oxygen in the overlying water column has a strong effect on sediment phosphorus fluxes. The fact that the model could not reproduce the low levels of dissolved oxygen in these areas of the lake may have contributed to the mis-calibration of the phosphorus dynamics. While the phosphorus loading to the lake is well documented, carbon loads to the lake are not as well documented. Improving estimates of carbon loads to the lake may improve the model's computations of dissolved oxygen resulting in an improved phosphorus calibration.

Other processes which may affect dissolved oxygen levels in the water column include submerged aquatic vegetation, benthic organisms and wind-induced sediment resuspension. The latter may also directly introduce sediment-bed stored phosphorus to the water column. None of these processes were directly included in the model framework, due to data and budget limitations.

However, two model sensitivity runs were performed in order to explore the two issues of dissolved oxygen mis-calibration and wind-induced sediment resuspension and their respective impacts on the model with respect to total phosphorus in the lake. One model sensitivity run involved the forced fit of dissolved oxygen to the observed data. The second sensitivity run attempted to simulate the effects of wind on the resuspension of phosphorus-rich lake sediments. Both sensitivity runs provided improved calibration results and therefore, merit additional research.

One important finding of this study, supported by analyses of both data and model computations, as well as by the work of other researchers (Martin et al., 1994), is that the response time of Lake Champlain to phosphorus reduction scenarios is on the order of decades. This is in part due to the low burial rates of phosphorus in the sediments of Lake Champlain.

#### CONCLUSIONS AND RECOMMENDATIONS

The sediment sampling program and coupled water quality/sediment model have provided useful information regarding the phosphorus cycle in Lake Champlain. The sediment data provide extensive temporal and spatial coverage of sediment fluxes, pore water and solid phase phosphorus concentrations. Estimates of sediment accretion rates have also been provided. The water quality/sediment model will prove to be a useful tool in order to determine how various remediation alternatives will effect Lake Champlain water quality.

However, additional research and study needs to be performed in order to determine why the model cannot reproduce the low dissolved oxygen observed in South Lake B, Missisquoi Bay and St. Albans Bay. Starting points for this analysis should include improved estimates of carbon loads to the system and additional studies of the effects of wind resuspension on phosphorus release from sediments. There also appears to be an under-estimation of the phosphorus load to St. Albans Bay. A sampling program designed to account for all phosphorus inputs to the Bay would improve the understanding of phosphorus cycling in the Bay. In particular, the sampling program should be designed to evaluate the role of the marshes as a potential phosphorus source to the lake.

Modifications to the water quality sampling programs are also recommended. The implementation of surface and bottom water sampling at locations where currently only composite samples are taken could improve the understanding of the role of stratification in Lake Champlain. Including a few more vertical sampling points in the deeper portions of the lake would also be desired, since bottom data taken at these stations represent only a small portion of the bottom surface area of the lake. Measurements of the individual fractions of phosphorus, including PO<sub>4</sub>, POP and DOP, would also improve the understanding of phosphorus cycling in the lake.

As for the model itself, finer horizontal segmentation in areas of concern and areas where there is an observable total phosphorus gradient could improve the model calibration. Also, extending the simulation period of the model to include several years of varying loading and meteorological conditions would be informative. Other analysis indicate that in high flow years there can be a greater phosphorus load to the system. For example, the phosphorus loading estimated by VTDEC for March 1990 through February 1992 was 884 mt/yr. However, the phosphorus load for the calibration period (1991) was only 600 mt/yr. Since 1991 appears to be

a low loading year, it may account, in part, for the underprediction of phosphorus in some locations. The model also appears to be sensitive to the partition coefficients assigned for phosphorus in the lake sediments. Additional solid phase and pore water data, as well as sediment density data, would allow for improved estimates of phosphorus distributions in the sediment of the lake.

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#### SECTION 1

#### INTRODUCTION

Phosphorus has long been recognized as the most critical nutrient controlling primary productivity and phytoplankton growth in most lakes (Vollenweider, 1968, Dillon, 1975, Carlson, 1977). Lake restoration programs aimed at reducing phytoplankton biomass in culturally eutrophic lakes have focused on reduction of external loads of phosphorus delivered to the lake. However, the response of these lakes to the phosphorus reduction programs has met with varied success. For example, Lake Washington's (located in the state of Washington) response to sewage diversion was rapid with marked reductions in the quantity of phytoplankton and the proportion of blue-green algae as well as in the concentrations of water column nutrients (Edmondson and Lehman, 1981). Lake Erie also responded favorably to reductions in point and nonpoint source phosphorus loadings with reductions in in-lake phosphorus, algal biomass and volume of anoxic water (Di Toro et al., 1987).

However, Shagawa Lake (Minnesota) failed to show significant positive response to major reductions in external phosphorus loading (Larsen et al., 1981). This failure to reduce algal biomass was attributed to internal cycling of phosphorus, associated with phosphorus release from the sediments. The recovery of Lake Sammamish (Washington) was slower than expected, based on consideration of flushing rate. The lake did, however, begin to show signs of recovery six years after phosphorus diversion. The cause for this slow recovery was attributed to internal cycling of phosphorus from the lake sediments (Welch, 1985).

Therefore, in order to ensure the predictive capability of water quality models used by water quality and living resource managers to assist in the development of a comprehensive management plan for Lake Champlain, it is important to fully understand sediment-water column interactions for phosphorus. It is also important to be able to incorporate information concerning phosphorus cycling gathered from field and laboratory experiments into a framework that can be included in water quality models of Lake Champlain.

#### 1.1 DESCRIPTION OF THE LAKE

Lake Champlain is a large freshwater body of water bordered by New York State to the west, Vermont to the east, and the Province of Quebec, Canada to the north. With a length of

170 km and a water surface area of 1,130 km<sup>2</sup>, it is one of the largest lakes in North America. The average depth of Lake Champlain is 22.8 meters with a maximum depth of 122 m. Lake Champlain is a morphologically complex body of water with numerous embayments (Figure 1-1). Due to its size, morphology, and loading sources, a variety of water quality conditions are found within its shores. Details of the lake's limnology, environment, and water uses have been previously reviewed by Meyer and Gruending (1979) and the Lake Champlain Basin Study (1978, 1979).

#### 1.2 HISTORY OF NUTRIENT MANAGEMENT

Eutrophication caused by phosphorus enrichment is a major water quality management issue for Lake Champlain. Measures for dealing with this issue, including implementation of a phosphorus detergent ban, were undertaken during the 1970's. Early studies were conducted to develop phosphorus loading estimates and compute a phosphorus budget. A subsequent study, the Lake Champlain Basin Study (1979), made recommendations concerning phosphorus management which were designed to hold constant or to reduce phosphorus loadings to the lake until 1990. These recommendations included continued phosphorus detergent bans, construction of phosphorus removal facilities and the implementation nonpoint source controls. The major recommendations of this study have been pursued and at least partially implemented. However, phosphorus levels in some areas of the lake continue to be of concern (Smeltzer, 1992).

In 1988, the states of New York and Vermont along with the Province of Quebec entered into a cooperative agreement by signing the Memorandum of Understanding on Environmental Cooperation on the Management of Lake Champlain. At the time of this agreement Vermont and New York developed a work plan which addressed eutrophication issues. The plan recognized that the eutrophication caused by phosphorus enrichment in Lake Champlain resulted from the cumulative affect of many individual sources and not a single major source. Knowing that broad based policies were needed, the 1988 Vermont and New York work plan developed management strategies to deal with the eutrophication issue.

Among the steps outlined in the 1988 work plan was to "Use [a] lake model to conduct a point and nonpoint source phosphorus load allocation and set basin-wide phosphorus management policies and priorities in a manner to attain the in-lake water quality criteria" (Vermont Agency of Natural Resources and New York State Department of Environmental Conservation, 1988).

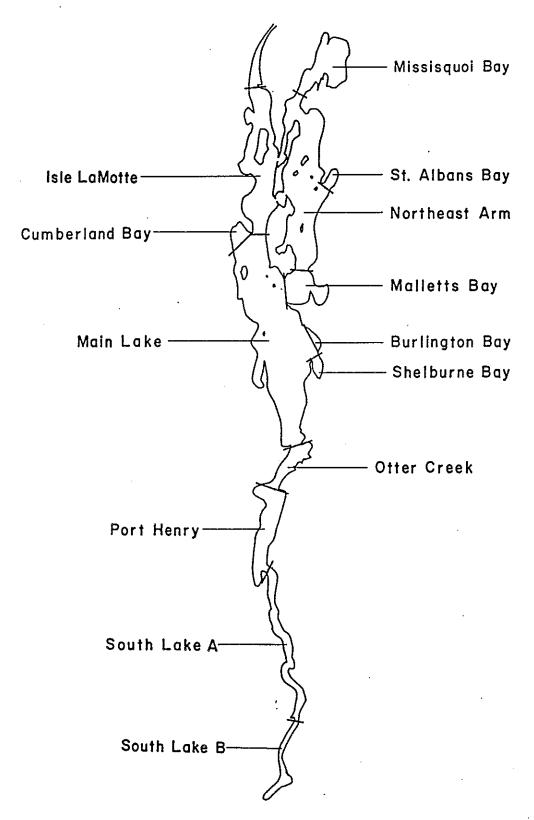


Figure 1-1. Lake Champlain Study Area

To address this step a modeling study was conducted by the Vermont Department of Environmental Conservation and the New York State Department of Environmental Conservation (1997). In that study a steady-state mass balance model was calibrated to data collected in 1990 and 1991. The model was used to determine the phosphorus load reductions necessary to attain in-lake total phosphorus concentration criteria.

#### 1.3 STUDY PURPOSE

While the 1997 Vermont Department of Environmental Conservation (DEC) and New York State Department of Environmental Conservation (DEC) study recognized the importance of internal sources of phosphorus; i.e., via sediment release, the model did not include an explicit mass balance based analysis of the sediment bed. This deficiency was noted in the recommendations of the study which called for conducting additional research on the internal phosphorus processes in the lake. To address this recommendation the Lake Champlain Management Conference and the U.S. EPA issued an RFP, which called for field investigations that would quantify the magnitude of the internal phosphorus sources in the lake and provide insight into the physical, biological, and chemical processes which affected them.

HydroQual, Inc. and researchers from the University of Maryland's Horn Point Environmental Laboratory responded with a proposal which included: (1) a field sampling program to measure sediment phosphorus flux and sediment composition, and (2) the application of a coupled water quality sediment nutrient flux model, which could be used to investigate the physical, biological, and chemical processes that affect internal phosphorus dynamics in Lake Champlain. The accepted proposal called for a phased study effort. In the first phase of the study the major emphasis was on the field studies which included sampling 14 stations within the lake. Also included in the first year effort was preliminary water quality modeling using a stand alone version of a sediment nutrient flux model developed as part of a water quality modeling package for Chesapeake Bay (DiToro and Fitzpatrick, 1993).

Recommendations made by HydroQual (1995) at the end of the first phase of the study included further sediment sampling and the development of a coupled water column/sediment model based on the Vermont DEC and New York State DEC 1990/1991 analysis. The Lake Champlain Management Conference agreed with these recommendations and funded the second phase of the study. This report summarizes the efforts of the calibration of the coupled water

column/sediment model. The results of the sediment surveys are included in a separate report (Cornwell and Owens, 1998).

#### 1.4 SCOPE OF MODEL DEVELOPMENT AND APPLICATION

Due to time and budget constraints, HydroQual relied heavily upon existing information available for Lake Champlain. A thorough phosphorus budget was developed by the VTDEC (1997) for the 1991 calendar year. Water quality data were also available to develop and calibrate a relatively simple eutrophication model of the lake. These data included phytoplankton biomass, (as indicated by chlorophyll-a), dissolved oxygen, BOD<sub>5</sub> and organic carbon. In-lake data were also available for organic and inorganic nitrogen and biogenic and dissolved silica. However, neither nitrogen nor silica data were available for the tributaries or waste water treatment facilities. Thus, it was not possible to estimate nitrogen or silica loading to the lake. Therefore, it was not possible to develop and calibrate a fully modern eutrophication model with nitrogen and silica state-variables. Rather a simplified framework, which included only phosphorus, carbon and dissolved oxygen state-variables, was chosen. Implicit in this framework is the assumption that phosphorus is the key nutrient limiting phytoplankton growth in Lake Champlain. Since it is known that freshwater lakes are generally phosphorus limited, this appears to be a reasonable assumption. A secondary assumption resulting from the framework chosen is that nitrification in the water column and sediments of the lake are small components of the overall oxygen balance within Lake Champlain.

The model developed during this study was designed to be an improvement over earlier modeling efforts conducted by the VTDEC (1997). The implementation of a time-variable, vertically-segmented water quality model with a coupled sediment submodel provides an improved tool to conduct analyses of remediation alternatives for Lake Champlain. It is hoped that the resultant model will be improved upon as more extensive data and field studies of phosphorus cycling in Lake Champlain become available.

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#### **SECTION 2**

#### **MODEL THEORY**

#### 2.1 INTRODUCTION

This section of the report details the theoretical basis used in the development of a time-variable vertically segmented model of phytoplankton growth and phosphorus cycling in Lake Champlain, including a coupled sediment nutrient flux submodel. The kinetic framework used for the coupled eutrophication/sediment nutrient flux model draws from modeling efforts on the Chesapeake Bay system (Cerco and Cole 1993, Di Toro and Fitzpatrick, 1993), Long Island Sound (HydroQual, 1991) and Massachusetts Bay (HydroQual, 1995). The importance of the sediment submodel is that it completes the lake mass balance for phosphorus and carbon, rather than treat the sediments as a boundary condition. This permits water quality managers to determine the role that sediment phosphorus may play in any remediation alternative chosen. In particular, the coupled model permits managers to determine the period of time required before the lake responds to planned phosphorus reductions.

In this study Lake Champlain was vertically segmented into two layers for the deeper sections of the lake. This was deemed necessary to more accurately reproduce the temperature, dissolved oxygen and dissolved inorganic phosphorus stratification observed in the water column data. The magnitude and timing of phosphate fluxes are strongly determined by water column temperature and dissolved oxygen concentrations. Therefore, it is necessary to properly model the observed temperature and dissolved oxygen in order to determine the role of the sediment in the phosphorus cycle in Lake Champlain.

#### 2.2 EUTROPHICATION MODEL

The eutrophication model utilizes the twelve state-variables shown in Table 2-1. Other variables, constructed from these primary variables, are also tracked within the lake. Phytoplankton chlorophyll-a (chl-a), is the most important of these secondary variables. The model framework, discussed below, incorporates these twelve state-variables and is designed to simulate the annual cycle of phytoplankton production, its relation to the supply of phosphorus and its effect on dissolved oxygen. The calculation is based on formulating the kinetics which

govern the interactions of the phytoplankton and the various forms of phosphorus, and the application of these kinetics to Lake Champlain within the context of mass conservation equations.

Table 2-1. State System Variables, Coupled Eutrophication/Chemical Equilibria Model

- 1. chlorinity (Cl)
- 2. phytoplankton carbon winter diatoms (Pc1)
- 3. phytoplankton carbon summer assemblage (Pc2)
- 4. particulate organic phosphorus (POP)
- 5. dissolved organic phosphorus (DOP)
- 6. orthophosphate (PO<sub>4</sub>)
- 7. particulate organic carbon (POC)
- 8. dissolved organic carbon (DOC)
- 9. algal exudate dissolved organic carbon (ExDOC)
- 10. dissolved oxygen equivalents (O₂)
- 11. dissolved oxygen (DO)
- 12. temperature (T)

#### 2.2.1 General Structure

Figures 2-1 through 2-3 present the principal kinetic interactions between phytoplankton, phosphorus, carbon and dissolved oxygen. In the phosphorus system kinetics (Figure 2-1), dissolved inorganic phosphorus or orthophosphate (PO<sub>4</sub>) is utilized by phytoplankton for growth. Phosphorus is returned from the phytoplankton biomass pool to the dissolved and particulate organic phosphorus pools and to PO<sub>4</sub> through endogenous respiration and predatory grazing. The various forms of organic phosphorus undergo hydrolysis and mineralization and are converted to PO<sub>4</sub> at temperature-dependent rates. Particulate organic phosphorus and phytoplankton also undergo settling to the sediment bed of the lake.

The kinetics of organic carbon are shown on Figure 2-2. Organic carbon sources can include anthropogenic inputs, terrestrial runoff and the by-products of biological production. Particulate organic carbon undergoes hydrolysis to form dissolved organic carbon. Dissolved organic carbon can undergo bacterially mediated oxidation. Particulate organic carbon also settles to the sediment bed.

Dissolved oxygen (Figure 2-3) is coupled to the other state-variables. The sources of oxygen included in the model are atmospheric reaeration and algal photosynthesis. The sinks of

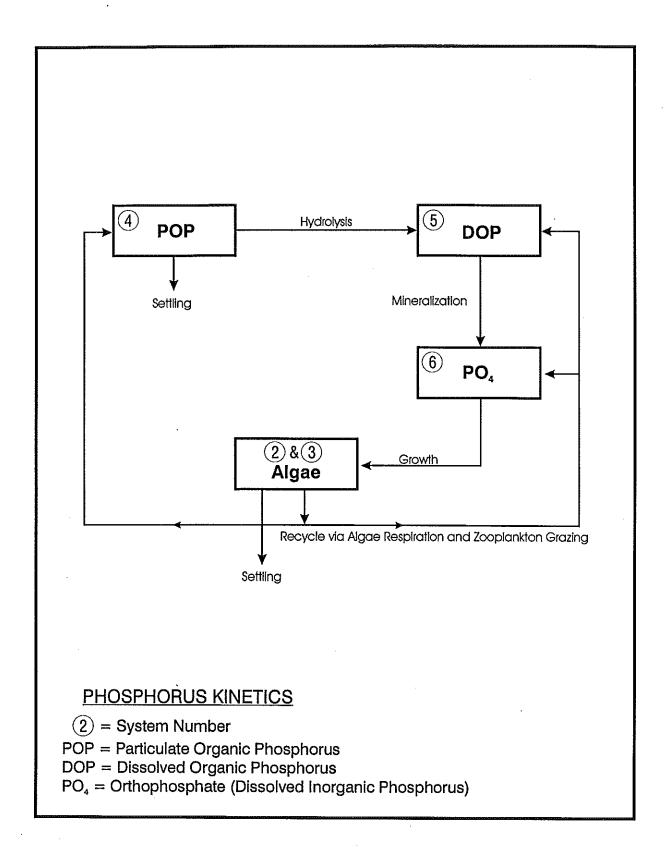


Figure 2-1. Phosphorus System Kinetics

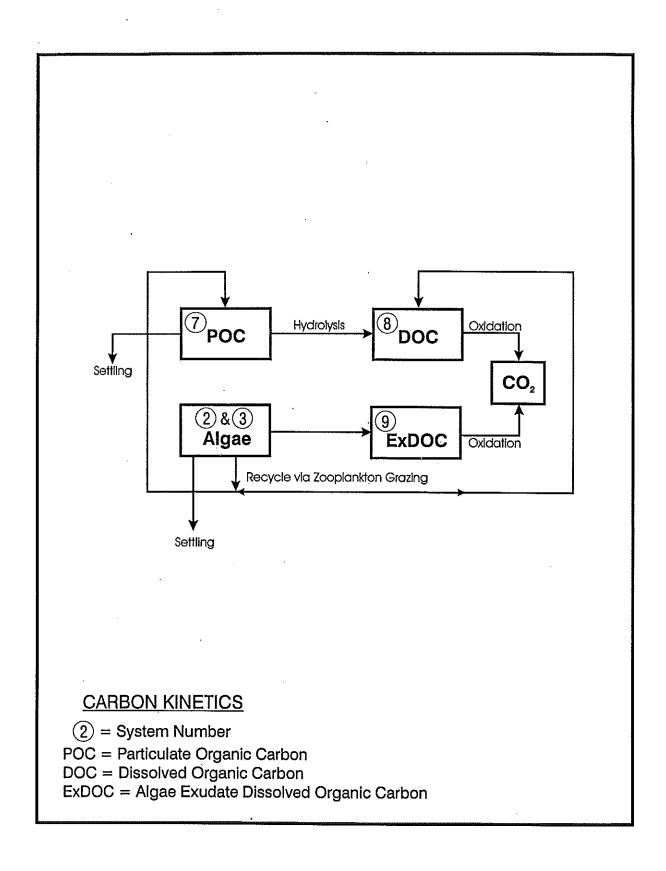


Figure 2-2. Carbon System Kinetics

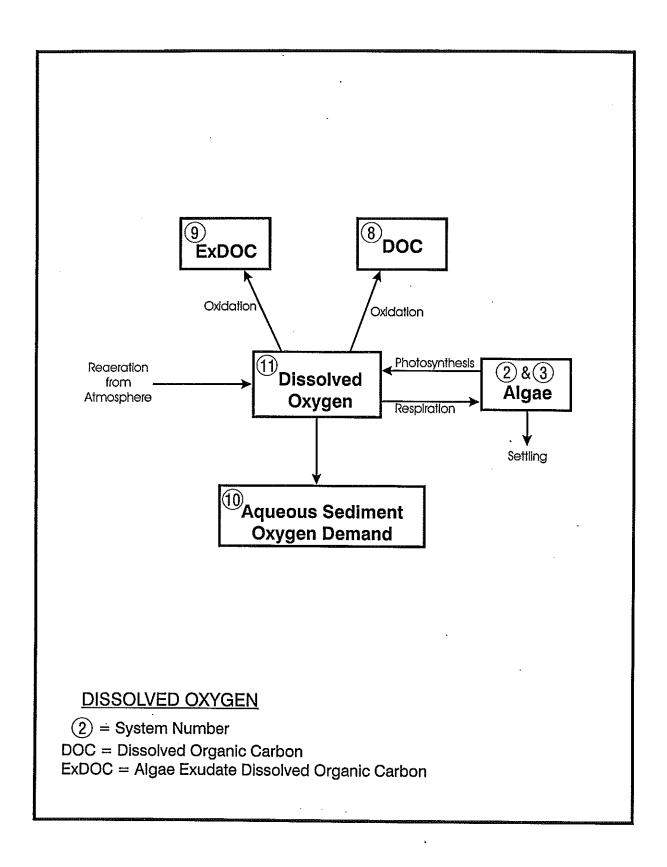


Figure 2-3. Dissolved Oxygen Kinetics

oxygen within the model include: algal respiration, oxidation of detrital algal carbon and organic carbon discharged from wastewater treatment plant facilities and nonpoint source discharges, and sediment oxygen demand (SOD).

The water quality model also includes a coupled sediment submodel. This model was originally developed by HydroQual (Di Toro and Fitzpatrick, 1993) for the joint U.S. EPA/U.S. Army Corps of Engineers study of Chesapeake Bay. The sediment submodel can be conceived of as modeling three processes: the deposition of particulate organic matter (POM) to the sediment from the water column; the decay or diagenesis of the POM in the sediment; and a balance between the flux of resulting dissolved end-products back to the overlying water column and the burial of dissolved and particulate end-products via sediment accretion.

#### 2.2.2 Chlorides and Temperature

Chlorides are modeled as a conservative substance and were used to verify the routing of freshwater flow within the lake and to calibrate the horizontal bulk exchange between model segments. The starting point for flow routing within the lake and for estimates of the bulk exchanges between model segments was work conducted by the VTDEC (1997). Temperature is modeled for two reasons. First, temperature was used to determine the bulk exchange between the vertically-segmented regions of the lake. This was accomplished by assigning a time-variable temperature profile to the surface layer of the lake and adjusting vertical dispersion coefficients to reproduce bottom temperatures. The second reason for modeling temperature is that temperature is very important in moderating the rates of chemical and biological reactions that occur within the lake.

#### 2.2.3 Phytoplankton

The present version of the water quality model considers two functional phytoplankton groups: winter diatoms and a summer mixed assemblage. These distinctions are made to recognize some of the physiological differences, in terms of optimal temperature, light, nutrient requirements, grazing pressures, etc., between the phytoplankton species that dominate in each of these seasons of the year. The diatom functional group is characterized as favoring low temperature and light conditions. The summer group represents a mixed population of phytoplankton, including greens, dinoflagellates and some diatoms. This group favors higher

temperature and light conditions. The winter and summer groups are not meant to represent any specific phytoplankton species. Rather, they attempt to reproduce the observation that species tend to change seasonally due to changing environmental conditions.

The kinetic framework used for both functional algal groups is largely the same. Differences between the groups are expressed by the choice of model coefficients. The growth rate formulation in the present model is affected by temperature, light and available nutrients  $(PO_4)$ , as per Equation 2-1:

$$G_{P} = G_{Pmax} \times G_{T}(T) \times G_{I}(I) \times G_{N}(N)$$
 (2-1)

(temperature) (light) (nutrients)

where

 $G_{T}(T)$  is the effect of temperature,

 $G_{I}(I)$  is the effect of light and light attenuation,

 $G_N(N)$  is the effect of nutrients (PO<sub>4</sub>) on growth.

Initial estimates of  $G_{Pmax}$  were based upon the literature and previous modeling studies and were subsequently refined during the calibration process. The selected maximum growth rates are then temperature-corrected using temporally and spatially dependent, water column temperature values computed by the water quality model. The temperature corrected growth rate is computed using one of the following equations, which relate  $G_{Pmax}(T)$ , the growth rate at ambient temperature, T, to  $G_{Pmax}(T_{opt})$ , the growth rate at the optimal temperature,  $T_{opt}$ :

$$G_{\text{Pmax}}(T) = G_{\text{Pmax}} \theta_{\text{P}}^{(T-T_{\text{opt}})} \qquad T < T_{\text{ont}}$$
 (2-2)

or

$$G_{p_{max}}(T) = G_{p_{max}} \theta_{p}^{(T_{opt}-T)} \qquad T > T_{opt}$$
 (2-3)

where  $\theta_P$  is the temperature correction coefficient. A principal difference between the winter diatom group and the summer group is that the diatom group has a much lower  $T_{opt}$  than does the summer group.

In the natural environment, the light intensity to which phytoplankton are exposed is not uniformly at the optimum value. At the surface and near-surface of the air-water interface, photo-inhibition can occur due to high light intensities, while at depths below the euphotic zone, light is not available for photosynthesis due to background and algal related turbidity. The modeling framework used in this study extends from a light curve analysis formulated by Steele (1962). This analysis accounts for the effect of the variations of available light as a function of depth. The light intensity, I(z), at any depth, z, is related to the incident surface intensity,  $I_{av}$ , by the extinction coefficient,  $k_e$ , through the formula  $I(z) = I_{av} \exp(-k_e z)$ . The reduction factor due to both the effect of non-optional light intensity and decreasing intensity as a function of depth is obtained by averaging the reduction factor over the depth H, and over time. Thus the light attenuated growth rate factor,  $G_I(I)$ , is represented by the following integral:

$$G_{I}(I) = \frac{1}{T} \int_{0}^{f} \frac{1}{H} \int_{0}^{H} \frac{I(z)}{I_{s}} e \left[ \frac{-I(z)}{I_{s}} + 1 \right] dz dt$$
 (2-4)

where:

 $I(z) = I_{av} e^{-kez}$ , (ly/day),

f = the photo period or fraction of daylight,

H = water column depth, (m),

 $k_e$  = the total extinction coefficient, computed from the sum of the base, non-algal related, light attenuation,  $k_{ebase}$ , and the self-shading attenuation due to the ambient phytoplankton population  $k_e P_{chl-a}$ ,  $(m^{-1})$ ,

 $k_{ebase}$  = the base extinction coefficient due to background conditions created by natural turbidity or exogenous inputs and absorption by water molecules, (m<sup>-1</sup>)

k<sub>c</sub> = the algal related extinction coefficient per unit of chlorophyll, (m<sup>2</sup>/mg chl-a),

 $P_{chl-a}$  = the ambient phytoplankton population as chlorophyll, (mg chl-a/L), where  $P_{chl-a}$  =  $P_c/a_{cchl}$ ,

 $P_c$  = the ambient phytoplankton population as carbon, (mg C/L),

 $a_{cchl}$  = the ratio of algal carbon to algal chlorophyll, (mg C/mg chl-a),

I<sub>o</sub> = the total daily incident light intensity at the surface, (ly/day), and

 $I_s$  = the saturating light intensity, (ly/day).

Integrating Equation 2-4 results in Equation 2-5

$$G_{I}(I) = \frac{ef}{k_{e}H} \left[ exp\left(\frac{-I_{o}}{I_{s}} e^{-k_{e}H}\right) - exp\left(-\frac{I_{o}}{I_{s}}\right) \right]$$
(2-5)

The effects of various nutrient concentrations on the growth of phytoplankton have been investigated, and the results are quite complex. As a first approximation to the effect of nutrient concentration on the growth rate, it is assumed that the phytoplankton population in question follows Monod growth kinetics with respect to the important nutrients. That is, at an adequate level of substrate concentration, the growth rate proceeds at the saturated rate for the ambient temperature and light conditions. However, at low substrate concentration, the growth rate becomes linearly proportional to substrate concentration. Thus, for a nutrient with concentration  $N_j$  in the  $j^{th}$  segment, the factor by which the saturated growth rate is reduced in the  $j^{th}$  segment is  $N_j/(K_m + N_j)$ . The constant,  $K_m$ , which is called the Michaelis, or half-saturation constant, is the nutrient concentration at which the growth rate is half the saturated growth rate. Since phosphorus is the sole nutrient considered in this analysis, the Michaelis-Menton expression is evaluated for phosphorus and the resulting value is chosen to reduce the nutrient saturated growth rate,

$$G_N(N) = \frac{PO_4}{K_{mp} + PO_4}$$
 (2-6)

Three terms have been included in the modeling framework to account for the loss of phytoplankton biomass: endogenous respiration, sinking or settling from the water column and grazing. Endogenous respiration is the opposite process of photosynthesis, and as such, contributes to the biomass loss rate of the phytoplankton population:

$$k_{rp} = k_{rg} G_p + k_{rb} \theta^{T-20}$$
 (2-7)

where  $k_{rp}$  is the net respiration rate,  $k_{rg}$  is respiration associated with growth,  $k_{rb}$  is the basal respiration rate, and  $\theta$  is the temperature correction for the basal respiration rate. If the respiration rate of the phytoplankton as a whole is greater than the growth rate, there is a net loss of phytoplankton carbon or biomass.

The sinking of phytoplankton is an important contribution to the overall mortality of the phytoplankton population. Published values of the sinking velocity of phytoplankton, mostly in quiescent laboratory conditions, range from 0.1 to 18.0 m/day. In some instances, however, the settling velocity is zero or negative. Actual settling rates in natural waters are a complex phenomenon, affected by vertical turbulence, density gradients and the physiological state of the different species of phytoplankton. An important factor shown to influence the physiological state of the algae is nutrient availability. Work by Bienfang et al. (1982) and Culver and Smith (1989) has shown that the settling rate of marine diatoms is increased primarily by low concentrations of silica, although low concentrations of nitrogen and low light availability were also found to increase diatom sinking rates. Sinking, then, can contribute to the overall mortality of the algal population. In addition, the settling of phytoplankton can be a significant source of nutrients to the sediments and can play an important role in the generation of sediment oxygen demand. For these reasons, a term representing phytoplankton settling has been included in the algal mortality expression, and is determined by:

$$k_{sP} = \frac{v_{sPb}}{H} \theta_{sP}^{(T-20)} + \frac{v_{sPn}}{H} [1 - G_N(N)] \theta_{sP}^{(T-20)}$$
 (2-8)

where  $k_{sP}$  is the net effective algal loss rate due to settling (day<sup>-1</sup>),  $v_{sPb}$  is the base settling velocity of phytoplankton (m/day),  $v_{sPn}$  is the nutrient dependent settling rate (m/day),  $G_N(N)$  is defined as per Equation 2-6,  $\theta_{sP}$  is the temperature correction coefficient, and H is the depth of the model segment, (m).

Zooplankton grazing may, depending upon the time of year and zooplankton biomass levels, be an important loss rate for phytoplankton. Rather than attempt to model the complex and dynamic process of zooplankton grazing and growth, a simple first order loss rate representing the effect of zooplankton grazing on algal biomass is included in the model. The loss rate due to grazing is temperature corrected as per Equation 2-9,

$$k_{grz}(T) = k_{grz}(20^{\circ}C) \theta_{grz}^{(T-20)}$$
 (2-9)

where  $k_{grz}(T)$  is the temperature corrected loss rate due to zooplankton grazing and  $k_{grz}(20^{\circ}\text{C})$  is the loss rate at 20°C. The units of  $k_{grz}$  are day<sup>-1</sup>. The total loss rate for phytoplankton is then the sum of Equations 2-7, 2-8 and 2-9.

#### 2.2.4 Stoichiometry and Phosphorus Uptake Kinetics

A principal component in the mass balance equation for the phosphorus state-variables in the model framework is phosphorus uptake associated with algal growth. In order to quantify phosphorus uptake by algae it is necessary to specify the phytoplankton stoichiometry in units of phosphorus uptake per mass of phytoplankton biomass synthesized. For carbon as the unit of phytoplankton biomass, the relevant ratio is the mass of phosphorus per unit mass of carbon. An analysis of a large and divergent number of marine data sets by Redfield (1963) indicated that, in general, nutrient-saturated algal biomass was comprised of carbon, nitrogen and phosphorus in the following molar or atomic ratio, 106C:16N:1P or the following ratio based on weight, 40C:7N:1P. Based on the nutrient status of Lake Champlain and a limited set of particulate organic carbon and particulate organic phosphorus data, it appears as if the assumption of in-lake phytoplankton being in constant Redfield stoichiometry is not valid.

It has been shown in the literature (Rhee 1978, Chalup and Laws, 1990) that phytoplankton can adjust their cellular structure during periods of nutrient limitation stress. Therefore, the Lake Champlain eutrophication model allows for variable stoichiometry of the cellular makeup of phytoplankton during periods of nutrient limitation. This process is implemented in the model framework via the use of the following equation:

$$\frac{P}{C} = \frac{1}{x_1 + (x_2 - x_1)e^{-x_3PO_4}}$$
 (2-10)

 $x_1$  = carbon to phosphorus ratio under nutrient saturated conditions,

x<sub>2</sub> = maximum carbon to phosphorus ratio under nutrient limited conditions,

 $x_3$  = coefficient which determines rate at which the algal stoichiometry changes

as a function of PO<sub>4</sub>,

 $PO_4$  = concentration of available  $PO_4$ .

The behavior of this equation is shown in Figure 2-4. At high concentrations of  $PO_4$ , i.e., nutrient saturated conditions, the carbon to phosphorus ratio for phytoplankton is at the Redfield ratio, i.e., 40:1. At  $PO_4$  concentrations less than 10  $\mu$ g P/L, there is a noticeable change in the carbon to phosphorus ratio. The maximum allowable carbon to phosphorus ratio for this model is 90:1 for the winter group and 200:1 for the summer group.

Once the stoichiometric ratio for phosphorus has been determined, the phosphorus mass balance equations may be written in much the same way as for the phytoplankton biomass. The principal processes determining the distribution of phosphorus among the various pools are: uptake of inorganic phosphorus by phytoplankton for cell growth, the release of inorganic and organic phosphorus algal respiration and predation processes, and the recycling of organic phosphorus to PO<sub>4</sub> via bacterial hydrolysis and mineralization.

Rather than attempt to model bacterial recycling of organic phosphorus by including a bacterial system (for which there are little or no data with which to calibrate against), a phytoplankton-dependent saturated recycle formulation (Di Toro and Matystik, 1980) was used. The assumption is made that bacterial biomass, and hence the recycling rate, is proportional to the phytoplankton biomass. A number of field and laboratory studies (Hendry, 1977, Lowe, 1976, Menon et al., 1972, Jewell and McCarty, 1971) support this hypothesis. The saturated recycling relationship may be written:

$$k(T) = k'(20^{\circ}C) \theta^{(T-20)} \frac{P_c}{K_{mPc} + P_c}$$
 (2-11)

where k(T) is the temperature corrected recycling rate, k'(20°C) is the saturated recycling rate at 20°C,  $P_c$  is the phytoplankton biomass,  $K_{mPc}$  is the half-saturation constant for recycling,  $\theta$  is the temperature correction coefficient. Basically, this mechanism employs a first-order recycling rate which decreases if the algal population is small, yet does not permit the recycling rate to

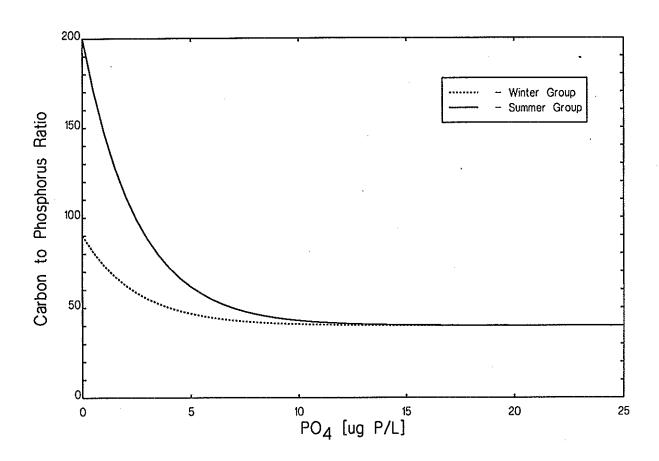


Figure 2-4. Behavior of Model's Variable Stoichiometry

increase in an unlimited fashion as phytoplankton biomass increases (instead the mechanism permits zero-order recycling when the phytoplankton greatly exceed the half-saturation constant). The latter assumes that at higher population levels, other factors are limiting recycling rates or kinetics, so that it proceeds at its maximum zero-order rate.

#### 2.2.5 Phosphorus

The Lake Champlain eutrophication model includes three principal phosphorus forms: dissolved organic phosphorus (DOP), particulate organic phosphorus (POP) and dissolved inorganic phosphorus (PO<sub>4</sub>). Dissolved inorganic phosphorus is utilized by phytoplankton for growth. Phosphorus is returned to the various organic and inorganic forms via respiration and predation. A fraction of the phosphorus released during phytoplankton respiration and predation is in the inorganic form and readily available for uptake by other viable algal cells. The remaining fraction released is in the dissolved and particulate organic forms. The organic phosphorus must undergo a mineralization or bacterial decomposition into inorganic phosphorus before it can be used by phytoplankton.

### 2.2.6 Organic Carbon

Three organic carbon state variables are considered: dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved algal exudate (ExDOC). The principal sources of organic carbon include: anthropogenic inputs and natural runoff; detrital algal carbon, which is produced as a result of algal death and predation; and dissolved organic carbon exudate from phytoplankton. Zooplankton utilize and redistribute algal carbon to the organic carbon pools via grazing, assimilation, respiration and excretion. Since zooplankton are not directly included in the model, the redistribution of algal carbon by zooplankton is simulated by empirical distribution coefficients. An additional term, representing the excretion of DOC by phytoplankton during photosynthesis, is included in the model. This algal exudate is quite reactive and has a reaction rate for oxidation which is greater than the DOC oxidation rate.

#### 2.2.7 Dissolved Oxygen

A by-product of photosynthetic carbon fixation is the production of dissolved oxygen. The rate of oxygen production (as well as nutrient uptake) is proportional to the growth rate of the

phytoplankton, since its stoichiometry is fixed. The source of oxygen produced via photosynthesis is accounted for by multiplying the phytoplankton growth by the oxygen to carbon ratio of  $32 \text{ mg O}_2/12 \text{ mg C}$ .

Oxygen-deficient or under-saturated waters are replenished via atmospheric reaeration. The reaeration coefficient is a function of the temperature and wind and is computed using Equation 2-12, as reported in the WASP 4.0 manual (Ambrose et al., 1988),

$$k_a(T) = \frac{(-0.46W + 0.136W^2)}{H} \theta_a^{(T-20)}$$
 (2-12)

where

W = wind speed, (m/s)

H = depth, (m),

 $\theta_a$  = temperature coefficient.

As per the formulation used by Ambrose et al. (1988) a minimum value of 1.6/H /day is imposed on  $k_a$  at 20°C. Dissolved oxygen saturation in freshwater is a function of temperature and is determined via Equation 2-13 (APHA, 1985):

$$DO_{sat} = \exp \left(-139.34411 + \frac{1.575701 \times 10^5}{T} - \frac{6.6423087 \times 10^7}{T^2}\right)$$
 (2-13)

$$+\frac{1.2438\times10^{10}}{T^3}-\frac{8.621949\times10^{11}}{T^4}$$

where T is temperature in Kelvin.

Dissolved oxygen is diminished in the water column model as a result of algal respiration, which is the reverse process of photosynthesis, as a result of the oxidation of carbonaceous material (including detrital phytoplankton), and as a consequence of sediment oxygen demand.

#### 2.3 SEDIMENT SUB-MODEL

Traditionally, models of phosphorus cycling and sediment flux have fit into one of two categories: (1) models which determine the interstitial water concentration distribution of phosphate, or (2) models specifically designed to compute phosphate fluxes. Models used to determine interstitial water concentrations of phosphate relate diagenetic production of phosphate to the resulting pore water concentration distribution (Berner, 1974, Berner, 1980, van Cappellen and Berner, 1988) and have usually been one-dimensional vertically and steady-state. Models designed to compute phosphate fluxes include empirical models relating phosphate flux to an extracted fraction of the phosphorus concentration of the sediment (Kamp-Nielsen, 1975, Jorgensen et al., 1975, Nurnberg, 1988) and more detailed, vertically segmented models (Ishikawa and Nishimura, 1989, Van der Molen, 1991), which consider iron oxyhydroxide trapping and relate phosphate flux to overlying water dissolved oxygen concentrations, but which also depend on observations of interstitial water phosphorus concentrations.

Recently, HydroQual (Di Toro and Fitzpatrick, 1993) developed a modeling framework which considers both the diagenetic production of phosphate and the mechanism of iron oxyhydroxide trapping. This modeling framework was developed as part of the Chesapeake Bay water quality modeling effort and was successfully calibrated against an extensive set of sediment flux, sediment composition and interstitial pore water measurements collected in Chesapeake Bay. This modeling framework has also been applied to an extensive set of water column and flux measurements obtained from the MERL mesocosm studies obtained from the University of Rhode Island and has been incorporated in water quality models developed for the Long Island Sound Study, the New York Harbor complex and the Massachusetts Bays system. An overview of this sediment nutrient flux submodel follows.

#### 2.3.1 Model Framework

The sediment model is based on the principle of mass balance. The sediment receives fluxes of particulate organic carbon (POC) and particulate organic phosphorus (POP). This is collectively referred to as particulate organic matter (POM). Mineralization, which is termed diagenesis, produces soluble end-products. These end-products can react in the aerobic and anaerobic layers of the sediment. The difference between the resulting aerobic layer dissolved concentration and the overlying water concentration determines the flux to or from the sediment.

The magnitude of the flux is determined by the surface mass transfer coefficient. The situation is diagramed in Figure 2-5.

#### 2.3.2 Diagenesis

The multi-class G model (Westrich and Berner, 1984) is used to model the diagenesis of POM. Each class represents a portion of the organic material that reacts at a specific rate. The reaction rates for each class are approximately an order of magnitude smaller than the previous class. For this application three G classes are chosen. The three classes represent three scales of reactivity: reactive (~20 day half-life); refractory (~1 year half-life); and inert (i.e., conservative).

The kinetic equations for particulate organic carbon and phosphorus are analogous. Let  $G_{POC,i}$  be the concentration of POC in the i<sup>th</sup> diagenesis class (I=1, 2, or 3). The kinetic equation used for diagenesis is:

$$H \frac{dG_{POC,i}}{dt} = -K_{GPOC,i}\theta_{GPOC,i}^{(T-20)}G_{POC,i}H + J_{GPOC,i}$$
(2-14)

where:

H = depth of the active sediment layer [m],

 $G_{POC,i}$  = concentration of particulate organic carbon in reactivity class I,

 $K_{GPOC,i}$  = first order reaction rate coefficient ( $K_{GPOC,3} = 0$ ) [day-1],

 $\theta_{GPOC,i}$  = temperature coefficient,

 $J_{GPOC,i}$  = POC flux of the i<sup>th</sup> G class to the sediment from the overlying water, [mg C/m<sup>2</sup>-day].

The water column sources that contribute to each reactivity class are:

 $J_{GPOC,1} = f_{GI}J_{POC},$ 

 $J_{GPOC,2} \ = \ f_{G2}J_{POC},$ 

 $J_{GPOC,3} = f_{G3}J_{POC}$ 

## SEDIMENT FLUX MODEL

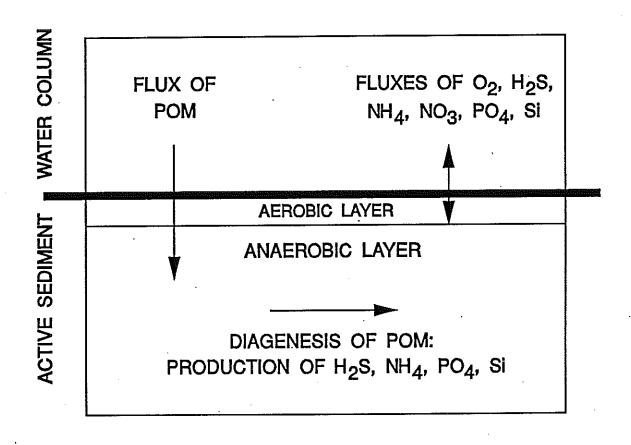


Figure 2-5. Sediment Model Framework

where:

 $f_{GI}$  = fraction of water column POC that is in reactivity class  $G_1$ ,  $f_{G2}$  = fraction of water column POC that is in reactivity class  $G_2$ ,  $f_{G3}$  = fraction of water column POC that is in reactivity class  $G_3$ .

Carbon diagenesis flux,  $J_c$ , is computed from the rates of mineralization of the labile and refractory G classes:

$$J_{C} = \sum_{i=1}^{2} K_{GPOC,i} \theta_{GPOC,i}^{(T-20)} G_{POC,i} H$$
 (2-15)

Phosphorus diagenesis flux,  $J_P$ , is completely analogous. The reaction rates and temperature coefficients are analogous to those listed above for carbon.

$$J_{P} = \sum_{i=1}^{2} K_{GPOP,i} \theta_{GPOP,i}^{(T-20)} G_{POP,i}^{H}$$
(2-16)

#### 2.3.3 The General Sediment Model Equations

The flux component of the sediment model is constructed using two mass balance equations: one for the aerobic layer, denoted as layer 1, and a second for the anaerobic layer, denoted as layer 2. Figure 2-6 presents the notation. The equations are expressed in terms of the total concentration of the chemical. The distribution between particulate and dissolved fractions is modeled using a linear partitioning model. The mass balance equations of the model can be expressed in a general from which is quite convenient for numerical solution. The layer 1 and 2 equations are:

$$H_{1} \frac{dC_{T1}}{dt} = K_{L01} (f_{d1}C_{T1} - C_{d0}) + W_{12} (f_{p2}C_{T2} - f_{p1}C_{T1})$$

$$+ K_{L12} (f_{d2}C_{T2} - f_{d1}C_{T1}) - K_{1}H_{1}C_{T1} + J_{T1}$$
(2-17)

# SEDIMENT FLUX MODEL

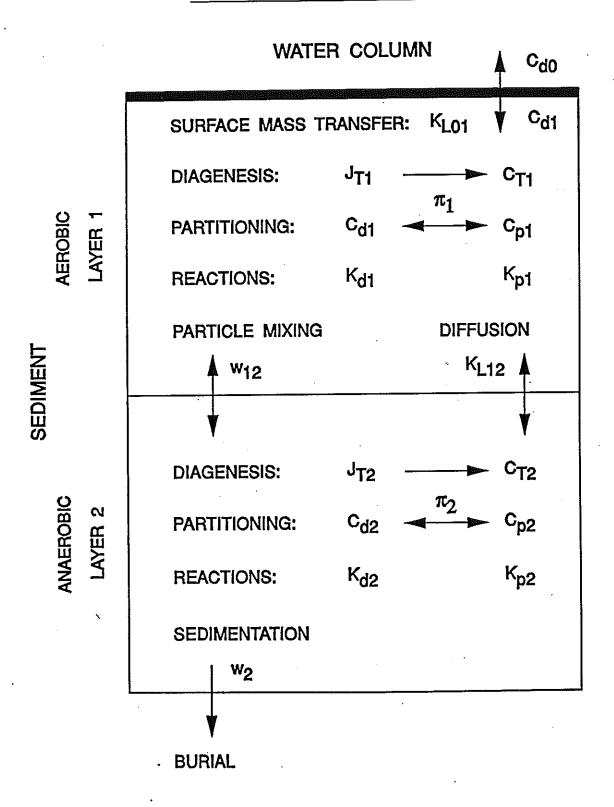


Figure 2-6. General Sediment Model Framework

$$H_{2} \frac{dC_{T2}}{dt} = -w_{12}(f_{p2}C_{T2} - f_{p1}C_{T1}) - K_{L12}(f_{d2}C_{T2} - f_{d1}C_{T1})$$

$$- K_{2}H_{2}C_{T2} - w_{2}C_{T2} + J_{T2}$$
(2-18)

where:

 $C_{T1}$  = total concentration in layer 1 [mg/m<sup>3</sup>],

 $C_{T2}$  = total concentration in layer 2 [mg/m<sup>3</sup>],

 $J_{T1}$  = total source into layer 1 [mg/m<sup>2</sup>-day],

 $J_{T2}$  = total source into layer 2 [mg/m<sup>2</sup>-day],

 $H_i$  = depth of layer 1 [m],

 $H_2$  = depth of layer 2 [m],

 $K_{L01}$  = aqueous mass transfer coefficient between layer 1 and the overlying water

[m/day],

 $K_{L12}$  = aqueous mass transfer coefficient between layer 1 and layer 2 [m/day],

 $w_{12}$  = particle mixing velocity between layer 1 and layer 2 [m/day],

w<sub>2</sub> = sedimentation velocity out of layer 2 [m/day],

 $K_1$  = first order decay rate coefficient removal process in layer 1 [day<sup>-1</sup>],

 $K_2$  = first order decay rate coefficient removal process in layer 2  $[T^{-1}]$ .

The dissolved and particulate concentrations and fractions are:

C<sub>d0</sub>, dissolved concentration in overlying water column, mg/m<sup>3</sup>

 $C_{d1}$ , dissolved concentration in layer 1, mg/m<sup>3</sup>,  $C_{d1} = f_{d1} C_{T1}$ 

 $f_{d1}$ , dissolved fraction in layer 1,  $f_{d1} = 1 / (1 + m_1 \pi_1)$ 

 $C_{p1}$ , particulate concentrations in layer 1, mg/m<sup>3</sup>,  $C_{p1} = f_{p1}C_{T1}$ 

 $f_{pl}$ , particulate fraction in layer 1,  $f_{pl} = 1 - f_{dl}$ 

 $C_{d2}$ , dissolved fraction in layer 2, mg/m<sup>3</sup>,  $C_{d2} = f_{d2}C_{T2}$ 

 $f_{d2}$ , dissolved fraction in layer 2,  $f_{d2} = 1 / (1 + m_2 \pi_2)$ 

 $C_{p2}$ , particulate concentration in layer 2, mg/m<sup>3</sup>,  $C_{p2} = f_{p2}C_{T2}$ 

 $f_{p2}$ , particulate fraction in layer 2,  $f_{p2} = 1 - f_{d2}$ 

where:

 $m_1$  = solids concentration in layer 1 (aerobic layer), kg/L,

m<sub>2</sub> = solids concentration in layer 2 (anaerobic layer), kg/L,

 $\pi_1$  = partition coefficient in layer 1, L/kg,

 $\pi_2$  = partition coefficient in layer 2, L/kg.

#### 2.3.3.1 Surface Mass Transfer Coefficient and Reaction Velocities

The surface mass transfer coefficient,  $K_{L01}$ , quantifies the mixing between layer 1 and the overlying water. The critical observation is that it can be related to the sediment oxygen demand, SOD. The SOD is the mass flux of dissolved oxygen into the sediment. Thus, it can be calculated from the mass transfer equation:

SOD 
$$\approx D_1 \frac{d[O_2]}{dz}|_{z=0} \approx D_1 \frac{[O_2(0)] - [O_2(H_1)]}{H_1} = \frac{D_1}{H_1} [O_2(0)]$$
 (2-19)

where a straight line approximation to the derivative is used. The second equality follows from  $[O_2(H_1)] = 0$ , since  $H_1$  is the depth of zero oxygen concentration. Therefore, the surface mass transfer coefficient can be expressed as:

$$K_{L01} = \frac{D_1}{H_1} = \frac{SOD}{[O_2(0)]} = s$$
 (2-20)

which is the ratio of SOD and overlying water oxygen concentration. For notational simplicity this ratio is termed s.

The reaction rate in the aerobic layer is formulated as a conventional first order reaction with reaction rate constant  $K_1$ . The term in the layer 1 equation is  $K_1H_1$ . The depth of the aerobic zone follows from the definition of the surface mass transfer coefficient:  $s = D_1/H_1$ . Hence  $K_1H_1 = K_1D_1/s$ . The reaction velocity, which has units m/day, is defined as:

$$\kappa_1 = \sqrt{D_1 K_1} \tag{2-21}$$

The square root is used to conform to the parameter group that appears in the spatially continuous form of the model. With these definitions the reaction rate - aerobic layer depth product becomes:

$$K_1 H_1 = \frac{\kappa_1^2}{s}$$
 (2-22)

The reaction velocity in layer 2 is defined for convenience of nomenclature only.

$$\kappa_2 = K_2 H_2 \tag{2-23}$$

It has units of m/day. However, it is not equivalent to the aerobic layer reaction velocities which include a diffusion coefficient as well as a reaction rate constant.

With these definitions the layer 1 and 2 equations become:

$$H_{1} \frac{dC_{T1}}{dt} = s(f_{d1}C_{T1} - C_{d0}) + w_{12}(f_{p2}C_{T2} - f_{p1}C_{T1})$$
 (2-24)

+ 
$$K_{L12}(f_{d2}C_{T2} - f_{d1}C_{T1}) - \frac{\kappa^2}{s}C_{T1} + J_{T1}$$

$$H_{2} \frac{dC_{T2}}{dt} = -w_{12}(f_{p2}C_{T2} - f_{p1}C_{T1}) - K_{L12}(f_{d2}C_{T2} - f_{d1}C_{T1})$$

$$- \kappa_{2}C_{T2} - w_{2}C_{T2} + J_{T2}$$
(2-25)

#### 2.3.3.2 Particulate Phase Mixing

The rate of mixing of sediment particles by macrobenthos (bioturbation) has been quantified by estimating the apparent particle diffusion coefficient. The variation has been found to be proportional to the biomass of the benthos. In addition, it has been found that bethic biomass is correlated to the carbon input to the sediment (Maughan, 1986; Robbins et al., 1989). In order to make the model self-consistent - that is to use only internally computed variables in the parameterization - it seems reasonable to assume that benthic biomass is proportional to the labile carbon in the sediment which is calculated by the model as  $G_{POC,1}$ .

A series of experiments have examined the relationship between particle mixing due to benthic organisms and the overlying water oxygen concentration. There is a general dependency of mixing rate on DO, with the lower rates occurring at the lower DO concentration. This dependency is modeled using a Michaelis Menton expression. The particle mixing mass transfer coefficient that results is:

$$\mathbf{w}_{12}^{*} = \mathbf{D}_{p} \frac{\theta_{Dp}^{(T-20)}}{\mathbf{H}_{2}} \frac{\mathbf{G}_{POC,1}}{\mathbf{G}_{POC,R}} \frac{[\mathbf{O}_{2}(0)]}{\mathbf{K}_{M,Dp} + [\mathbf{O}_{2}(0)]}$$
(2-26)

with units [L/T]. The superscript \* is used to denote this formulation from the final expression for  $w_{12}$  that is developed below. The parameter values are:

 $D_p$  = diffusion coefficient for particle (m<sup>2</sup>/d),

 $\theta_{Dp}$  = temperature coefficient for  $D_p$ ,

 $G_{POC,R}$  = reference concentration for  $G_{POC,1}$  (mg/m<sup>3</sup>),

 $K_{M,Dp}$  = particle mixing half saturation constant for oxygen (mg/L).

#### 2.3.3.3 Benthic Stress

In addition to the reduction in particle mixing velocity due to the instantaneous oxygen concentration, it has been found necessary to include a more lasting effect. In particular, if anoxia occurs the benthic fauna population is reduced or eliminated. This is modeled using a first order differential equation that accumulates stress, S, when overlying water dissolved oxygen is below the particle mixing half saturation constant for oxygen,  $K_{M,Dp}$ . Thus:

$$\frac{dS}{dt} = -K_s S + \frac{K_{M,Dp}}{K_{M,Dp} + [O_2(O)]}$$
 (2-27)

where:

= accumulated benthic stress, day,

= first order decay coefficient for accumulated stress, day-1.

The behavior of this formulation can be understood by evaluating the limiting steady state stresses at the two oxygen extremes:

as 
$$[O_2(0)] \rightarrow 0$$
 then  $K_s S \rightarrow 1$  and  $(1 - K_s S) \rightarrow 0$   
as  $[O_2(0)] \rightarrow \infty$  then  $K_s S \rightarrow 0$  and  $(1 - K_s S) \rightarrow 1$ 

as 
$$[O_2(0)] \rightarrow \infty$$
 then  $K_s S \rightarrow 0$  and  $(1 - K_s S) \rightarrow 1$ 

Note that as [O<sub>2</sub>(0)] approaches zero at the onset of anoxia, the term (1 - K<sub>s</sub>S) is the proper variable to quantify the degree of benthic stress. The expression is unitless and requires no additional parameter - for example a half saturation constant for benthic stress. The final formulation for the particle mixing velocity which includes the benthic stress is:

$$w_{12} = w_{12}^* \min \{ (1 - K_s S) \}$$
 (2-28)

where  $w_{12}^*$  is defined above. The stress is continued at its minimum value through the end of the year, in order to conform to the observation that once the benthos has been suppressed by low oxygen, it does not recover until the next year.

#### 2.3.3.4 **Dissolved Phase Mixing**

Dissolved phase mixing between layers 1 and 2 is via passive molecular diffusion which is enhanced by the mixing activities of the benthic organisms (bio-irrigation). This is modeled by increasing the diffusion coefficient by a factor of 10 over the molecular diffusion coefficient.

W.

$$K_{L12} = \frac{D_d \theta_{Dd}^{(T-20)}}{H_2}$$
 (2-29)

 $D_d$  = pore water diffusion coefficient, m<sup>2</sup>/day,

 $\theta_{Dd}$  = temperature coefficient for  $D_d$ .

#### 2.3.3.5 Solids Burial

The deposition of solids to the sediment causes an increase in the depth of the sediment relative to a fixed datum. If the sediment surface is regarded as the point of reference, then the increase in the depth of sediment is a loss of mass due to burial from the active sediment layer.

 $w_2$  = sedimentation velocity, m/d.

#### 2.3.3.6 Active Layer Depth

The active layer depth is chosen to represent the depth of organism mixing. Particles buried below this depth can no longer be recycled to the aerobic layer. They are permanently buried.

 $H_2$  = depth of the anaerobic layer, m.

#### 2.3.4 Parameter Values for Individual Solutes

The parameters that vary with the solute being considered are the reaction velocities, the partition coefficients, and the source terms. The specific form for these parameters are given below for each of the modeled solutes.

#### 2.3.4.1 Sulfide

Sulfide is produced by carbon diagenesis, as shown in equation 2-30,

$$J_{T2} = J_c \tag{2-30}$$

where:

 $J_c$  = carbon diagenesis

 $J_{T2}$  = aerobic layer sulfide source, g  $O_2^*/m^2$ -day,

Dissolved and particulate sulfide are oxidized in the aerobic layer. The reaction rate is linear in oxygen concentration, consistent with reported formulations for these reactions. The constant  $K_{M,HS,O2}$  scales the overlying water oxygen concentration.

$$\kappa_1^2 = (\kappa_{s,d1}^2 f_{d1} + \kappa_{s,p1}^2 f_{p1}) \theta_{HS}^{(T-20)} \frac{[O_2(0)]}{K_{M,HS,O2}}$$
(2-31)

Partitioning between dissolved and particulate sulfide represents the formation of iron sulfide, FeS(s). No other reactions occur. The parameters are:

 $\kappa_{s,d1}$  = reaction velocity for dissolved sulfide oxidation in the aerobic layer, m/d,

 $\kappa_{s,pl}$  = reaction velocity for particulate sulfide oxidation in the aerobic layer, m/d,

 $\theta_{HS}$  = temperature coefficient for sulfide oxidation,

 $K_{M,HS,O2}$  = sulfide oxidation normalization constant for oxygen, mg  $O_2/L$ ,

 $f_{d1}$  = dissolved faction,

 $f_{p1}$  = particulate fraction,

 $\kappa_1$  = an aerobic layer reaction velocity, m/d,

where  $0_2$ \* represents the oxygen equivalents of sulfide.

#### 2.3.4.2 Oxygen

Oxygen is consumed by the oxidation reactions in the aerobic layer. Carbonaceous sediment oxygen demand (CSOD) - so named because it originates with carbon diagenesis - is computed from the rate of oxygen utilization during sulfide oxidation. No stoichiometric coefficient is needed because the sulfide concentrations are computed in oxygen equivalents.

CSOD = 
$$\frac{(\kappa_{s,d1}^2 f_{d1} + \kappa_{s,p1}^2 f_{p1}) \theta_{HS}^{(T-20)}}{s} \frac{[O_2(0)]}{K_{M,HS,O2}} [\Sigma H_2 S(1)]$$
(2-32)

where:

 $[\Sigma H_2S(1)]$  = total aerobic layer sulfide concentration (g  $O_2^*/m^3$ ),

#### 2.3.4.3 Phosphate

Phosphate is conservative in both layers, with partitioning controlling the fraction that is dissolved and particulate. Phosphorus flux is strongly affected by the overlying water oxygen concentration,  $[O_2(0)]$ . The mechanism usually suggested is that the phosphorus which is transferred to the aerobic layer is sorbed to freshly precipitated iron oxyhydroxides which prevents it from diffusing into the overlying water. At low oxygen concentrations, the iron oxyhydroxides are reduced and dissolved, the sorption barrier is removed, and the phosphorus flux escapes unimpeded. A simple way to implement this mechanism is to make the aerobic layer partition coefficient larger than in the anaerobic layer during oxic conditions and to remove this additional sorption as  $[O_2(0)]$  approaches zero. Hence if  $[O_2(0)] > [O_2(0)]_{crit}$ , sorption in the aerobic layers is enhanced by an amount  $\Delta \pi_{Fe,PO4}$ . However, if oxygen falls below a critical concentration,  $[O_2(0)] < [O_2(0)]_{crit}$ , then:

$$\pi_{\text{PO4,1}} = \pi_{\text{PO4,2}} (\Delta \pi_{\text{Fe,PO4}})^{[O_2(0)]/[O_2(0)]_{\text{crit}}} \qquad [O_2(0)] \leq [O_2(0)]_{\text{crit}} \qquad (2-33)$$

which smoothly reduces the aerobic layer partition coefficient to that in the anaerobic layer as  $[O_2(0)]$  goes to zero. No other reactions affect the phosphorus concentrations. The parameter values are:

 $\kappa_1$  = aerobic layer reaction velocity, m/day,

 $\kappa_2$  = anaerobic layer reaction velocity, m/day,

 $J_{T1}$  = aerobic layer phosphorus source, mg P/m<sup>2</sup>-day,

 $J_{T2} = J_P$  = phosphorus diagenesis, computed from Equation 2-16, mg P/m<sup>2</sup>-day,

 $\Delta \pi_{\text{Fe,PO4}}$  = incremental partition coefficient for phosphate in the aerobic layer, L/kg,

 $\pi_{PO4,2}$  = partition coefficient for phosphate in the anaerobic layer, L/kg,

 $\pi_{PO4.1}$  = partition coefficient for phosphate in the aerobic layer, L/kg,

 $[O_2(0)]$ crit = overlying water oxygen concentration at which aerobic layer incremental partitioning starts to decrease, mg/L.

#### 2.3.5 The Finite Difference Equations

The most convenient method of solution is to use an implicit integration scheme. This is due to the similarity of the equations that results to the steady state equations for which a simple solution algorithm is available. Given the concentrations at t, the finite difference equations are solved for the unknown concentrations at  $t + \Delta t$ . Since layer 1 is quite thin,  $H_1 \sim 1 \text{mm} = 10^{-3}$  m, and the surface mass transfer coefficient is or order  $s \sim 0.1$  m/day, the residence time in the layer is:  $H_1/s \sim 10^{-2}$  days. Hence it can be assumed to be at steady state without any loss of accuracy. The layer 1 equation is:

$$0 = H_{1} \frac{dC_{T1}^{(t+\Delta t)}}{dt} = s \left( f_{d1} C_{T1}^{(t+\Delta t)} - C_{d0}^{(t+\Delta t)} \right)$$

$$+ w_{12} \left( f_{p2} C_{T2}^{(t+\Delta t)} - f_{p1} C_{T1}^{(t+\Delta t)} \right)$$

$$+ K_{L12} (f_{d2} C_{T2}^{(t+\Delta t)} - f_{d1} C_{T1}^{(t+\Delta t)}) - \frac{\kappa_{1}^{2}}{s} C_{T1}^{(t+\Delta t)} + J_{T1}$$

$$(2-34)$$

The layer 2 mass balance finite difference equation which is implicit in time is:

$$H_{2} \frac{C_{T2}^{t+\Delta t} - C_{T2}^{t}}{\Delta t} = -w_{12} (f_{p2} C_{T2}^{(t+\Delta t)} - f_{p1} C_{T1}^{(t+\Delta t)})$$

$$- \kappa_{L12} (f_{d2} C_{T2}^{(t+\Delta t)} - f_{d1} C_{T1}^{(t+\Delta t)})$$
(2-35)

$$- \ \kappa_2^{} C_{T2}^{\;(t+\Delta t)} \; - \ w_s^{} C_{T2}^{\;(t+\Delta t)} \; + \; J_{T2}^{\;(t+\Delta t)}$$

which can be put into a form that is similar to the steady state equations:

$$0 = -w_{12}(f_{p2}C_{T2}^{(t+\Delta t)} - f_{p1}C_{T1}^{(t+\Delta t)})$$

$$-\kappa_{L12}(f_{d2}C_{T2}^{(t+\Delta t)} - f_{d1}C_{T1}^{(t+\Delta t)})$$

$$-\kappa_{2}C_{T2}^{(t+\Delta t)} - w_{s}C_{T2}^{(t+\Delta t)} - \frac{H_{2}C_{T2}^{(t+\Delta t)}}{\Delta t} + J_{T2}^{(t+\Delta t)} + \frac{H_{2}C_{T2}^{t}}{\Delta t}$$
(2-36)

The terms corresponding to the derivatives:  $H_2C_{T2}^{(t+\Delta t)}/\Delta t$  and  $H_2C_{T2}^t/\Delta t$ , simply add to the layer two removal rate and the forcing function respectively. Hence the solution algorithm for these equations is the same as the steady state model.  $C_{T1}^{(t+\Delta t)}$  and  $C_{T2}^{(t+\Delta t)}$  are the two unknowns in the two equations which are solved at every time step.

For the sake of symmetry the diagenesis equations are also solved in implicit form:

$$H_{2} \frac{G_{POC,i}^{(t+\Delta t)} - G_{POC,i}^{(t)}}{\Delta t} = -K_{G,i} \theta_{G,i}^{(T-20)} G_{POC,i}^{(t+\Delta t)} H_{2} + J_{GPOC,i}^{(t+\frac{\Delta t}{2})}$$
(2-37)

so that:

$$G_{POC,i}^{(t+\Delta t)} = \begin{bmatrix} G_{POC,i}^{(t)} + \frac{\Delta t}{H_2} J_{GPOC,i}^{(t+\frac{\Delta t}{2})} \end{bmatrix} \begin{bmatrix} 1 + \Delta t K_{G,i} \theta_{G,i}^{(T-20)} \end{bmatrix}^{-1}$$
(2-38)

#### 2.3.5.1 Solution Technique

The solution of the layer 1 and layer 2 mass balance equations require an iterative technique since the surface mass transfer coefficient,  $s = SOD/[O_2(0)]$ , is a function of the SOD which, in turn, is a function of the ammonia and sulfide mass balance equations. A simple back substitution method can be used to solve the equations at each time step. The procedure is:

- (1) Guess an SOD,
- (2) Solve layer 1 and 2 equations for sulfide,
- (3) Compute SOD = CSOD,
- (4) Refine the estimate of SOD. A root finding method is used to make the new estimate,
- (5) Go to (2) if no convergence,
- (6) Compute the phosphorus fluxes.

This method has been found to be quite reliable (Di Toro and Fitzpatrick, 1993).

#### 2.3.6 Sediment Initial Conditions

The solution of the diagenesis and sediment model equations require initial conditions, the concentrations at t=0:  $G_{poc.i}(0)$ , and the total concentrations for sulfide and phosphate,  $C_{TI}(0)$ , and  $C_{T2}(0)$ , to start the computations. Strictly speaking these initial conditions should be based on data and would reflect the past history of the lake. While the Lake Champlain field sampling program conducted by the HPEL provided some information with which to estimate initial conditions, there was some data variability across stations within a model segment. This is to be expected given the spatial heterogeneity of lake sediments. However, this also made spatial extrapolation of initial conditions practically impossible. Therefore, to assign initial conditions the model was run to equilibrium or periodic steady-state by cycling the model for a multi-year period using the available overlying water column data. In other words the model equations were solved using an arbitrary set of initial conditions. The model was then integrated for one year. The final concentrations at the end of the year were then used as the initial conditions and the equations solved again for another year. This procedure was repeated until the final conditions at the end of the year were equal, within a tolerance, to the initial conditions. At this point the model is in periodic steady state. When changes were made in the kinetic parameters to improve the calibration, the initial conditions were recalculated using the new model coefficients.

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#### **SECTION 3**

#### **MODEL CALIBRATION**

#### 3.1 CALIBRATION DATA

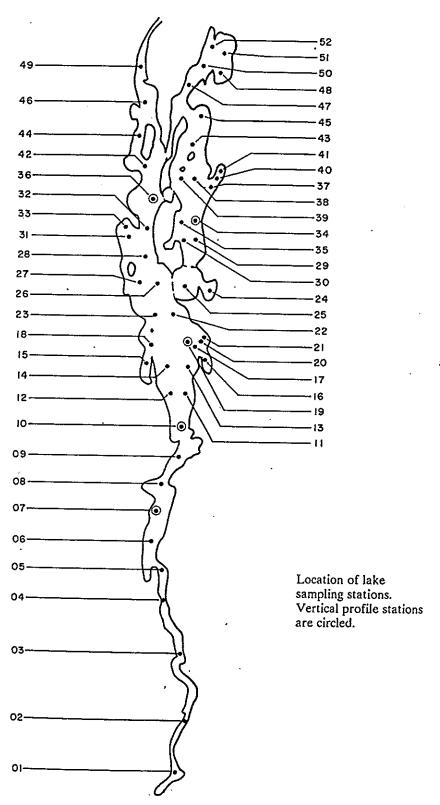
#### 3.1.1 Introduction

A properly validated deterministic model is a powerful tool because it represents, as closely as possible, the mechanisms which affect the system under study and, therefore, can be used to evaluate the effects of perturbations, such as changes in pollutant inputs, on the system. The credibility of model calculations is judged, to a large degree, on the basis of the agreement of the model with observed data. Beyond the constraint that the model must behave reasonably well and conform with general scientific principles, observed data offer perhaps the only external criteria available to assess the validity and, hence, the utility of a complex water quality model. However, it is equally important that the data, by which the model is judged to be representative of the system, are themselves representative of the system.

The period chosen for calibration was the 1991 calendar year. This year was selected primarily due to the amount of information available from a previous modeling study of the lake previously performed by the VTDEC. However, due to limited water column and sediment data for this period, the 1991 data set was supplemented by data collected between 1990 and 1996.

#### 3.1.2 Water Column

During the 1990-96 period, the Vermont Department of Environmental Conservation and the New York State Department of Environmental Conservation collected water column data at 52 stations within Lake Champlain. These stations included 47 locations where composite samples were taken and 5 locations where vertical profile samples were taken (Figure 3-1). Vertical profile sampling was generally performed in the deeper portions of the lake. Sampling cruises were generally conducted between the months of April, after ice-out, and November before the surface of the lake became locked in ice. Not all of the stations were sampled during each cruise. The water quality constituents that were sampled at the vertical profile stations included: total phosphorus (TP), dissolved phosphorus (DP), orthophosphorus (PO<sub>4</sub>),



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\$ \$ m.

Figure 3-1. Sampling Station Locations

chlorophyll-a (chl-a), total organic carbon (TOC), dissolved organic carbon (DOC), dissolved oxygen (DO), chlorides, and temperature. At the composite stations, chlorides and TP were measured.

#### 3.1.3 Sediment

Measurements of sediment nutrient fluxes and sediment pore water and composition were made by the Horn Point Environmental Laboratory as part of this study. The first series of sediment data were obtained during three surveys conducted in July 1994, October, 1994 and April 1995. The second series of sediment data were obtained during three surveys conducted in August, October and November, 1996. In July 1994, duplicate sediment cores were taken at 14 locations within the lake. The July 1994 survey provided a broad overview of phosphorus fluxes and sediment phosphorus content in the lake. The next two surveys focused on areas of the lake that were of particular interest to the water quality managers. The selected sites correspond to water quality stations 2, 7, 37, 41, 50 and 51. Although good replication was obtained using duplicate cores during the first survey, it was decided to take triplicate cores during the second and third field surveys.

The fourth, fifth and sixth sediment surveys were conducted to increase the temporal and spatial data on sediment phosphorus conditions in the lake. Data were collected at the six stations chosen from the second sampling survey and at five additional locations. These five extra locations included stations 10, 12, 19, 21, and a new station in Shelburne Bay. Measurements taken during each survey included sediment oxygen demand (SOD), phosphate flux (J<sub>PO4</sub>), pore water PO<sub>4</sub>, particulate organic phosphorus (POP) and particulate inorganic phosphorus (PIP). In addition to these measurements, <sup>210</sup>Pb profiles were examined to determine sedimentation rates at 16 locations in Lake Champlain.

#### 3.2 POLLUTANT LOADS

The carbon and nutrient loads discharged into Lake Champlain emanate from two major sources: waste water treatment facilities (WWTFs), and tributary runoff. The loads used for this calibration were based on the methods developed by VTDEC/NYSDEC (1997). This analysis was expanded, however, in order to provide time variable estimates of the phosphorus and carbon loads entering the lake. A brief summary of the load estimation procedure and the resultant loads

follows. The reader is, however, referred to VTDEC/NYSDEC (1997) for a more detailed account of procedures and data sources.

#### 3.2.1 Wastewater Treatment Facilities

Seventeen WWTFs are known to discharge directly into Lake Champlain, nine from the Vermont side and eight from New York. Monthly flows were available from January 1990 through December 1991. Measurements of chlorides and TP were available on a bimonthly basis and monthly averaged BOD<sub>5</sub> measurements were also available. Monthly flows and the monthly averaged concentrations were used to calculate the monthly loads for each facility. If data were missing for a particular month at a WWTF, the average concentration for that facility was used. In cases where no data were available for a particular WWTF, the average concentration from all of the remaining facilities was used. Since the model does not include BOD<sub>5</sub> as a state-variable, but rather models organic carbon, the BOD<sub>5</sub> loads were converted to equivalent organic carbon loads using a regression relationship developed by HydroQual (1991). This regression was based on paired observations of TOC and BOD<sub>5</sub> from New York City WWTFs. Total phosphorus and TOC loads were then split into the various dissolved and particulate fractions using Table 3-1. These fractions were also estimated from data available from New York City WWTFs. Uncertainties in the estimates of these fractions should have a small effect on the lake as a whole because on an annual basis only 7.9% of the estimated TP load emanates from WWTFs discharging directly into Lake Champlain.

Table 3-1. WWTF Loading Fractions

DOP = 0.125 TP	
POP = 0.125  TP	
$PO_4 = 0.75 \text{ TP}$	
$TOC = 0.7 BOD_5 + 18$	
DOC = 0.75 TOC	
POC = 0.25 TOC	
L	

#### 3.2.2 Tributaries

The thirty-one tributaries that flow into Lake Champlain contribute more than 90 percent of the carbon and phosphorus loads. Continuous daily flows were available for 30 of the 31

tributaries for the period of March 1990 through April 1992. When data were missing, linear interpolation was used to fill the data gaps.

Approximately one to two measurements per month were available for tributary chlorides, TP, DP, TOC and DOC. Using these data, piecewise linear concentration versus flow relationships were developed for each tributary via Equation 3-1,

$$c = e^{(m \ln Q + 2.303 (b + 0.5d^2))}$$
 (3-1)

where c is the concentration, Q is the flow and m, b, and d are constants computed from a linear regression analysis of the tributary data. For Equation 3-1, m is the slope estimated from a log-log plot, b is the intercept estimated from a log-log plot and d is the standard deviation of the residuals about the log-log line of best fit.

These relationships were separated into high and low flow conditions depending on observed breaks in the flow versus concentration relationships. An example is shown in Figure 3-2 for the Poultney River. Table 3-2 presents the flow breakpoints and Table 3-3 presents the regression constants for each tributary. These equations were then used with 1991 flow data to develop corresponding concentrations and loads. These loads were then averaged on a weekly basis. For the ungaged area of a tributary, a unit load was estimated using the ratio of gaged load to gaged area. This unit load was then multiplied by the ungaged area. In areas where no gaged tributaries existed, the unit load from a nearby drainage basin was used. After all the tributary loads were calculated, they were split among the various state-variables according to the equations presented in Table 3-4. The equations in Table 3-4 were created by grouping all of the limited tributary data that were available and computing ratios from the averaged values.

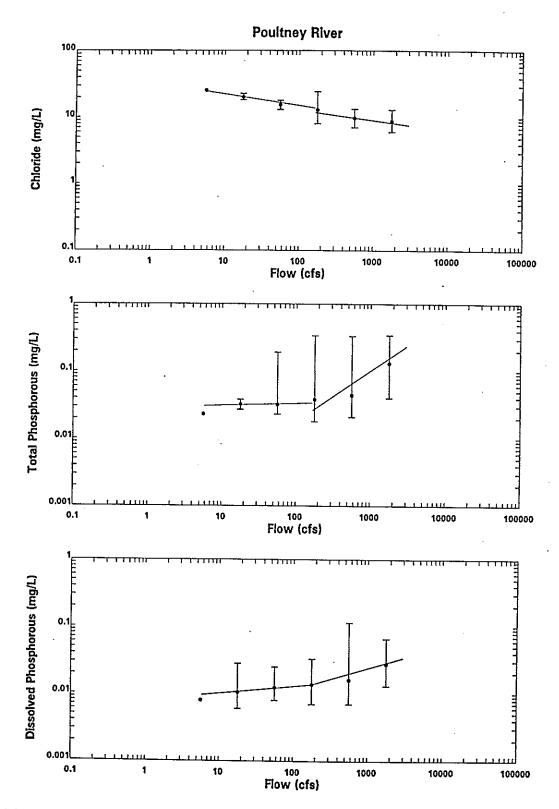


Figure 3-2. Example Flow Versus Concentration Relationships Used for Tributary Loading Estimates

Table 3-2. Flow Regime Breaks for Flow/Concentration Relationships and Total Area/Gaged Area Ratios

		Total/			Total/
	Break	Gaged		Break	Gaged
Tributary	(cfs)	Ratio	Tributary	(cfs)	Ratio
East	25	2.31	Richelieu	999	1.00
Indian	13	1.11	Ausable	336	1.14
Lamoille	784	1.07	Bouquet	500	1.00
LaPlatte	100	1.18	Great Chazy	500	1.20
Lewis	200	1.05	Highlands Forge	17	10.7
Little Otter	90	1.25	Hoisington	15	1.65
Malletts	23	1.81	Mt. Hope	11	1.00
Mill	5.6	1.02	Little Ausable	45	1.07
Missisquoi	2240	1.01	Little Chazy	50	1.01
Otter	1500	1.51	Mettawee/Barge Canal	560	2.53
Pike	101 .	1.28	Mill (Port Henry)	80	1.04
Poultney	168	1.43	Mill (Putnam Sta.)	9	1.00
Rock	392	1.21	Putnam	500	1.19
Stevens	22	2.27	Salmon	224	1.09
Stone Bridge	5	1.45	Saranac	2240	1.00
Winooski	1680	1.05	LaChute	999	1.19

Table 3-3. Correlation Results for Lake Champlain

- 10 ma <sup>270</sup> - 10 ma - 10 m				Flow 1	Regime		
			Upper			Lower	
Tributary	Variable	В	M	D	В	M	D
Winooski	CL	1.8407	-0.2266	0.1310	1.3850	-0.0606	0,1100
	TP	-5.0195	1.0513	0.2712	-1.2904	-0.0980	0.1266
	DP	-2.8565	0.2537	0.2016	-2.2484	0.0760	0.1660
Lewis	CL	1.0203	-0.0729	0.1006	1.0472	-0.0835	0.0491
	TP	-3.4687	0.9811	0.2966	-2.1820	0.3497	0.2159
	DP	-3.3920	0.7147	0.2882	-2.0776	0.1370	0.1628
Little Otter	CL	1.0788	-0.0309	0.1173	1.1790	-0.0758	0.1198
	TP	-2.1229	0.4977	0.2141	-0.7169	-0.2351	0.2097
	DP	-2.0871	0.3917	0.2246	-0.8656	-0.2608	0.2182
LaPlatte	CL	2.0999	-0.3568	0.1436	2.1185	-0.3775	0.1738
	TP	-1.0998	0.1478	0.2170	-0.2579	-0.1934	0.2218
	DP	-0.9313	0.0104	0.2138	-0.1809	-0.3025	0.2061
East	CL	0.8298	0.0589	0.1438	1.0020	-0.0563	0.1464
	TP	-2.0944	0.3997	0.2482	-0.7781	-0.4479	0.2407
	DP	-2.2729	0.4275	0.2369	-1.0812	-0.3896	0.2398
Mill	CL	1.7539	-0.1582	0.1003	1.5155	0.1095	0.0916
	TP	-1.8297	0.3727	0.2377	-1.3089	-0.2811	0.2839
	DP	-1.7739	0.2188	0.2316	-1.7009	0.1012	0.2831
Stevens	CL	2.0692	-0.2262	0.3005	1.7737	0.0317	0.1909
	TP	-1.2851	0.3868	0.2787	-0.9932	-0.0122	0.3486
	DP	-0.9937	0.0025	0.2832	-1.2765	0.0312	0.3291
Malletts	CL	1.4815	-0.1913	0.1077	1.6166	-0.3570	0.1296
	TP	-2.3422	0.6075	0.2555	-0.8975	-0.4748	0.1479
	DP	-2.0440	0.1839	0.2195	-1.1895	-0.4190	0.1678
Stone Bridge	CL	1.5332	-0.2438	0.0827	1.4797	-0.1989	0.0499
	TP	-1.6632	0.3788	0.2889	-0.8679	-0.9803	0.1478
	DP	-1.6245	0.0728	0.2535	-1.5697	-0.1251	0.2582
Pike	CL	1.6992	-0.2305	0.0808	1.4775	-0.1432	0.0606
	TP	-2.1541	0.4479	0,2929	-0.5777	-0.3664	0.2509
	DP	-1.7420	0.1760	0.2923	-0.3919	-0.5979	0.2943
Rock	CL	2.8383	-0.6917	0.1233	1.0546	-0.0136	0.1006
	TP	-6.1051	2.0383	0.3430	-1.0416	0.0907	0.2306
	DP	-1.9552	0.3179	0.2750	-1.3695	0.1345	0.2366
Indian	CL	2.0287	-0.3075	0.1357	1.7938	-0.0720	0.1262
	TP	-2.7639	1.0785	0.2568	-1.3724	-0.1623	0.0879
	DP	-1.9895	0.1201	0.1609	-1.6050	-0.1815	0.1337
Saranac	CL	3.2534	-0.7440	0.0919	1.2005	-0.1550	0.0886
	TP	-5.3249	1.0830	0.1930	-1.2658	-0.1603	0.1432
•	DP	-3.1042	0.2832	0.1711	-1.1911	-0.3146	0.1420
Mettawee/Barge	CL	1.3563	-0.1223	0.1059	1.4837	-0.1666	0.0774
Canal	TP	-3.6393	0.8888	0.2275	-0.8519	-0.1836	0.1926
	DP	-3.7963	0.7769	0.1888	-1.6396	-0.0285	0.2110
Bouquet	CL	1.9257	-0.3473	0.1183	1.6429	-0.2471	0.0636
— - ··· ** *-	TP	-5.8564	1.4981	0.3299	-2.8386	0.3757	0.3380
	DL	-2.7303	0.2335	0.3255	-2.4376	0.0655	0.2584
		-2.1303	0.2333	0.2700	-2.7J/U	0.0000	0,2364

Table 3-3. Correlation Results for Lake Champlain

		Flow Regime					
			Upper			Lower	
Tributary	Variable	В	M	D	В	M	D
Little Chazy	CL	1.6377	-0.2282	0.0935	1.3373	-0.1343	0.0866
	TP	-2.5440	0.5799	0.3074	-0.9254	-0.3115	0.2372
	DP	-2.5940	0.5311	0.3445	-0.9929	-0.3789	0.2469
Putnam	CL	-0.0052	0.1716	0.0501	1.3496	-0.2854	0.0917
	TP	-1.7872	0.0940	0.2197	-2.7129	0.4348	0.2997
	DP	5.0771	-2.6530	0.2997	-2.2729	0.0121	0.1518
Little Ausable	CL	1.0684	-0.0563	0.1466	0.9753	0.0745	0.0390
	TP	-2.0317	0.3168	0.2537	-1.4347	-0.0388	0.2706
	DP	-1.6269	-0.0183	0.1837	-1.4523	-0.1734	0.2444
Mt. Hope	CL	0.0860	-0.1008	0.1105	-0.0956	-0.0461	0.1311
	TP	-2.8744	0.4308	0.2193	-2.3390	-0.1516	0.0882
	DP	-2.2054	-0.1520	0.1317	-2.3180	-0.2286	0.0735
Mill	CL	1.7026	-0.3605	0.0923	1.3870	-0.2280	0.0679
(Port Henry)	TP	-3.4706	0.9376	0.2174	-2.5069	0.4560	0.2752
	DP	-0.3890	-0.7836	0.1732	-2.0574	-0.1365	0.2508
Highlands Forge	CL	1.2151	-0.2326	0.0987	0.8322	0.0762	0.0785
	TP	-2.3541	0.2717	0.1703	-2.1199	0.1165	0.2229
•	DP	-3.0843	0.4643	0.1501	-2.2290	-0.1215	0.1243
Mill	CL	1.0553	-0.1428	0.1659	0.9263	-0.0312	0.1554
(Putnam Sta.)	TP	-1.7590	0.2400	0.2863	-1.2010	-0.2603	0.1965
	DP	-1.7578	0.0414	0.3161	-1.6106	-0.1272	0.1594
Salmon	CL	0.5860	0.0128	0.2680	0.5226	0.1323	0.0995
	TP	-2.9207	0.6882	0.2972	-2.5912	0.4416	0.2089
	DP	-4.7759	1.1601	0.3791	-2.2276	0.0920	0.1717
Hoisington	CL	1.1234	-0.1173	0.1416	1.1333	-0.1739	0.1250
	TP	-2.9159	1.1147	0.2590	-1.7878	0.1680	0.3460
	DP	-2.7660	0.6648	0.2048	-1.8837	-0.0374	0.3475
Ausable	CL	1.7512	-0.3313	0.1171	1.4342	-0.1957	0.0583
	TP	-3.6602	0.6366	0.2975	-1.2935	-0.2684	0.0917
	DP	-1.7571	-0.1425	0.2241	-2.4362	0.1669	0.1438
Great Chazy	CL	2.1697	-0.4029	0.0895	1.7647	-0.2965	0.0845
•	TP	-3.6453	0.7558	0.2113	-1.9228	0.1333	0.2826
	DP	-2.4163	0.2374	0.2106	-2.2047	0.1566	0.2875
Otter	CL	1.2961	-0.1062	0.0822	1.6757	-0.2178	0.0992
	TP	-3.4223	0.6771	0.2429	-0.7421	-0.1078	0.1811
	DP ·	-2.1572	0.2245	0.2305	-1.1215	-0.0344	0.2010
Missisquoi	CL	1.7511	-0.2689	0.0950	1.2706	-0.1368	0.0881
•	TP	-5.3017	1.1300	0.2194	-1.8104	0.0808	0.1429
	DP	-2.1810	0.1246	0.2002	-2.1879	0.0916	0.1699
Lamoille	CL	1.6681	-0.2249	0.1326	2.4829	-0.5190	0.0607
	TP	-3.9755	0.7025	0.2345	-2.0749	0.0679	0.0826
	DP	-3.3477	0.3872	0.2151	-2.3251	0.0350	0.1526
Poultney	CL	1.4017	-0.1508	0.0672	1.5196	-0.1726	0.0737
_ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~					*****		
•	TP	-3.3008	0.7552	0.2929	-1.5568	0.0304	0.2005

**Table 3-4. Tributary Loading Fractions** 

DOP = 0.14 DP		
POP = TP-DP		
$PO_4 = 0.86 DP$		
DOC = 0.84 TOC		
 POC = 0.16 TOC		 

Table 3-5 presents a comparison between the TP loads computed by VTDEC and by HydroQual for 1991 based on an annual basis. As can be seen from this table, estimates of total phosphorus loading to the lake made by VTDEC and this study agree to within approximately 5 percent, although differences in loading estimates to a few "segments" within the lake were as large as 10 percent, and one "segment" (Isle LaMotte) was about 30 percent.

Table 3-5. Total Phosphorus Loading

Segment	VTDEC 1991 (mt/yr)	HydroQual, Inc. 1991 (mt/yr)
South Lake B	56.2	45.9
South Lake A	15.5	16.6
Port Henry	4.7	4.2
Otter Creek	121.8	121.4
Main Lake	126.9	115.7
Shelburne Bay	16.4	14.8
Burlington Bay	<b>11.5</b> .	11.3
Cumberland Bay	38.0	32.9
Malletts Bay	32.9	30.3
St. Albans Bay	8.0	7.6
Missisquoi Bay	167.3	172.4
Isle LaMotte	28.9	20,2
Northeast Arm S.	3.2	2.1
Northeast Arm N.	<u> </u>	0.7
Total	631.3	596.1

## 3.3 MODEL SEGMENTATION

The model segmentation employed in this study was based on the segmentation developed by the VTDEC for use with the BATHTUB model. This segmentation scheme corresponded to the 13 lake segments for which in-lake total phosphorus criteria had been established. During this study, some modifications were made to the original model segmentation. For example, the Northeast Arm segment was divided into northern and southern segments. In addition, the deeper portions of the lake were divided into two vertical layers. The number of segments increased from 13 to 22 with these changes. These changes were made for several reasons. In the deeper sections of the lake, model segments were divided into two layers in order to better represent the vertical stratification that is observed in the temperature and DO data. Reproduction of the observed stratification was deemed necessary because sediment phosphorus fluxes are highly dependent on the overlying water column temperature and dissolved oxygen concentration. The Northeast Arm was divided into two segments based on differences in depth between the northern and southern portion of this region of the lake.

Model segment volumes and depths used in this study were computed in the following manner. General segment locations were based on maps included in the VTDEC report (1997). The volume of each segment was computed using available bathymetry data in a GIS format. Average segment depths were calculated using the segment volume and the segment surface area computed at a depth of five meters. The maximum surface layer depth of a particular segment was chosen to be 10 meters based on an analysis of the vertical profile data. The five meter depth surface area was then the midpoint of the surface segment. Any lake segment with a computed average depth of less than 10 meters contained only one vertical layer in the model. When the computed average depth of a segment exceeded 10 meters, the volume of the bottom segment was calculated as the difference between the total segment volume and the surface layer volume. The depth of the bottom segment was determined by using one of two surface areas. If the depth within a lake or model segment appeared to be uniform, the five meter surface area was used. If a lake or model segment contained a deep narrow bathemetric feature then the lake surface area at a depth of 15 meters was used together with the bottom segment volume to compute an average segment depth. This allowed the model to better represent the lake's deeper portions where all of the vertical profile data were collected. Table 3-6 presents segment volumes and depths.

Table 3-6. Model Segmentation

	Segment	Layer	Volume (km³)	Depth (m)
1	South Lake B	1	0.02567	2.75
2	South Lake A	1	0.13225	3.15
<b>3</b> .	Port Henry	1	0.72862	10.00
14	Port Henry	2	0.52281	7.175
4	Otter Creek	1	0.30360	10.00
15	Otter Creek	2	0.69989	23.034
5	Main Lake	1	3.99045	10.00
16	Main Lake	2	11.78003	29.521
6	Shelburne Bay	1	0.09402	10.00
17	Shelburne Bay	2 .	0.02886	7.261
7	Burlington Bay	1	0.05253	10.00
18	<b>Burlington Bay</b>	2	0.00058	0.11
8	Cumberland Bay	1	0.09586	6.61
9	Malletts Bay	1	0.54655	10.00
19	Malletts Bay	2	0.13814	5.769
10	Northeast Arm S.	1	0.90503	10.00
20	Northeast Arm S.	2	0.69842	20.00
11	St. Albans Bay	1	0.03234	3.66
12	Missisquoi Bay	1	0.21529	2.66
13	Isle LaMotte	1	1.56993	10.00
21	Isle LaMotte	2	0.23862	1.517
22	Northeast Arm N.	1	1.52442	10.148

## 3.4 EXOGENOUS INPUTS

# 3.4.1 Surface Water Temperature

In lieu of detailed hydrodynamic computations, estimates of net circulation and vertical mixing in the lake were based on observed chloride and temperature data. Water temperature was assigned to the surface layer of each model segment. Five different temporal surface temperature profiles were developed to represent the varying temperatures observed in various regions of the lake based on VTDEC/NYSDEC data. Temperatures were modified on a monthly basis. The five surface temperature time-series profiles are shown in Figure 3-3.

## 3.4.2 Extinction Coefficients

Water transparency and, therefore, light extinction coefficients, play an important role in primary productivity. Phytoplankton productivity is usually greater in areas of high light penetration than in light limited areas, given the same nutrient availability. A monthly base extinction coefficient was estimated for each segment using measured Secchi depth data obtained during VTDEC/NYSDEC sampling surveys. Base extinction coefficients are shown in Figure 3-3. Higher base extinction coefficients in the spring may be due to high flow events associated with snow melt which transport higher solids concentrations to the lake. Base extinction coefficients were observed to be higher at the South Lake B, South Lake A, St. Albans Bay and Missisquoi Bay stations. These higher values may be due to higher solids loading or resuspension of sediment due to wind.

## 3.4.3 Solar Radiation

Solar radiation is a principal exogenous input that plays a major role in determining phytoplankton growth. Short wave radiation from the sun is used by phytoplankton for photosynthesis. As this radiation passes through the atmosphere it can be absorbed and scattered by gases in the air and by water vapor, clouds and dust. As a result of these processes, solar radiation reaching the earth's surface is comprised of two forms, direct and diffuse radiation. Values of total incident solar radiation data were available at Burlington Airport for the period of 1986-1990. From these data, monthly average values were calculated and used in the model.

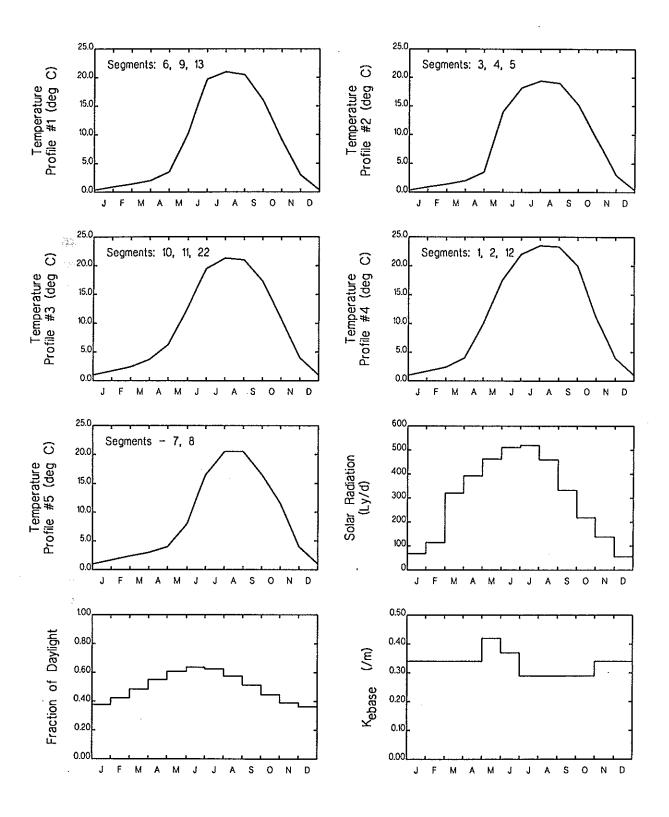


Figure 3-3. Exogenous Inputs

The solar radiation inputs are presented in Figure 3-3. The reported solar radiation values were halved in January and February to simulate the effect of ice cover in the lake.

# 3.4.4 Fraction of Daylight

The growth rate formulation for phytoplankton used in the model, as described by Equation 2-4, depends on the length or fraction of daylight, as photosynthesis takes place only in the presence of sunlight. The fraction of daylight for each day of the year may be calculated using basic trigonometry assuming the earth is a perfect sphere. (Corrections of six to eight minutes per day, which account for atmospheric refraction of the sun's rays at sunrise and sunset are assumed to be negligible.) Daily fractions of daylight were calculated using a methodology developed by Duffie and Beckman (1970), which depends on the latitude of the location of interest and the declination of the sun as a function of the time of year. The latitude chosen for Lake Champlain was 44.5 N. These daily values were then averaged on a monthly basis. The fraction of daylight used in the model is presented in Figure 3-3.

## 3.4.5 Sedimentation Rate

As part of the 1996 sediment sampling program, researchers from the Horn Point Environmental Laboratories collected cores at 17 sites for <sup>210</sup>Pb profiling. <sup>210</sup>Pb profiles can be used to estimate the sedimentation rate at each site sampled within the lake. The sedimentation rates varied from 163 g/m²-year at Port Henry and Northeast Arm to 1413 g/m²-year in Main Lake. Computed accretion rates ranged from 0.11 cm/yr in Northeast Arm to 1.09 cm/yr in Missisquoi Bay. The measured accretion rates were used as input to the sediment submodel. Table 3-7 presents the accretion rates used in the model.

# 3.4.6 Sediment Density

Sediment density was estimated from percent water measurements taken during the sediment sampling program. Using a particle density of 2.5 g/cc, sediment densities were calculated and ranged from 0.116 to 0.541 g/cc. Table 3-7 presents the values used in the model.

Table 3-7. Sediment Parameters

Segment	Accretion Rate	m <sub>I</sub> /m <sub>2</sub>	$\pi PO_{41}$	πPO <sub>42</sub>
	cm/yr	kg/L	L/kg	L/kg
South Lake B	0.38	0.40	7500	1000
South Lake A	0.38	0.30	15000	1000
Port Henry	0.22	0.21	40000	1000
Otter Creek	0.22	0.20	40000	1000
Main Lake	0.30	0.20	40000	1000
Shelburne Bay	0.20	0.50	40000	1000
Burlington Bay	0.20	0.21	40000	1000
Cumberland Bay	0.26	0.20	40000	1000
Malletts Bay	0.30	0.14	50000	1000
Northeast Arm S.	0.30	0.12	40000	1000
St. Albans Bay	0.18	0.30	7500	1000
Missisquoi Bay	0.475	0.40	12000	1000
Isle LaMotte	0.11	0.32	30000	1000
Northeast Arm N.	0.12	0.20	40000	1000

## 3.4.7 Phosphorus Partition Coefficients

Sediment pore water dissolved inorganic phosphorus and solid phase particulate inorganic phosphorus data were available to estimate aerobic and anaerobic layer phosphorus partition coefficients. Near the sediment-water column interface, pore water phosphate was measured every 0.5 cm and solid phase inorganic phosphorus was measured every 1.0 cm. Aerobic and anaerobic layer partition coefficients were estimated by assuming the aerobic layer was 1.0 cm in depth. The partition coefficients calculated from the observed data were used as rough guidelines to estimate model partition coefficients for each model segment as shown in Table 3-7.

Phosphorus partitioning is effected by the sorption of phosphate to iron oxides. When more iron is available more phosphorus trapping should theoretically occur. Figure 3-4 presents a comparison phosphorus partition coefficients to measured solid phase iron concentrations. The plotting numbers refer to station numbers where the samples were taken. While the data show an increased aerobic layer partition coefficient, as expected, there does not appear to be any correlation between partition coefficients and solid phase iron concentrations. This would appear, then, to be an area of further research for the Management Conference to consider.

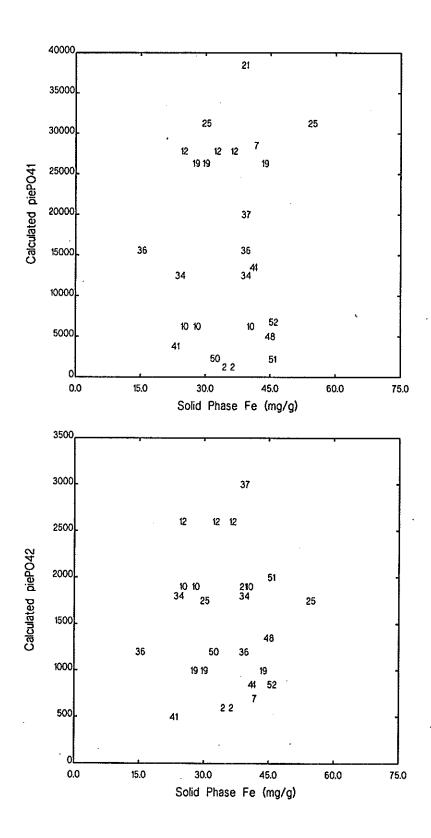


Figure 3-4. Estimated Phosphorus Partition Coefficients for the Aerobic Layer  $(\pi_{PO41})$  and Anaerobic Layer  $(\pi_{PO42})$  Verses Solid Phase Iron Concentrations

# 3.5 MODEL CALIBRATION

The final calibration, presented below, is the result of over 60 model runs, which were made to obtain a consistent set of model coefficients that are reasonable and reproduce the observed data for all the state variables considered. The method of determining the values for the modeling coefficients is essentially one of trial and error. The starting point is a set of rate constants and parameters which have been used in previous studies including the Long Island Sound study (HydroQual, 1991), the Massachusetts and Cape Cod Bays outfall relocation study (HydroQual, 1995) and previous work on Lake Champlain (HydroQual, 1995). The final set of water quality model constants and parameters are reported in Appendix A. The final set of sediment model constants and parameters are reported in Appendix B.

The model was run for a simulation period of fifty years with estimated historical loads so that the water column and sediment could achieve an equilibrium. The rather lengthy time to reach equilibrium is due to the fact that phosphorus is essentially conservative in the sediment bed and its only loss pathways are via flux to the overlying water column or burial to the deep sediments of the lake bed. Historical loads were crudely estimated by assuming that there has been a 40 percent reduction in phosphorus loadings from wastewater treatment facilities in all areas of the lake except for St. Albans Bay where a 90 percent reduction has occurred (Smeltzer, 1997).

Historical point source loads were estimated by dividing 1991 treatment plant loads by 0.60, except for St. Albans Bay where 1991 loads were divided by 0.10. This procedure was performed for all WWTFs that discharge directly into Lake Champlain and for WWTFs that discharge into the tributaries. To simplify the addition of historical WWTF loads to the model, the 1991 total phosphorus loads for each model segment were multiplied by a scale factor. This scale factor was computed by adding the historical WWTF loads to the estimated nonpoint source loads for that segment and then dividing by the sum of 1991 WWTF loads and the nonpoint source loads. The resultant phosphorus loading scale factors are presented in Table 3-8.

The model was then run for an additional ten years using 1991 freshwater inflows and loading conditions. This latter 10 year simulation attempts to account for the reduced loading that has occurred over the decade preceding 1991. Ideally, one would like to perform the 10 year simulation using actual 1982 through 1991 inflows and loads but data limitations and budget constraints precluded this analysis.

Table 3-8. Historical Loading Scale Factors

	······································
South Lake B	1.08
South Lake A	1.45
Port Henry	1.25
Otter Creek	1.34
Main Lake	1.18
Shelburne Bay	1.21
Burlington Bay	1.65
Cumberland Bay	1.51
Mallets Bay	. 1.06
Northeast Arm	1.00
St. Albans Bay	2.00
Missisquoi Bay	1.06
Isle LaMotte	1.17

Model versus data comparisons for the water column will be presented for six locations in Lake Champlain: South Lake B, Port Henry, Main Lake, Northeast Arm, St. Albans Bay and Missisquoi Bay. These locations were chosen due to the quantity of available data and the diversity of water quality conditions. Figure 3-5 presents the locations of these stations within the lake. The South Lake B, St. Albans Bay and Missisquoi Bay regions of the lake had only composite data with which to compare against the model and include sampling stations 1 and 2, 40 and 41, and 50 and 51, respectively. These lake regions were each modelled with one completely mixed segment. The Port Henry, Main Lake and Northeast Arm South model segments results are compared against data from vertical profile stations 7, 10 and 19, and 34, respectively. These three locations were each represented by two vertical layers in the model. The data collected in the top 10 meters of the water column were considered surface measurements and the remaining data were considered bottom measurements. The model results represent the last year of the simulation. Additional calibration figures for the remaining lake locations are presented in Appendix C. Figures which show model computations for the 50th year of the 50 year historical loading period are presented in Appendix D.

### 3.5.1 Chlorides

Chloride data were used to verify the flow routing and to estimate horizontal mixing or bulk exchange between the model segments. Figure 3-6 presents model versus data comparisons of chlorides for the six chosen locations. The data show fairly low concentrations of chlorides

# Lake Champlain Missisquoi Bay St. Albans Bay Northeast Arm Main ( Lake Port Henry South Lake B

Figure 3-5. Stations Used for Model Versus Data Comparisons in this Report

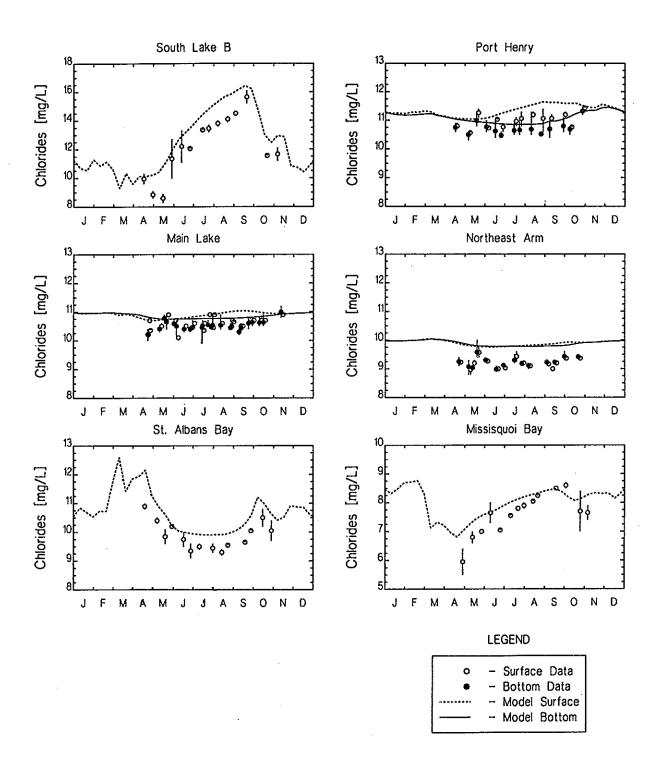


Figure 3-6. Calibrated Model Results Versus Data for Chlorides

within the lake ranging from less than 6 mg/L in Missisquoi Bay to almost 16 mg/L in South Lake B (higher concentrations are observed in South Lake A). The larger deep sections of the lake show only small temporal variations in the chloride concentration, while the smaller shallower areas have larger temporal variations of as much as 8 mg/L over the year. While the model slightly over-estimates the observed chlorinity at most locations and the Northeast Arm in particular, it does reproduce most of the temporal patterns observed in the data as well as the spatial differences between regions of the lake. Over-estimation of the chloride concentrations may be due to the fact that the model was run to a periodic steady-state using 1991 inflows and chloride loads and, therefore, ignores any carry over of water quality conditions from 1990. As noted the model captures the temporal variations observed throughout 1991 at South Lake B, St. Albans Bay and Missisquoi Bay. In addition, the model is also able to reproduce the observed stratification between top and bottom data at Port Henry, Main Lake and Northeast Arm. The horizontal bulk exchange rates used for model calibration are shown in Table 3-9.

Table 3-9. Horizontal Bulk Exchange

Segments	Layer	Bulk Exchange (hm³/yr)
South Lake B - South Lake A	1	15.6
South Lake A - Port Henry	1	660
Port Henry - Otter Creek	1	18,000
Port Henry - Otter Creek	2	7,750
Otter Creek - Main Lake	1	20,000
Otter Creek - Main Lake	2	38,000
Main Lake - Isle La Motte	1	6500
Main Lake - Isle La Motte	2	4,700
Missisquoi Bay - Northeast Arm N.	1	*
Northeast Arm N Northeast Arm S.	1	25,000
Mallets Bay - Northeast Arm S.	1	5.0
Main Lake - Shelburne Bay	·1	3,550
Main Lake - Shelburne Bay	2	1,300
Main Lake - Burlington Bay	1	2,900
Main Lake - Burlington Bay	2	100
Main Lake - Mallets Bay	1	20.4
Northeast Arm N Isle LaMotte	1	1,950
St. Albans Bay - Northeast Arm S.	1	<b>1,850</b>
Cumberland Bay - Main Lake	1	6,500
*seasonally dependent values ranging from 10 to 2	200 hm³/yr were used	
$1 \text{ hm}^3 = 10^6 \text{m}^3$		

## 3.5.2 Temperature

Temperature is an important parameter in the model that affects reaction rates computed within the model. Using available data, temperature profiles are assigned to the surface layer of the model. Vertical dispersion rates were then calibrated on a weekly basis in order to reproduce the bottom layer temperature. Five different temperature profiles, based on observed data, were developed to represent the various locations within the lake. Temperatures during the winter months were estimated. Figure 3-7 presents the bulk vertical dispersion and the vertical dispersion coefficients used in the temperature calibration of Port Henry, the Main Lake and the Northeast Arm. The bulk dispersion reflects the actual vertical exchange of water whereas the dispersion coefficient displays the relative dispersion normalized by cross-sectional area and segment depth.

Higher water column temperatures were observed in the data for the shallower regions of the lake, reaching 27°C in July and August (Figure 3-8). At the deeper locations the water column appears to be well mixed from October through April. During the remaining portion of the year temperature stratification was observed. At Port Henry and the Main Lake, a temperature difference between surface and bottom of greater than 10°C was observed. Bottom water temperatures were higher in the Northeast Arm than were observed at Port Henry and Main Lake; and the greatest temperature difference between surface and bottom was 8°C. The model is able to reproduce these observations.

# 3.5.3 Phosphorus

The in-lake phosphorus data collected included total phosphorus, dissolved phosphorus and soluble reactive phosphorus. For the purpose of this report and to be consistent with how the data are reported, soluble reactive phosphorus will be called ortho-phosphorus (PO<sub>4</sub>). For the purposes of model versus data comparisons dissolved organic phosphorus "data" were assumed to be the difference between the dissolved phosphorus data and the PO<sub>4</sub> data, and the particulate organic phosphorus "data" were assumed to be the difference between the total phosphorus and the dissolved phosphorus data. For plotting purposes, any data values that were negative were assumed to be zero.

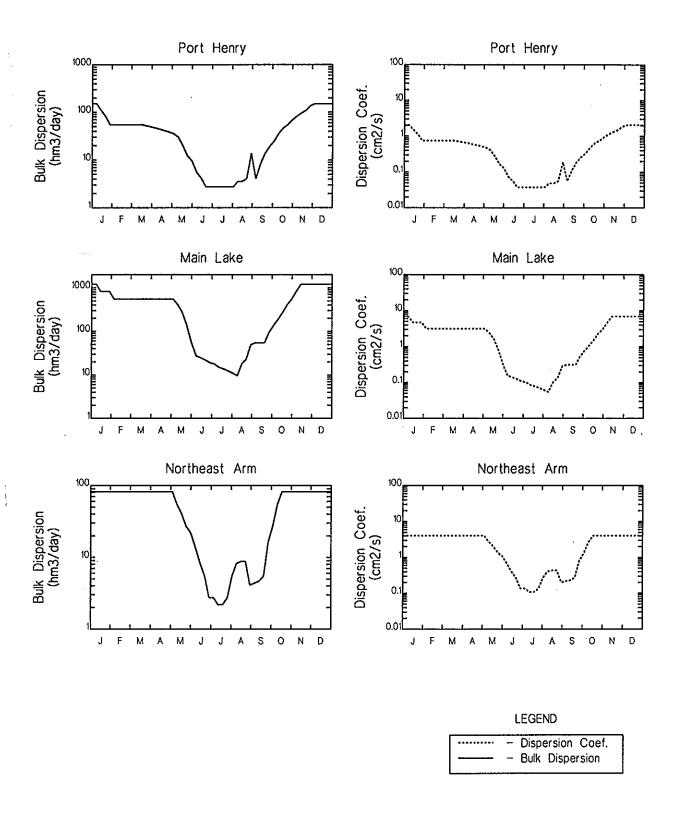


Figure 3-7. Model Bulk Vertical Dispersion and Vertical Dispersion Coefficients for Port Henry, Main Lake and Northeast Arm

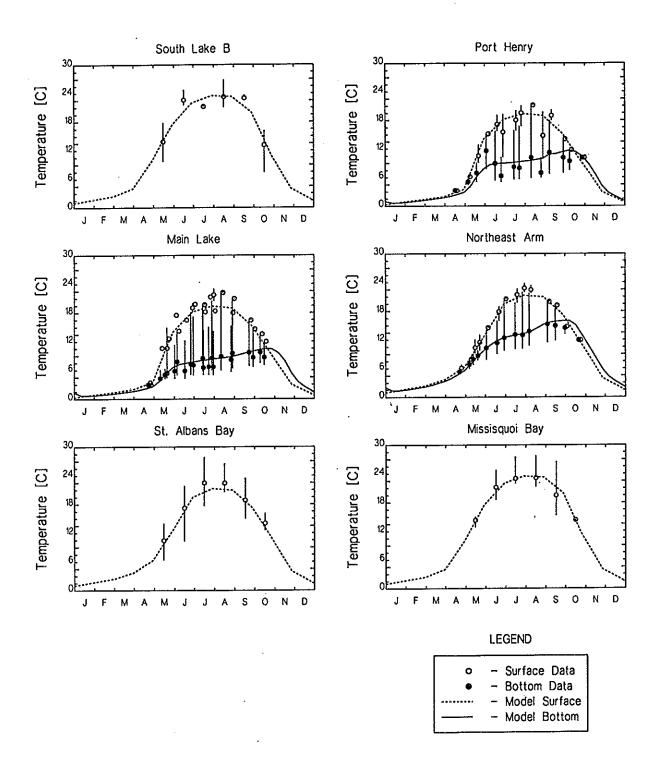


Figure 3-8. Calibrated Model Results Versus Data for Temperature

## 3.5.3.1 Total Phosphorus

Figure 3-9 presents the model versus data comparison for total phosphorus (TP). The areas with the highest observed TP concentrations tended to be the shallower sections of the lake. These areas were also observed to have low dissolved oxygen levels and may have been subjected to sediment resuspension associated with wind events. In three of these locations, South Lake B, St. Albans Bay and Missisquoi Bay, the highest concentrations of TP were observed in the summer. In the deeper sections of the lake, where the observed TP concentrations were lower, the highest concentrations of TP were observed in the spring and, in the case of the Northeast Arm, the fall.

The model is able to reproduce the measured TP concentrations fairly well for the deeper stations in the lake. In the deeper areas, the model predicts the proper magnitude and seasonal patterns of TP concentrations, but the computed surface and bottom concentrations are more stratified than the data indicate. The model under-predicts summertime peak TP concentrations in St. Albans Bay, Missisquoi Bay and South Lake B. For St. Albans Bay, three stations have been plotted separately. There appears to be a spatial gradient in TP extending from Station 41, in the back end of the bay with the highest concentrations, to Station 37, just outside the entrance to the bay with the lowest concentrations. The model cannot, of course, reproduce this feature using one completely mixed model segment. Therefore, the model will be compared to the data reported for these three stations. The model will be assumed to be calibrated if the model computations lie within the range of the data. However, even using this procedure, as a measure of model calibration, indicates that the model computes low relative to the observed data. The model computes TP concentrations just a little lower than the values observed at Station 37.

# 3.5.3.2 Orthophosphate (PO<sub>4</sub>)

The detection limit for the PO<sub>4</sub> measurements by VTDEC/NYSDEC was 0.002 mg P/L. In cases where the data were below the detection limit, the data were plotted at the detection limit. PO<sub>4</sub> data for South Lake B, St. Albans Bay and Missisquoi Bay were limited and were supplemented with data from 1990-96. Data collected at the deeper stations show stratification in PO<sub>4</sub> concentrations. This is due, in part, to algal uptake of PO<sub>4</sub> in the surface layer. In the deeper sections of the lake, algae become light limited and, therefore, do not grow and utilize PO<sub>4</sub>. Also contributing to higher bottom water PO<sub>4</sub> concentrations are release from phytoplankton cell, mineralization of detrital organic phosphorus, and flux of PO<sub>4</sub> from the sediment bed.

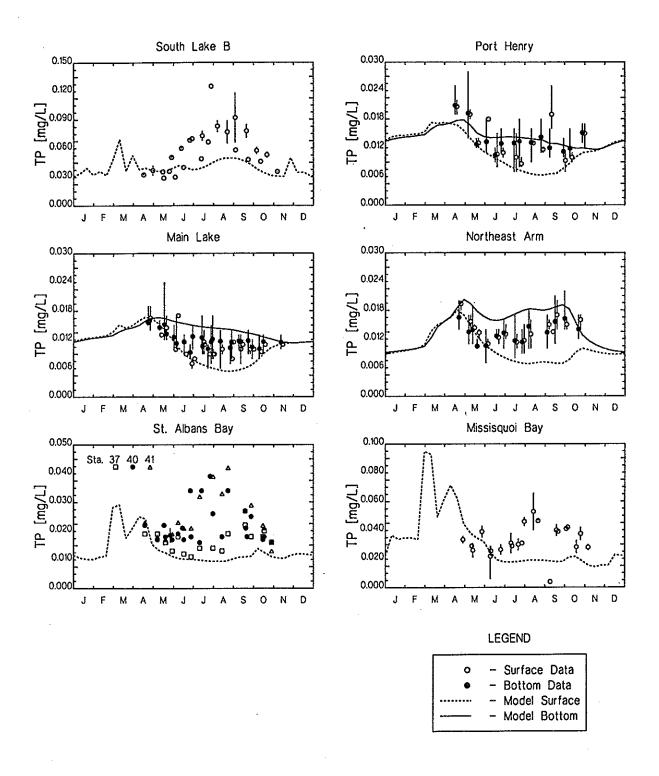


Figure 3-9. Calibrated Model Results Versus Data for Total Phosphorus

Figure 3-10 displays the model versus data comparison for PO<sub>4</sub>. The model predicts high PO<sub>4</sub> concentrations in the spring resulting from spring runoff, followed by potentially nutrient-limiting PO<sub>4</sub> concentrations in the summer. PO<sub>4</sub> concentrations increase in the fall as the algal biomass beings to decrease. The model overpredicts the PO<sub>4</sub> concentrations in South Lake B, in part, due to an underprediction of the algal biomass (to be shown subsequently). The model compares favorably to the limited data in St. Albans Bay and Missisquoi Bay. In the deeper two layer segments of the lake, the model compares favorably to the observed surface and bottom PO<sub>4</sub> concentrations. The model predicts nutrient limitation in the surface waters of the deeper stations during July, August and September. This corresponds reasonably well to the data. Bottom water PO<sub>4</sub> concentrations are generally less than 0.012 mg P/L.

## 3.5.3.3 Particulate Organic Phosphorus

Particulate organic phosphorus (POP) concentrations in the water column are a combination of external inputs of POP to the lake, phytoplankton biomass and algal detritus. POP concentrations could only be estimated at the vertical profile stations where both TP and total dissolved phosphorus were measured. Temporally, the highest concentrations of POP were observed in the spring, when POP loadings are high due to spring runoff and when high phytoplankton biomass was observed, and in the fall, when a fall phytoplankton bloom appeared to have been taken place. Surface water POP concentrations are generally greater than bottom water POP concentrations. Data at the three deep locations show that POP concentrations were generally less than 0.01 mg P/L, but occasional values greater than 0.015 mg P/L were also observed. Figure 3-11 presents the model versus data comparison for POP. The model performs adequately, generally reproducing the magnitude of concentrations of POP and temporal patterns observed in the data for the Main Lake and Port Henry stations. However, the model computes vertical POP concentrations which are opposite to those observed in the Northeast Arm. For this model segment, the model approximately reproduces the proper concentrations of POP. However, the model over-estimates bottom concentrations while under-estimating surface concentrations.

## 3.5.3.4 Dissolved Organic Phosphorus

Dissolved organic phosphorus (DOP) is produced from hydrolysis of POP and is a byproduct of respired and grazed algae. DOP is also found in treatment plant effluent and tributary runoff. DOP concentrations could only be estimated for the vertical profile stations,

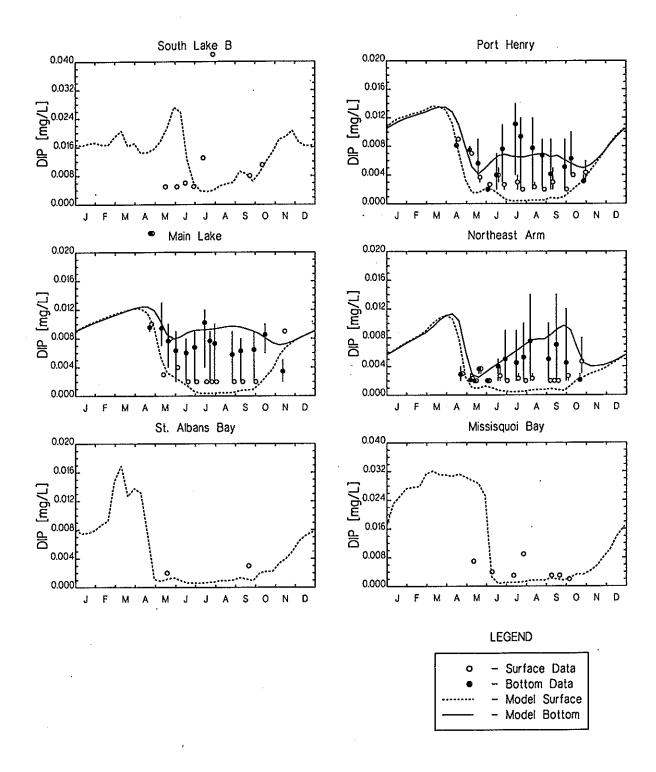


Figure 3-10. Calibrated Model Results Versus Data for Ortho-Phosphate

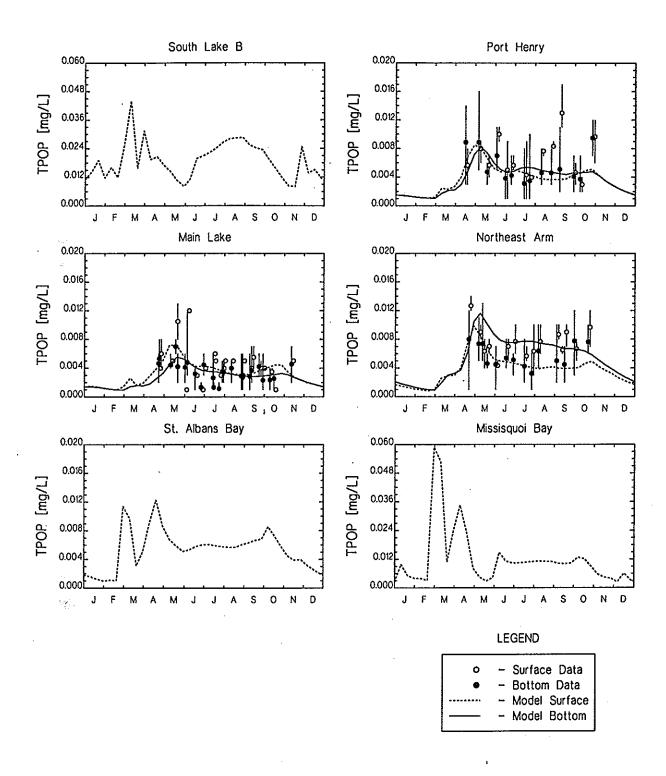


Figure 3-11. Calibrated Model Results Versus Data for Particulate Organic Phosphorus

where total dissolved phosphorus and PO<sub>4</sub> were measured. During the spring, DOP locations were observed to be greater in the surface layer. High DOP concentrations were also observed in the fall in the Northeast Arm. DOP concentrations were generally below 0.006 mg P/L. Figure 3-12 presents the comparison of model versus data for DOP. In general, the model reproduces the magnitude and timing of the measured DOP concentrations. However, in the Main Lake segment the model under-estimates surface DOP.

## 3.5.4 Chlorophyll-a

Chlorophyll-a is an estimate of phytoplankton biomass. The highest chlorophyll-a concentrations were observed in South Lake B, St. Albans Bay and Missisquoi Bay during July, August and September, when concentrations exceeded 20 ug/L. In the deeper sections, the highest chlorophyll-a concentrations were observed in the spring. Generally, chlorophyll-a concentrations were less than 15 ug/L at these deeper stations.

Model versus data comparisons for chlorophyll-a are presented in Figure 3-13. In general, the model predicts a spring bloom in the April/May time frame, a subsequent decline in June, and then elevated concentrations from July through October. For the deeper stations, the model is able to reproduce the observed surface and bottom chlorophyll-a concentrations fairly well. However, the model underpredicts chlorophyll-a concentrations in South Lake B and does not compute a spring bloom. The comparison between model and data is more favorable in St. Albans Bay, but the model does not compute the highest chlorophyll-a values observed in the data. In Missisquoi Bay, the model misses the timing of the spring bloom and predicts concentrations that are generally higher than observed values. In this model, only South Lake B received a chlorophyll-a "load", since POC and chl-a data suggest that phytoplankton inputs from the tributaries are small. However, small seed populations, entering the lake during the high flow period of April and May, may help trigger the spring bloom. Other than South Lake, this is not accounted for in the model.

#### 3.5.5 Extinction Coefficient

The extinction coefficient is a measure of how quickly light declines vertically in the water column and is a function of water clarity. Light extinction coefficients were estimated from Secchi depth measurements using Equation 3-2:

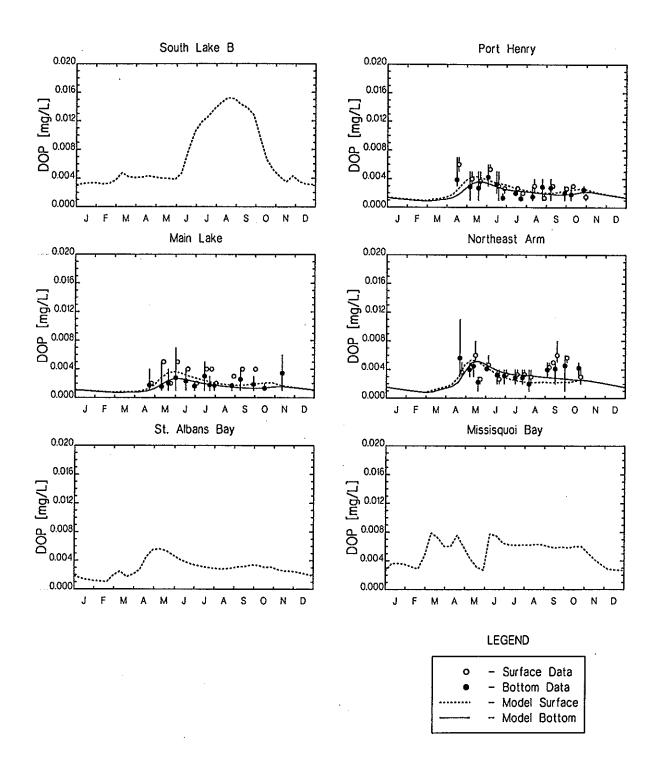


Figure 3-12. Calibrated Model Results Versus Data for Dissolved Organic Phosphorus

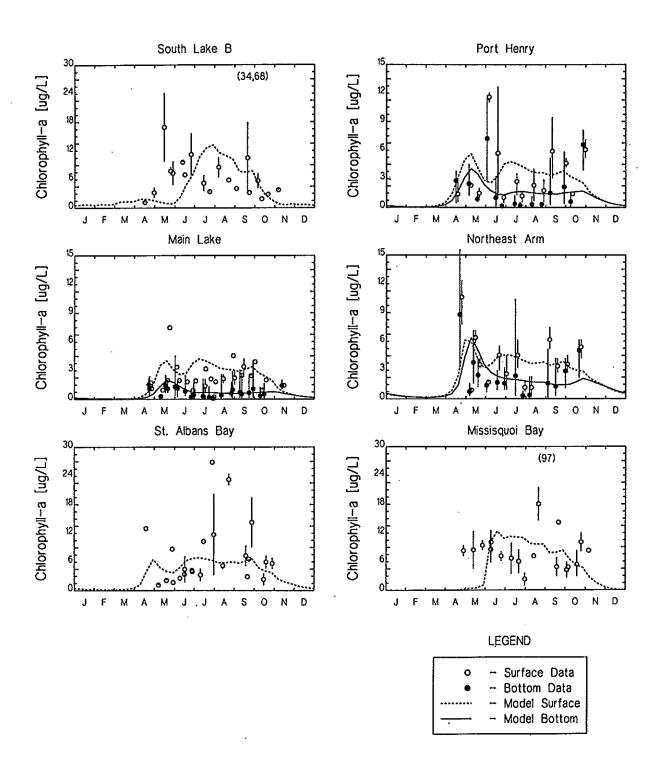


Figure 3-13. Calibrated Model Results Versus Data for Chlorophyll-a

$$K_{e} = \frac{1.7}{\text{Secchi Depth}}$$
 (3-2)

For each model segment the model calculates an extinction coefficient, which can be compared to the observed data. The model extinction coefficients are computed using a base extinction coefficient, (which includes light attenuation due to absorption by water molecules, background color and suspended solids), and the attenuation of light due to absorbance by algae as shown in Equation 3-3:

$$K_e = K_{e_{base}} + 0.017 \text{ chl-a}$$
 (3-3)

where  $K_{ebase}$  is the base extinction coefficient in m<sup>-1</sup> and chl-a is in  $\mu g/l$ . The base extinction coefficient is varied monthly based on available secchi depth and chlorophyll-a data.

Comparisons of model computed and observed extinction coefficients are presented in Figure 3-14; the base extinction coefficient is also presented for information purposes. Apart from South Lake B, it is apparent from the data that high extinction coefficients generally correspond to periods of high chlorophyll-a concentrations. When the model fails to reproduce the chlorophyll-a it also fails to reproduce the extinction coefficient. In South Lake B, the observed light extinction coefficients are extremely high and must be attributed to other factors than just high algal biomass. If high base extinction coefficients are assigned to South Lake B in the model, the model computes very little algal growth.

## 3.5.6 Organic Carbon

The majority of the carbon entering the lake via tributaries appears to be a fairly refractory DOC. This is based on the tributary organic carbon data which indicate that nearly all the TOC entering the lake is as DOC and model computations which indicate that only by using a slow DOC oxidation rate can the model reproduce the observed in-lake DOC data. Although concentrations of DOC as high as 10 mg C/L were measured in Northeast Arm, the majority of the data were between 2 and 6 mg C/L. DOC concentrations were highly variable and showed no discernable temporal trend. The model computes concentrations of approximately 4 mg C/L

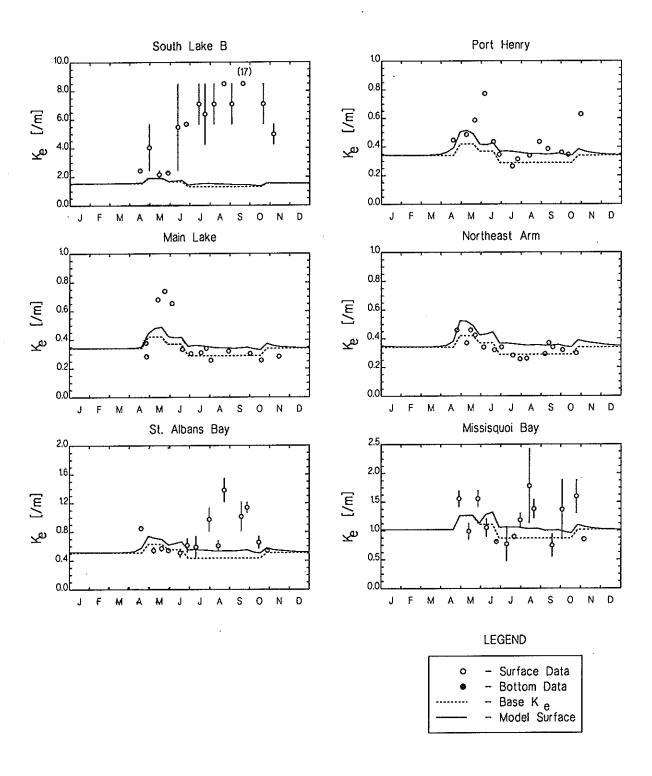


Figure 3-14. Calibrated Model Results Versus Data for the Extinction Coefficient

in the southern portions of the lake and concentrations of 5 to 7 mg C/L in northern portions of the lake (Figure 3-15). While the model overpredicts DOC concentrations in the Northeast Arm and St. Albans Bay, the model does reproduce the central tendency of the observed data at the remaining stations.

Based on a data and model analysis, it appears that the majority of the in-lake POC is associated with algal biomass. As has been noted above, measurements of tributary TOC and DOC suggest that the majority of the tributary TOC load is in the form of DOC. In addition, the highest POC measurements occur spatially and temporally when high chlorophyll-a measurements were recorded. The model generally reproduces the temporal trends in POC, although it underestimates the maximum observed POC concentrations (Figure 3-16).

# 3.5.7 Dissolved Oxygen

Dissolved oxygen plays an important role in the cycling of phosphorus between the water column and the sediment. In the aerobic layer of the sediment, iron oxyhydroxide forms via the oxidation of ferrous iron. This particulate species strongly sorbs pore-water phosphate and prevents its escape to the overlying water via diffusion. When the overlying water column dissolved oxygen decreases (due to algal respiration, oxidation of organic carbon and sediment oxygen demand), the aerobic layer in the sediment diminishes and the ferric oxyhydroxide is reduced to soluble ferrous iron which does not sorb phosphate as strongly. This allows phosphate to diffuse into the water column which may in turn provide nutrients for additional phytoplankton growth.

The 1991 data indicate that the lowest dissolved oxygen concentrations were found in the three shallow locations as well as the Northeast Arm. These low dissolved oxygen concentrations were usually observed when water column temperatures were the highest. In the shallow locations this occurred during the summer months, and in the Northeast Arm, just before the fall overturn. Hypoxic conditions (D.O. less than 3.0 mg/L) were observed for short periods of time at the South Lake B and St. Albans Bay stations during the summer months. For the Main Lake and Port Henry stations, the surface D.O. concentrations were generally near saturation while the bottom layer D.O. concentrations were slightly higher during the summer months. This was probably due to strong vertical stratification at these stations and due to relatively low oxygen demand below the thermocline. The model is able to reproduce this feature for these two stations. The model over-estimates D.O. concentrations in South Lake B, St. Albans Bay and

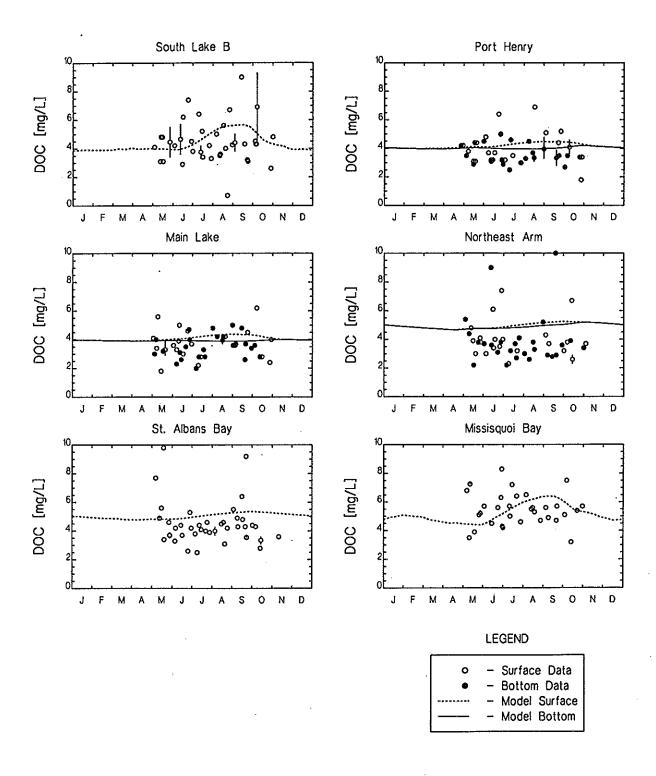


Figure 3-15. Calibrated Model Results Versus Data for Dissolved Organic Carbon

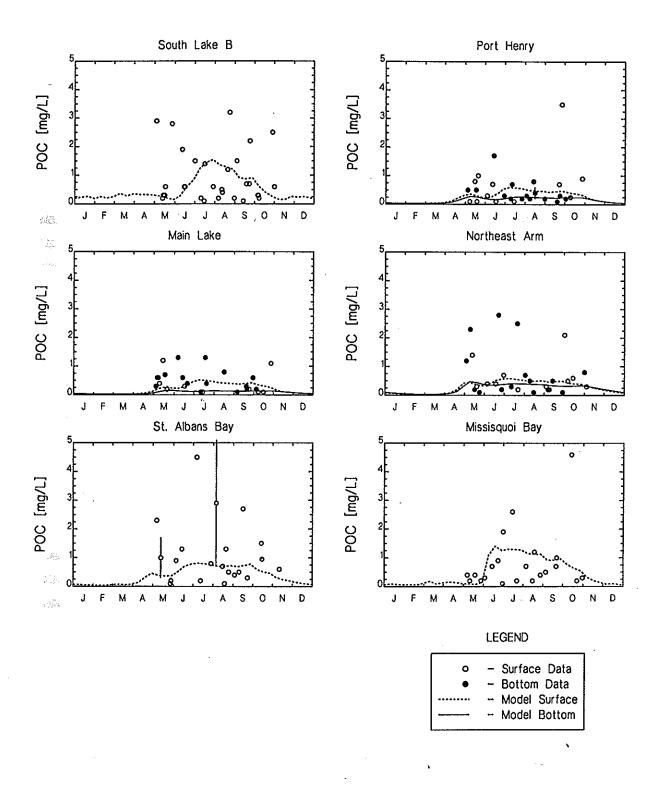


Figure 3-16. Calibration Model Results Versus Data for Particulate Organic Carbon

Missisquoi Bay. This may be due to a number of factors, including: an over-estimation of the phytoplankton biomass, inaccurate carbon loadings, local sources of detrital carbon from submerged aquatic vegetation, benthic fauna respiration, the omission of nitrification from the model framework, inadequate model segmentation, or more likely, a combination of these factors.

## 3.5.8 Sediment Composition

Sediment data were collected during April, July and October 1994 and August and October 1996 by the Horn Point Environmental Laboratory (HPEL). These data are used for comparison against model results. Figure 3-18 presents comparisons between data and model output for pore water PO<sub>4</sub>, solid phase PIP, and solid phase POP. The open bars represent data while the black bars are model output. Both bars represent an average of the data, or model output. The data are the average of core sections taken in the top 10 cm of the sediment while the model represents the yearly average. The lines intersecting the tops of the bars indicate the standard deviation of the data or model output. The top panel of Figure 3-18 displays the pore water PO<sub>4</sub> model versus data comparisons. In general, the model underpredicts the observed concentrations of PO<sub>4</sub>, but is within a factor of two of the data averages. At four of the six locations the model is within the standard deviation ranges of the data. The middle panel of Figure 3-18 presents the model versus data comparisons of solid phase PIP. Although the model underpredicts the PIP concentrations, it is within a factor of two at all locations except for the Main Lake stations. The reason for low Main Lake PIP concentrations may, in part, be due to sediment focusing which can occur in deeper sections of the lake. However, this phenomenon is not accounted for in the model. Additional horizontal segmentation, which might better represent lake bathemetry, might remedy this problem. As was noted previously, the observed pore water PO<sub>4</sub> and solid phase PIP data were used to estimate the partition coefficients assigned in the model. Model versus data comparisons for solid phase POP are displayed in the bottom panel of Figure 3-18. Again the model is in fair agreement with the data, but generally underpredicts the data especially in the Main Lake and Missisquoi Bay.

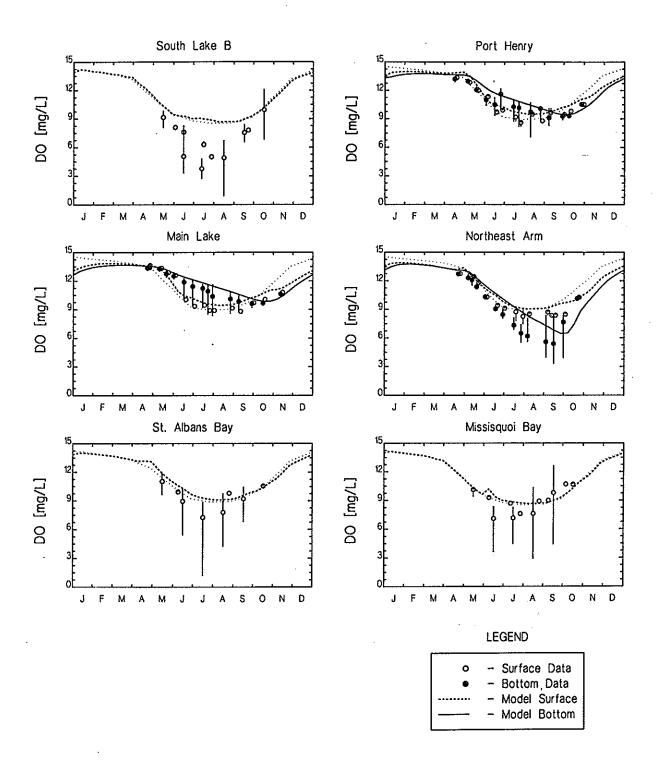


Figure 3-17. Calibrated Model Results Versus Data for Dissolved Oxygen

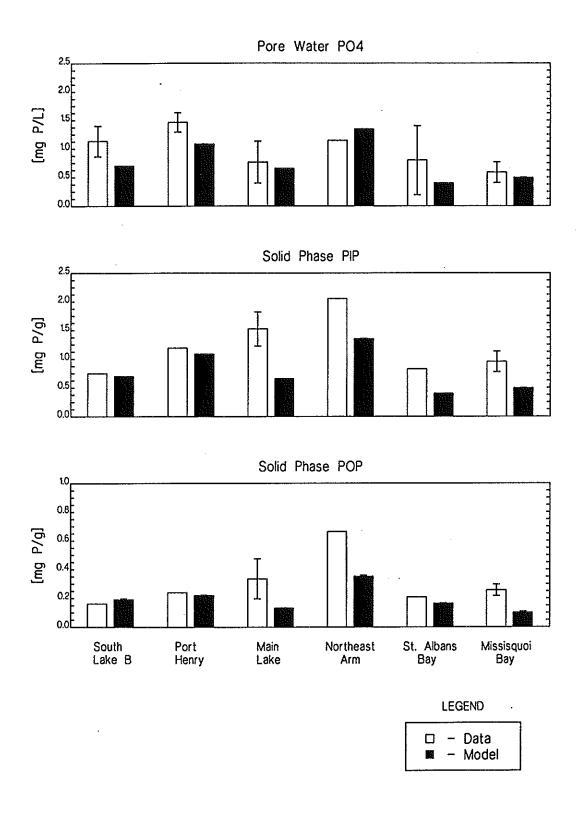


Figure 3-18. Comparison of Annually Averaged Data and Calibrated Model Results for Pore Water PO<sub>4</sub>, Solid Phase PIP and Solid Phase POP

## 3.5.9 Sediment Fluxes

Measured phosphate fluxes and model computed phosphate fluxes are compared in Figure 3-19. Data are represented by filled circles. In cases where two different sampling locations were sampled within one model segment, the second location is represented by an open circle. The flux data show a high correlation to bottom water temperature (Figure 3-8) and dissolved oxygen concentration (Figure 3-16). In April and October, when temperatures are low and dissolved oxygen concentrations are high, fluxes of less than 2 mg P/m²-d were generally observed. Higher phosphate fluxes were observed throughout the lake in July and August as temperatures rise and D.O. concentrations decrease. Two of the highest phosphate fluxes (25.6 and 44.7 mg P/m²-day) observed in this study were found in Missisquoi Bay. These high fluxes have been attributed to benthic organisms collected in the sediment cores. It is believed that these organisms were stressed during the sediment incubations and increased the rate of exchange between the sediment and overlying water (Cornwell, private communication). Therefore, these two values are omitted from the analysis and from Figure 3-19.

During the 1994 sediment sampling study, phosphate fluxes were measured using cores whose overlying water had been raised to dissolved oxygen saturation rather than using ambient *in-situ* conditions. Thus it is believed, that in areas which experience hypoxia, such as South Lake B and St. Albans Bay, the actual summertime phosphate flux measurements may have been under-estimated as a consequence of core re-aeration prior to the incubation experiments. As can be seen in Figure 3-19, the model overpredicts fluxes measured in South Lake B. This may, in part, be related to the fact that the cores at the South Lake B station were fully aerated as discussed. The model compares favorably to the observed fluxes in the Main Lake, St. Albans Bay and Missisquoi Bay, but underpredicts fluxes at Port Henry and the Northeast Arm.

The model versus data comparisons for sediment oxygen demand (SOD) are displayed in Figure 3-20. The SOD data show a similar pattern to that of the phosphate fluxes, i.e., lower fluxes in April and October (0.22-0.72 gm  $O_2/m^2$ -d) and high fluxes in July and August (0.04-1.43 gm  $O_2/m^2$ -d). The August 1996 fluxes were quite a bit higher than the July 1994 fluxes. The highest SOD measurements were observed in the locations with the highest phytoplankton populations. Settling phytoplankton provide a carbon source to the sediment that undergoes diagenesis or decay resulting in a sediment and oxygen demand.

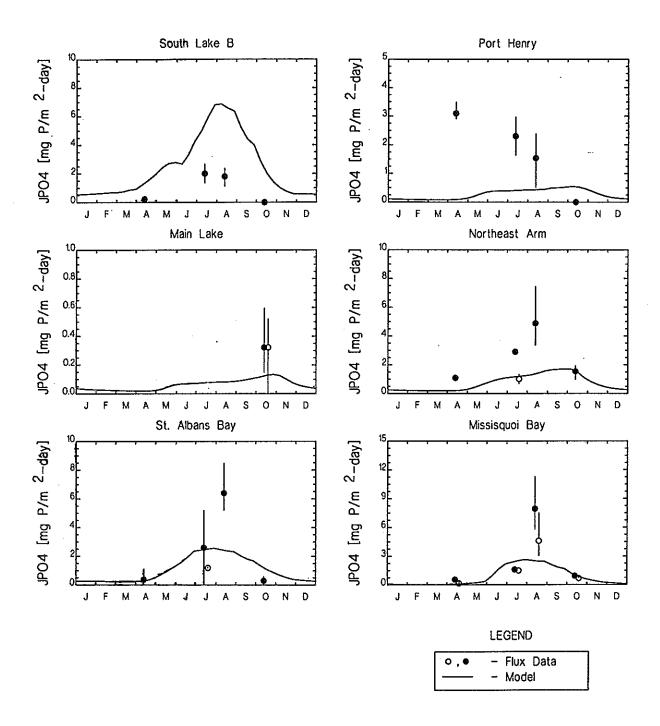


Figure 3-19. Calibrated Model Results Versus Data for Sediment Phosphate Flux

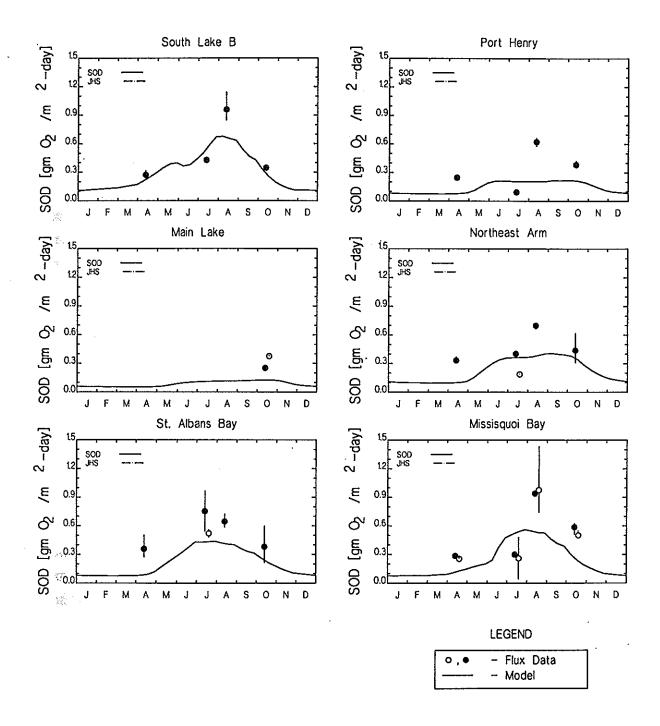


Figure 3-20. Calibrated Model Results Versus Data for Sediment Oxygen Demand

The model produces similar spatial and temporal patterns to those observed in the data. The model versus data comparisons for the single layer segments are generally good. In the two layer segments the model versus data comparisons are also favorable, although the model SODs are lower than the observed SODs.

#### 3.6 PHOSPHORUS BUDGET

The VTDEC, using data from March 1990 to February 1992, estimated total phosphorus inputs to Lake Champlain as 884 mt/yr and total outputs as 182 mt/yr. The difference between the input and output rates reflects a lake retention of approximately 80 percent of the phosphorus entering the lake. Using the water quality/sediment model developed in this study, a similar calculation of the phosphorus budget was made. For the 1991 calibration year the estimated total phosphorus load was 596 mt/yr and the model computed phosphorus outflow was 109 mt/yr. Therefore, by mass balance the model estimates that approximately 82 percent of the total phosphorus entering the lake remains in the lake. This value is very similar to the VTDEC estimate.

The model compares somewhat less favorably with published estimates of the mass of phosphorus in the sediments. Martin et al. (1994) made an estimate of total phosphorus incorporated in the sediment, for St. Albans Bay. Using a depth averaged sediment total phosphorus concentration, bottom surface area, and sediment porosity an estimate was made of the total phosphorus pool in the top 8.0 cm of sediment in St. Albans Bay. Separate estimates were made for the four geographic regions of St. Albans Bay, including the wetland, inner bay, middle bay and outer bay. Depth averaged mean total phosphorus concentrations of 1012 and 921  $\mu$ g/g, reported for the inner and middle bay by Martin et al. (1994), compare favorably with the St. Albans Bay measurement of 1090  $\mu$ g/g found in this study (Cornwell and Owens, 1998). However, the sediment solids concentrations differ significantly between the two studies. Martin et al. (1994) estimated an areally averaged sediment concentration of approximately 0.65 kg/L while Cornwell and Owen's estimates were 0.24 and 0.39 kg/L.

Based on Cornwell and Owen's sediment data a sediment concentration of 0.3 kg/L was used for model calibration. Using the model, an estimate was made of the total phosphorus pool in St. Albans Bay. In order to compare Martin's estimate and the model's estimate of the mass of total phosphorus, the two estimates had to be put on the same basis. The depth of the sediment layer in the model is 10 cm, so it was assumed that Martin's depth averaged total phosphorus

concentrations were the same for the top 10 cm therefore Martin's estimate of the total mass of phosphorus was multiplied by 1.25 to put it on an equivalent 10 cm basis. The surface area of the inner bay and middle bay is larger than the model segment of St. Albans Bay, so both total phosphorus mass estimates were divided by their respective surface areas to put the estimates on an areal basis. Martin's analysis estimated that there was 61.8 g P/m² in St. Albans in 1992. Model computations indicate a value of 16.7 g P/m² for St. Albans Bay. A little more than half of this difference may be due to the difference between the reported solid concentrations. The remaining difference between the two estimates of the total mass of phosphorus in the sediment is the model's acknowledged under-estimation of phosphorus in the sediment. The remaining model mis-calibration may reflect the use of just 1991 loading conditions for the last 10 years simulation period versus accounting for the actual year to year variation in phosphorus inputs.

#### 3.7 MODEL SENSITIVITIES

#### 3.7.1 Introduction

In general, the Lake Champlain Eutrophication Model reproduces many of the features observed in the phosphorus cycle of Lake Champlain. However, in areas with high total phosphorus concentrations and low dissolved oxygen levels, the model generally compares less favorably with the observed data. There are a number of explanations as to why the model performs less favorably in these locations. It is possible that the horizontal grid resolution of the model is not fine enough or that the model does not contain enough vertical layers to properly represent these areas. Also the model may not be able to reproduce low dissolved oxygen levels due to: under-estimation of carbon loadings to the lake; effects from submerged aquatic vegetation (SAV) or benthic organisms; lack of nitrification in the model kinetics; or sediment resuspension. Many of these processes are outside the scope of the modeling effort and cannot be simply parameterized and incorporated in the model. However, two sensitivity runs were developed to investigate how dissolved oxygen and resuspension may play a role in the phosphorus cycle of Lake Champlain. The first sensitivity run performed forced the dissolved oxygen concentrations through the observed data. The second sensitivity run attempted to investigate the effects on wind-resuspension by applying a time-variable scale factor to the mass transfer term between the water column and sediment. This scale factor was correlated to the observed wind data.

#### 3.7.2 Dissolved Oxygen Sensitivity

Phosphorus fluxes from the sediment are very sensitive to overlying water dissolved oxygen concentrations. Iron oxides sorb phosphorus very strongly and act as a trapping mechanism in the aerobic layer. As the aerobic layer shrinks and/or disappears the iron oxides are reduced to soluble forms of iron which do not sorb phosphorus as strongly and phosphorus is released to the water column. As a sensitivity, the overlying water column D.O. was forced through the observed data (Figure 3-21). Modifications were made to the D.O. temporal profiles in South Lake B, St. Albans Bay and Missisquoi Bay.

The effects of the sensitivity changes to D.O. on phosphorus fluxes are presented in Figure 3-22. The lower D.O. levels in the water column reduce the aerobic layer in the sediment. The reduction in the aerobic layer increases release of PO<sub>4</sub> into the water column. During the summer months, when D.O. concentration were reduced, the computed phosphate fluxes increase to levels as high or higher than observed in the data. Remember though that the sediment flux data were measured in cores which had D.O. levels in the overlying water higher than observed *in situ* conditions, especially at South Lake B and St. Albans Bay. Therefore, in core PO<sub>4</sub> flux measurements may have under-estimated actual *in situ* fluxes.

The increased sediment flux of phosphate in South Lake B, St. Albans Bay and Missisquoi Bay has an effect on the water column TP. The model now reproduces more of the observed temporal behavior in TP at these locations (Figure 3-23). The increased levels of TP also effect the phytoplankton. Model now computes the high chlorophyll-a values observed in South Lake B and Missisquoi Bay (Figure 3-24). Increased levels of phytoplankton also affect the amount of carbon reaching the sediment as more algae settle to the bottom. This increased organic carbon load increases the sediment oxygen demand. Figure 3-25 presents the model SOD results for this sensitivity. The model now reproduces the high values observed in the data.

The model calibration is not improved everywhere however. The increased flux from the sediment reduces the amount of phosphorus in the sediment, especially in St. Albans Bay. Figure 3-26 shows the sediment phosphorus composition resulting from running the sensitivity D.O. profile for 10 years. These results suggest that low D.O. concentrations may not occur every year or that the historical loading to St. Albans Bay may have been under-estimated or inappropriately distributed over the year.

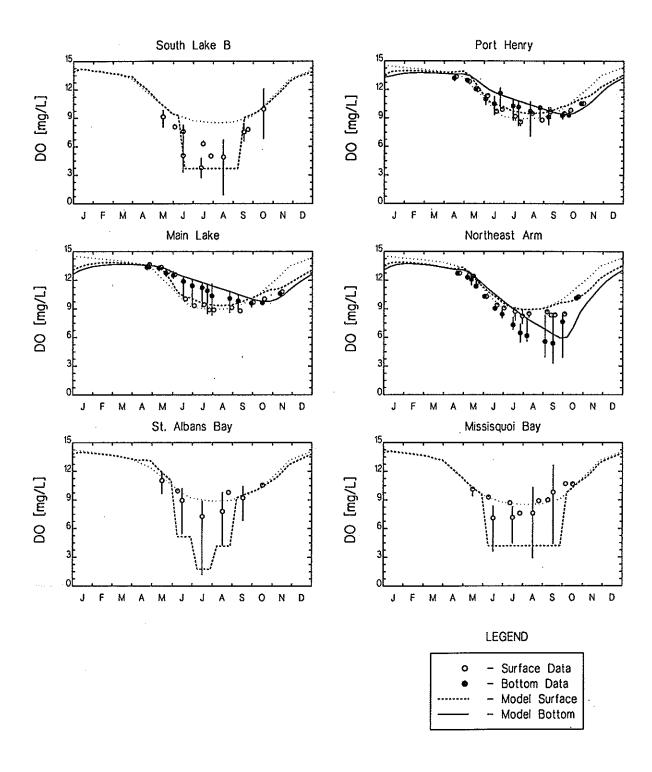


Figure 3-21. Dissolved Oxygen Sensitivity Model Results Versus Data for Dissolved Oxygen

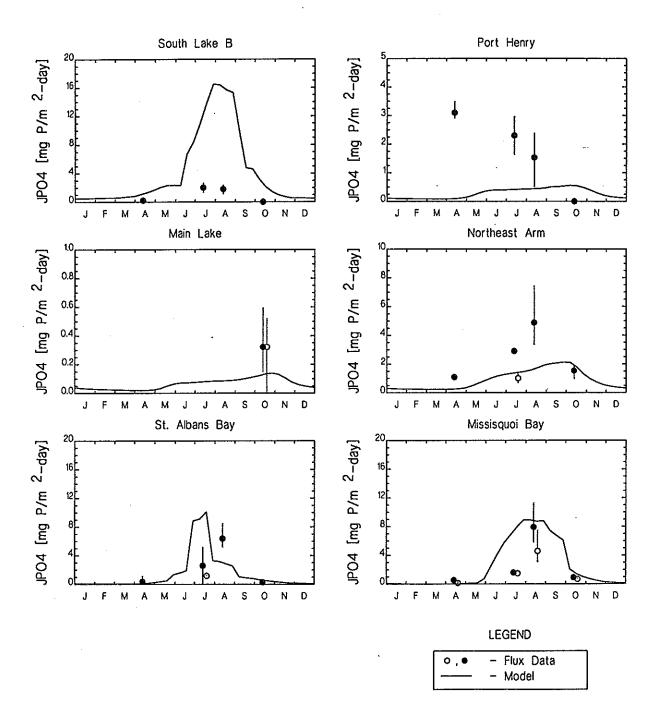


Figure 3-22. Dissolved Oxygen Sensitivity Model Results Versus Data for Sediment Phosphate Flux

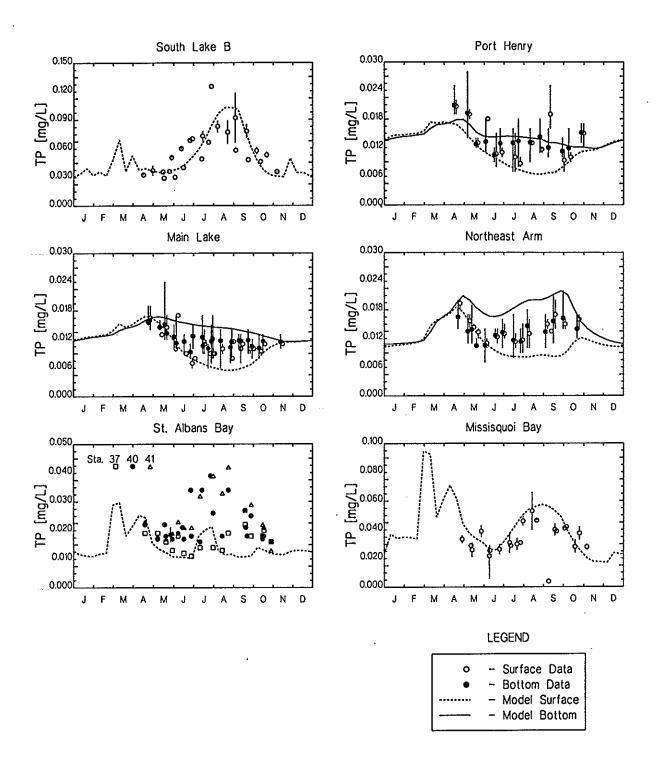


Figure 3-23. Dissolved Oxygen Sensitivity Model Results Versus Data for Total Phosphorus

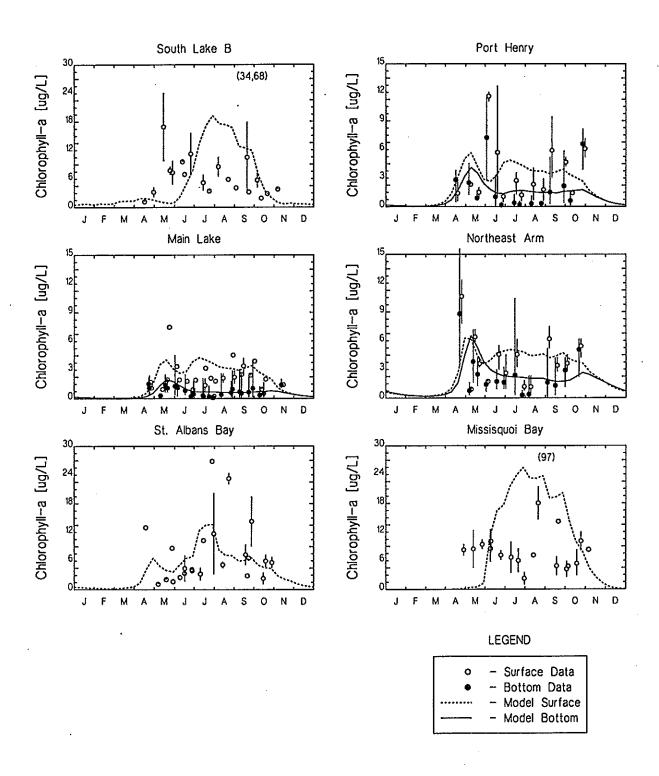


Figure 3-24. Dissolved Oxygen Sensitivity Model Results Versus Data for Chlorophyll-a

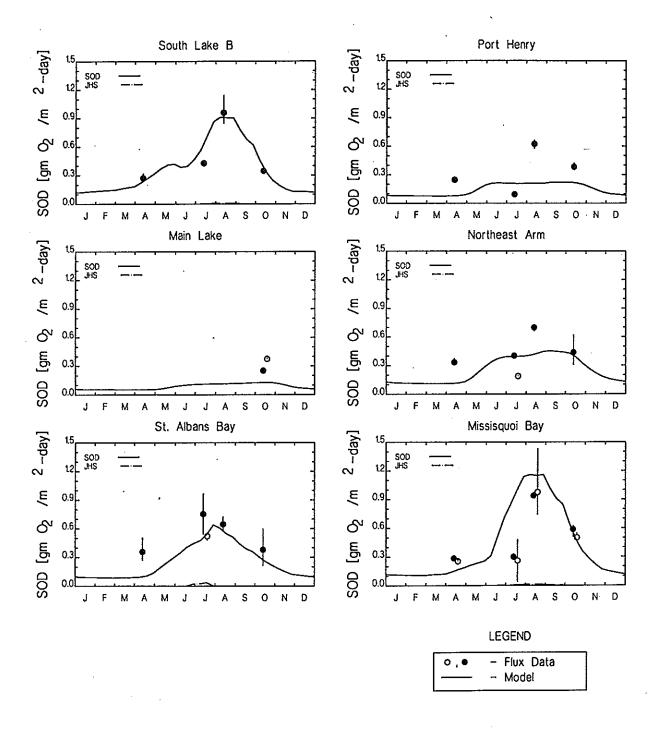


Figure 3-25. Dissolved Oxygen Sensitivity Model Results Versus Data for Sediment Oxygen Demand

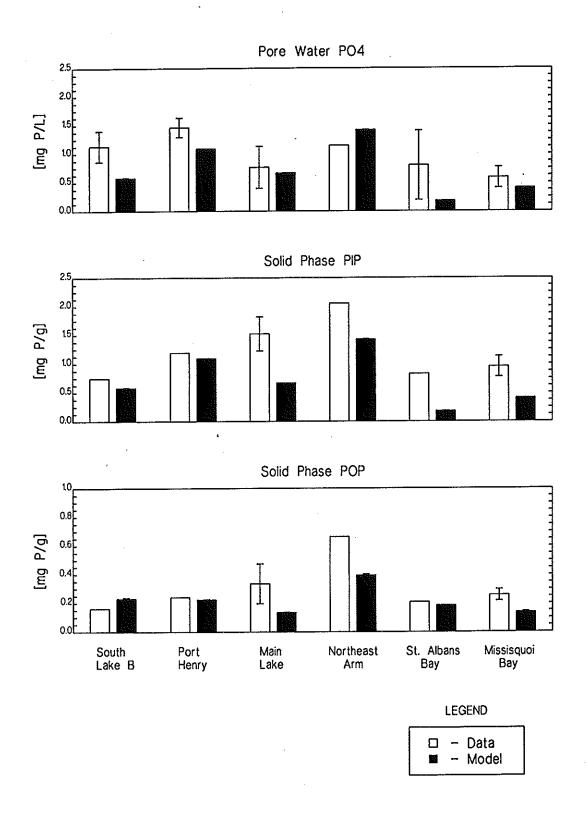


Figure 3-26. Comparison of Annually Averaged Dissolved Oxygen Sensitivity Model Results and Data for Sediment Pore Water PO<sub>4</sub>, Solid Phase PIP and Solid Phase POP

#### 3.7.3 Sediment Resuspension

In natural and man-made water systems sediment can be resuspended from the bottom due to a shear stress caused by high flows or high wind conditions. The current model framework does not account for sediment resuspension and, in the absence of detailed hydrodynamic computations, could not be easily modified to model particle resuspension. However, a sensitivity run was conducted which attempted to simulate the effects of sediment resuspension due to wind stresses. This run was performed by modifying the sediment submodel's mass transfer term, which governs the interchange between the water column and the sediment. The surface mass transfer coefficient, s, as defined by Equation 2-21, was multiplied by a scale factor as described by Equation 3-4, based on the north-south component of the observed wind velocities at Burlington Airport,

$$W_{s} = (1 + aW_{ns}^{2}) (3-4)$$

where  $W_s$  is the wind shear stress factor, a is a coefficient, and  $W_{ns}$  is the north-south component of the wind velocity. The north-south component of the wind was used due to the orientation of the lake. The north-south component of the wind can travel, unimpeded, great distances across the lake creating internal seiches. These seiches can result in higher bottom shear stresses which resuspend sediment.

As with the calibration and the D.O. sensitivity, the model was run for fifty years with estimated historical loads. Then the model was run with ten years of current loads and 1991 wind conditions. The wind stress coefficient, a, in Equation 3-4 coefficient was set equal to 0.16. Figure 3-27 shows that the calibration for TP is improved for South Lake B and Missisquoi Bay. However, there is only marginal improvement in the TP calibration for St. Albans Bay. Part of the reason for the minor improvement in St. Albans Bay can be seen in Figure 3-28. By the time that the tenth year of the simulation is reached, the solid phase particulate inorganic phosphorus is almost depleted in the sediments. During the first few years of the wind resuspension sensitivity run, there are increased concentrations of TP in St. Albans Bay, but as the sediment TP becomes depleted there is no TP to be resuspended from the sediments in the later years.

The wind resuspension sensitivity does not improve the D.O. calibration (Figure 3-29). Although the sediment oxygen demand is increased, the expected decrease in D.O. is offset by

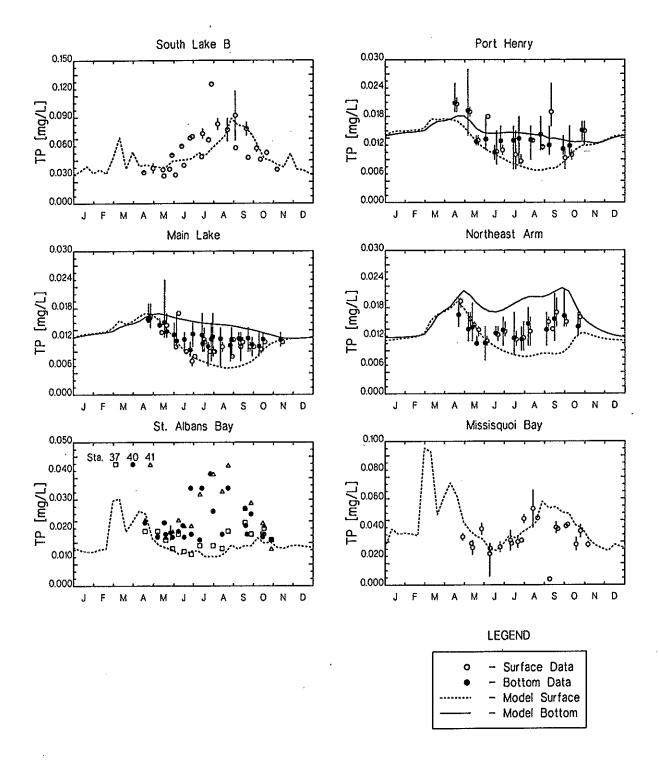


Figure 3-27. Wind Resuspension Sensitivity Model Results Versus Data for Total Phosphorus

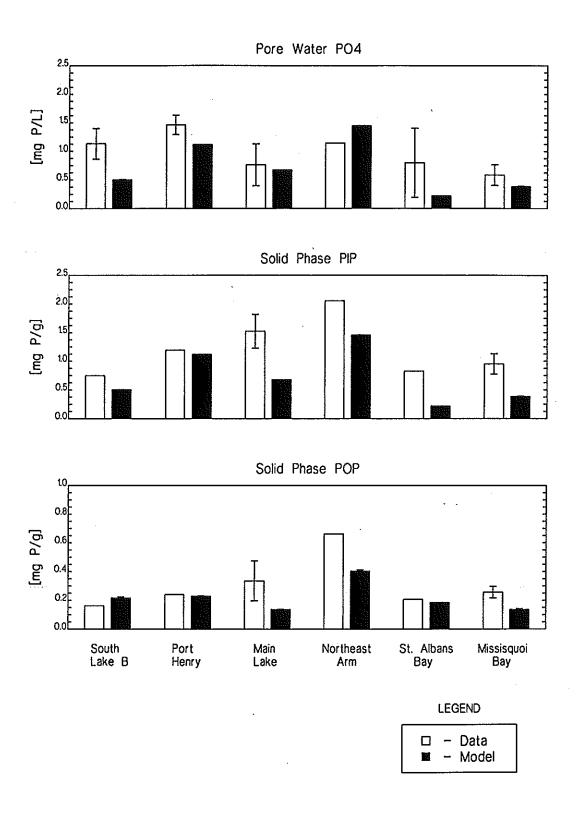


Figure 3-28. Comparison of Annually Average Wind Resuspension Sensitivity Model Results Versus Data for Sediment Pore Water PO<sub>4</sub>, Solid Phase PIP and Solid Phase POP

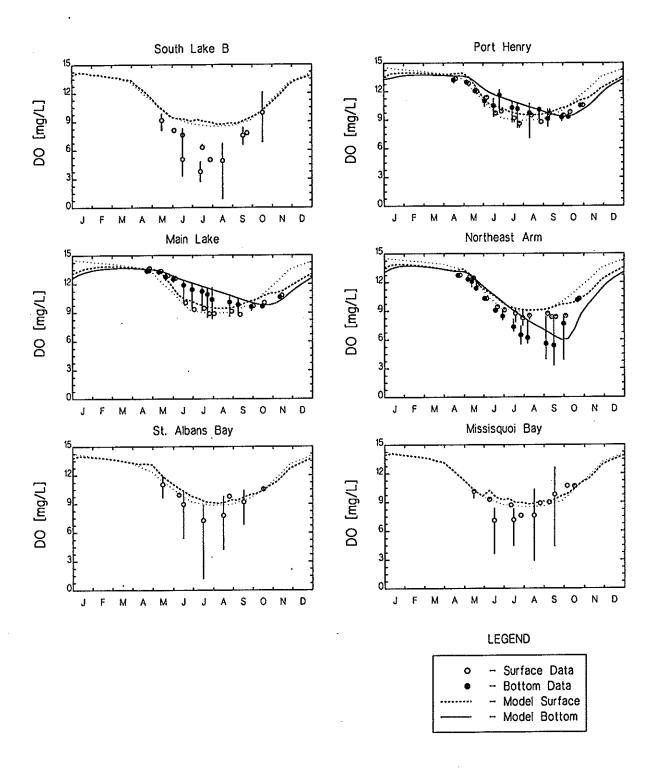


Figure 3-29. Wind Resuspension Sensitivity Model Results Versus Data for Dissolved Oxygen

the oxygen production from increased levels of phytoplankton. It is clear that wind resuspension is not the only feature lacking in the model which may contribute to reduced D.O. levels in parts of Lake Champlain.

#### 3.7.4 Summary of Sensitivities

The dissolved oxygen sensitivity indicates that improving the D.O. calibration will improve the overall model calibration. In addition, the sediment resuspension sensitivity run shows that wind resuspension may be an important factor in the total phosphorus cycle, and therefore, the phytoplankton cycle in some of the shallower embayments of Lake Champlain. An analysis of both sensitivies indicates that there is not enough phosphorus in the sediment of the Lake. A number of factors may contribute to the calibration problem, including: the use of 1991 loadings for long-term simulations; effects of submerged aquatic vegetation on phosphorus and D.O. dynamics; seasonal inputs of refraction phosphorus and carbon from "leaf-litter"; and sediment focusing to the deeper portions of the main lake and embayments. The model, however, can be used to test these hypotheses provided that additional data are collected and/or additional research is conducted.

#### 3.8 TIME TO SEDIMENT EQUILIBRIUM

In a technical report titled "Assessment of Sediment Phosphorus Distribution and Long-Term Recycling in St. Albans Bay, Lake Champlain" (Martin et al. 1994), an estimate was made of the rate of depletion of excess sediment TP in St. Albans Bay after phosphorus load reductions were initiated. A simple first order rate analysis was performed which used sediment data collected in 1982 and 1992. The analysis resulted in estimates of the time for 50, 75 and 90 percent depletion of the excess TP. Table 3-10 presents these results.

Using the calibrated model developed in this study, a similar estimate was made for St. Albans Bay. The calibrated water quality model was run, from a starting point approximately equivalent to 1981, for 150 years with 1991 loading conditions. The results of this simulation are consistent with Martin et al. (1994) and are presented in Table 3-10. Another simulation run was performed using wind resuspension formulation described earlier in this report. It was found that, for this scenario, the model took 27.5 years to reach 90 percent depletion, approximately 40 percent faster than the calibration time to equilibrium. However, the total sediment TP equilibrium mass in St. Albans Bay was lower in this scenario than in the normal calibration.

Table 3-10. Time to Equilibrium

· · · · · · · · · · · · · · · · · · ·	Time (	(years)
Reduction of TP	Martin et al.	HydroQual
50%	15.1	11
75%	30.1	24
90%	50.1	45



#### **SECTION 4**

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# APPENDIX A WATER COLUMN KINETICS

# TABLE A-1. STATE SYSTEM VARIABLES, COUPLED EUTROPHICATION/CHEMICAL EQUILIBRIA MODEL

- 1. chlorinity (Cl)
- 2. phytoplankton carbon winter diatoms (Pc1)
- 3. phytoplankton carbon summer assemblage ( $P_{\rm C2}$ )
- 4. particulate organic phosphorus (POP)
- 5. dissolved organic phosphorus (DOP)
- 6. dissolved inorganic phosphorus (DIP)
- 7. particulate organic carbon (POC)
- 8. dissolved organic carbon (DOC)
- 9. algal exudate dissolved organic carbon (ExDOC)
- 10. dissolved oxygen equivalents (O<sub>2</sub>\*)
- 11. dissolved oxygen (DO)
- 12. temperature (T)

#### TABLE A-2. PHYTOPLANKTON NET GROWTH EQUATIONS

#### **Net Growth Rate**

$$S_{p} = G_{pmax} \times G_{T}(T) \times G_{I}(I) \times G_{N}(N) \times P_{c}$$
 Phytoplankton Growth 
$$-k_{pR}(T) \times P_{c}$$
 Endogenous Respiration 
$$-k_{sp}(T) \times P_{c}$$
 Algal Settling 
$$-k_{grz}(T) \times P_{c}$$
 Zooplankton Grazing

#### **Temperature Correction**

$$G_{T}(T) = \Theta_{T}^{(T_{opt}-T)} \qquad T \leq T_{opt}$$

$$G_T(T) = \Theta_T^{(T-T_{opt})} \qquad T > T_{opt}$$

#### **Light Reduction**

$$G_{I}(I) = \frac{ef}{k_{e}H} \cdot \left(e^{-\alpha_{1}} - e^{-\alpha_{0}}\right)$$

$$\alpha_1 = \frac{I_o}{I_s} e^{-k_e H}$$
  $\alpha_o = \frac{I_o}{I_s}$ 

$$k_{\rm e} = k_{\rm ebase} + k_{\rm c} \times \frac{P_{\rm c}}{a_{\rm cch1}}$$

### TABLE A-2. PHYTOPLANKTON NET GROWTH EQUATIONS (Continued)

#### **Nutrient Uptake**

$$G_N(N) = \left(\frac{DIP}{K_{mP} + DIP}\right)$$

DIP = dissolved inorganic phosphorus

#### **Algal Settling**

$$k_{sP} = \frac{v_{sPb}}{H} \times \theta_{sP}^{(T-20)} + \frac{v_{sPn}}{H} \times \left[1 - G_N(N)\right] \times \theta_{sP}^{(T-20)}$$

#### **Endogenous Respiration**

$$k_{PR}(T) = k_{PRbase} + f_r \times G_p(T)$$
  $G_p = G_{Pmax} \times G_T(T) \times G_I(T) \times G_I(T)$ 

#### **Zooplankton Grazing**

$$k_{grz}(T) = k_{grz}(20^{\circ}C) \times \theta_{grz}^{(T-20)}$$

# TABLE A-2. PHYTOPLANKTON NET GROWTH EQUATIONS (Continued)

	Exogenous Variables	
<u>Notation</u>	<u>Description</u>	
${ m P_c}$	Phytoplankton Population as Carbon	
$k_{e}$	Total Extinction Coefficient	
$\mathbf{k}_{ebase}$	Base Extinction Coefficient	
$I_o$	Total Daily Surface Solar Radiation	
T	Temperature	
${ m H}$	Segment Depth	
${f f}$	Fraction of Daylight	

TABLE A-2. PHYTOPLANKTON NET GROWTH EQUATIONS (Continued)

#### Rate Constants

Description	<u>Notation</u>	Phytoplankton <u>Group</u>		<u>Units</u>
•		<u>Winter</u>	Summer	
Maximum Specific Growth Rate at Topt	$G_{\text{Pmax}}$	1.75	1.9	/day
Temperature Optimum	$\mathbf{T}_{ ext{opt}}$	6	18	°C
Effect of Temperature on growth	$\theta_{\mathtt{T}}$	1.068	1.068	
Phytoplankton Self-Light Attenuation	$k_c$	0.017	0.017	m²/mg chla
Half-Saturation Constant for Phosphorus	$K_{mP}$	0.001	0.001	mg/L
Algal Endogenous Respiration Rate	$k_{PR}$			
Basal Respiration Rate	$k_{PRbase}$	0.050	0.050	1/day
Respired Fraction of Growth	$f_r$	0.20	0.20	
Base Algal Settling Rate	$V_{sPb}$	0.40	0.20	m/day
Nutrient Dependent Algal Settling Rate	$\boldsymbol{v}_{sP\pi}$	1.20	0.00	m/day
Temperature Coefficient	$\theta_{sP}$	1.00	1.00	
Loss Due to Zooplankton Grazing	$\mathbf{k}_{grz}$	0.100	0.050	/day
Temperature Coefficient	$\theta_{grz}$	1.08	1.08	
Carbon/Chlorophyll Ratio	$a_{cchl}$	50	100	mgC/mg chla
Saturating Light Intensity	$\mathbf{I_s}$	250	350	Ly/day

#### TABLE A-3. PHYTOPLANKTON/NUTRIENT STOICHIOMETRY

$$\frac{x}{c} = \frac{1}{x_1 + (x_2 - x_1) e^{-x_3DIX}}$$

x = nutrient of interest (DIP)

 $x_1$  = carbon to nutrient ratio under nutrient saturated conditions

 $x_2$  = maximum carbon to nutrient ratio under nutrient limited conditions

x<sub>3</sub> = coefficient which determines rate at which the algal stoichiometry changes as a

function of DIX

DIX = concentration of available nutrient (DIP)

#### TABLE A-4. ORGANIC CARBON REACTION EQUATIONS

#### Particulate Organic Carbon (POC)

$$S_7 = f_{POC} \times k_{grz} (T) \times P_c$$

$$- k_{7,8} \Theta_{7,8}^{(T-20)} \times POC \times \frac{P_c}{K_{mP_c} + P_c}$$

$$- \frac{V_{sPOM(T)}}{H} \times POC$$

$$Settling$$

#### Dissolved Organic Carbon (DOC)

$$S_{8} = f_{DOC} \times k_{grz} (T) \times P_{c} \qquad Zooplankton \ Recycle$$
 
$$+ k_{7,8} \Theta_{7,8}^{(T-20)} \times DOC \times \frac{P_{c}}{K_{mP_{c}} + P_{c}} \qquad Hydrolysis$$
 
$$- k_{8,0} \Theta_{8,0}^{(T-20)} \times DOC \times \frac{P_{c}}{K_{mP_{c}} + P_{c}} \times \frac{DO}{K_{DO} + D} \qquad Oxidation$$

#### Algal Exudate Dissolved Organic Carbon (ExDOC)

$$S_9 = f_{E \times DOC} \times G_P \times P_C$$
 Algal Exudation 
$$-k_{9,0} \Theta_{9,0}^{(T-20)} \times E \times DOC \times \frac{P_C}{K_{mP} + P_C} \times \frac{L}{K_{DO}}$$
 Oxidation

TABLE A-4. ORGANIC CARBON REACTION EQUATIONS (Numbering scheme refers to the variable list in Table A-1) (Continued)

Description	Notation	Value	Units
Phytoplankton Biomasss	P <sub>c</sub>	-	mg C/L
Specific Phytoplankton Growth Rate	G <sub>P</sub>		day-1
Half Saturation Constant for Phytoplankton Limitation	K <sub>mPc</sub>	0.05	mg C/L
Fraction of Grazed Organic Carbon Recycled to:		,	
the POC pool	$\mathbf{f}_{\mathtt{POC}}$	0.50	
the DOC pool	${ m f_{DOC}}$	0.50	
Fraction of Primary Productivity Going to the Algal Exudate DOC pool	$f_{\text{ExDOC}}$	0.10	
Hydrolysis Rate for POC	k <sub>7,8</sub>	0.04	day-1
Temperature Coefficient	$\theta_{7,8}$	1.08	
Base Settling Rate of POM (POC)	$v_{sPOM}$	0.5	m/đay
Segment depth	H		m
Oxidation Rate of DOC	$k_{8,0}$	0.002	day-1
Temperature Coefficient	$\theta_{8,0}$	1.08	
Oxidation Rate of ExDOC	k <sub>9,0</sub>	0.150	day-1
Temperature Coefficient	$\theta_{9,0}$	1.080	
Half Saturation for Oxygen Limitation of Organic Carbon Oxidation	$K_{DO}$	0.20	$mg O_2/L$
Dissolved Oxygen	DO	-	$mg O_2/L$

#### TABLE A-5. PHOSPHORUS REACTION EQUATIONS

#### Particulate Organic Phosphorus (POP)

$$\begin{split} S_4 &= a_{PC} \times f_{POP} \times \left[ k_{PR}(T) + k_{grz}(T) \right] \times P_c \\ &- k_{4,5} \theta_{4,5} \stackrel{(T-20)}{\longrightarrow} \times POP \times \frac{P_c}{K_{mP_c} + P_c} \\ &- \frac{V_{sPOM(T)}}{H} \times POP \end{split}$$

Algal Respiration and Zooplankton Recycle

Hydrolysis

Settling

#### Dissolved Organic Phosphorus (DOP)

$$S_{5} = a_{PC} \times f_{DOP} \times \left[ k_{PR}(T) + k_{grz}(T) \right] \times P_{c}$$

$$+ k_{4,5} \theta_{4,5} \stackrel{(T-20)}{\times} \times POP \times \frac{P_{c}}{K_{mP_{c}} + P_{c}}$$

$$- k_{5,6} \theta_{5,6} \stackrel{(T-20)}{\times} \times DOP \times \frac{P_{c}}{K_{mP_{c}} + P_{c}}$$

Algal Respiration and Zooplankton Recycle

Hydrolysis

Mineralization

## TABLE A-5. PHOSPHORUS REACTION EQUATIONS (Continued)

#### Dissolved Inorganic Phosphorus (DIP)

$$S_{6} = a_{PC} \times f_{DIP} \times \left[k_{PR}(T) + k_{grz}(T)\right] \times P_{c} \qquad \qquad Algal Respiration and Zooplankton Recycle \\ + k_{5,6} \theta_{5,6} \stackrel{(T-20)}{\times} \times DOP \times \frac{P_{c}}{K_{mP_{c}} + P_{c}} \qquad \qquad DOP \ \textit{Mineralization} \\ - a_{PC} \times (1 - f_{ExDOC}) \times G_{P} \times P_{c} \qquad \qquad \textit{Uptake by Phytoplankton}$$

TABLE A-5. PHOSPHORUS REACTION EQUATIONS (Continued)

Description	Notation	<u>Value</u>	<u>Units</u>
Phytoplankton Biomass	$P_c$	-	mg C/L
Temperature Corrected Algal Respiration Rate	$k_{PR}(T)$		day <sup>-1</sup>
Temperature Corrected Grazing Rate	$k_{grz}(T)$		day-1
Specific Phytoplankton Growth Rate	$G_{\mathtt{P}}$		day <sup>-1</sup>
Half Saturation Constant for Phytoplankton Limitation	$K_{mPc}$		
Phosphorus to Carbon Ratio	$a_{PC}$		
Fraction of Primary Productivity Going to the Algal Exudate DOC pool	$\mathbf{f}_{\mathtt{ExDOC}}$	0.10	
Fraction of Respired and Grazed Algal Phosphorus Recycled to			
the POP pool	$f_{POP}$	0.35	
the DOP pool	$f_{DOP}$	0.40	
the DIP pool	$\mathbf{f}_{DIP}$	0.25	
POP Hydrolysis Rate at 20°C	k <sub>4,5</sub>	0.040	day-1
Temperature Coefficient	$\theta_{4,5}$	1.08	
Base Settling Rate of POM (POP)	$V_{sPOM}$	0.50	m/day
DOP Mineralization Rate at 20°C	k <sub>5,6</sub>	0.10	day-1
Temperature Coefficient	$\theta_{5,6}$	1.08	

## TABLE A-6. DISSOLVED OXYGEN AND AQUEOUS OXYGEN EQUIVALENT REACTION EQUATIONS

#### Dissolved Oxygen (DO)

$$S_{11} = a_{OC} \times G_p \times P_c \qquad \qquad Phytoplankton Photosynthesis (Ammonia and Nitrite Derived)$$

$$+ k_a \theta_a^{(T-20)} \times (DO_{sat} - DO) \qquad \qquad Atmospheric Reaeration$$

$$- a_{OC} \times k_{PR}(T) \times P_c \qquad \qquad Algal Respiration$$

$$- k_{8,0} \theta_{8,0}^{(T-20)} \times DOC \times \frac{P_c}{K_{mP_c} + P_c} \times \frac{DC}{K_{DO} +} \qquad DOC \text{ Oxidation}$$

$$- k_{9,0} \theta_{9,0}^{(T-20)} \times ExDOC \times \frac{P_c}{K_{mP_c} + P_c} \times \frac{I}{K_{DC}} \qquad ExDOC \text{ Oxidation}$$

$$- k_{9,0} \theta_{9,0}^{(T-20)} \times O_2^* \times \frac{DO}{K_{DO_{obs}} + DO} \qquad Aqueous \text{ Sediment Oxygen Demand}$$

### Aqueous Sediment Oxygen Equivalents (O2)

$$S_{10} = k_{o_2^*} \Theta_{o_2^*}^{(T-20)} \times O_2^* \times \frac{DO}{K_{DO_{o_2^*}} + DO}$$
Aqueous Sediment Oxygen Demand

TABLE A-6. DISSOLVED OXYGEN AND AQUEOUS SEDIMENT OXYGEN EQUIVALENT REACTION EQUATIONS (Continued)

Description	<u>Notation</u>	<u>Value</u>	<u>Units</u>
Phytoplankton Biomass	$P_c$	-	mg C/L
Specific Phytoplankton Growth Rate	$G_p$		day <sup>-1</sup>
Half Saturation Constant for Phytoplankton Limitation	$K_{mPc}$		
Reaeration Rate at 20°C	$k_a$		day-1
Temperature Coefficient	$\theta_{\mathtt{a}}$	1.024	
Oxygen Transfer Coefficient	$\mathbf{k_{L}}$	1.83	m/day
Dissolved Oxygen Saturation	$DO_{sat}$		$mg O_2/L$
Oxidation Rate for DOC at 20°C Temperature Coefficient	$\begin{matrix}k_{8,0}\\\theta_{8,0}\end{matrix}$	0.002 1.047	day-1
Oxidation Rate of Oxygen Equivalents at 20°C	k <sub>O2*</sub>	0.30	day-1
Temperature Coefficient	$\theta_{\text{O2*}}$	1.080	
Half Saturation for Oxygen Limitation for Oxygen Equivalents	$K_{DO02*}$	0.20	mg 0 <sub>2</sub> /L
Half Saturation for Oxidation Oxygen Limitation	$K_{DO}$	0.20	mg 0 <sub>2</sub> /L

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# APPENDIX B SEDIMENT MODEL COEFFICIENTS

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Table B-1. Sediment Model Coefficients

Description	Notation	Value	Units
Aerobic layer solids concentration	$m_1$	0.12 - 0.50	kg/L
Anaerobic layer solids concentration	$m_2$	0.12 - 0.50	kg/L
Particle mixing diffusion coefficient	$D_p$	0.00012	m <sup>2</sup> /d
Sedimentation velocity	$w_2$	3.01x10 <sup>-6</sup> - 1.30 x 10 <sup>-5</sup>	m/d
Pore water diffusion coefficient	$D_d$	0.001	m <sup>2</sup> /d
Temperature coefficient	$ heta_{ m Dp}$	1.117	
Temperature coefficient	$\theta_{\mathrm{Dd}}$	1.08	
Water-sediment diffusion coefficient	$D_{d0}$	0.0001	m²/d
Temperature coefficient	$ heta_{ m Dd0}$	1.08	
Reaction velocity for dissolved sulfide oxidation in the aerobic layer	$\kappa_{ m d1}$	0.2	m/d
Reaction velocity for particulate sulfide oxidation in the aerobic layer	$\kappa_{\mathrm{p1}}$	0.4	m/d
Partition coefficient for sulfide in the aerobic layer	$\pi_{ m hs1}$	100	L/kg
Partition coefficient for sulfide in the anaerobic layer	$\pi_{ m hs2}$	100	L/kg
Temperature coefficient	$\theta_{ ext{dp1}}$	1.08	
Sulfide oxidation normalization constant for oxygen	k <sub>mhso2</sub>	4.	mg O <sub>2</sub> /L
Depth of anaerobic layer	H <sub>20</sub>	0.1	m
Incremental partition coefficient for phosphate in the aerobic layer	$\pi_{\mathrm{po4i}}$	7.5	L/kg
Partition coefficient for phosphate in the anerobic layer	$\pi_{ m po42}$	1000.	L/kg
Overlying water oxygen concentration at which aerobic layer incremental partitioning starts to decrease	O <sub>2crit</sub>	2.0	mg O <sub>2</sub> /L
Particle mixing half saturation constant for oxygen	k <sub>mo2Dp</sub>	4.	mg O <sub>2</sub> /L
Temperature which benthic community begins to recover after an anoxic event	tempbnth	10.0	°C
Rate at which benthic stress is dissipated	.k <sub>bnthstr</sub>	0.03	day <sup>-1</sup>
Scale factor for enhancement of dissolved phase mixing due to benthic activity	klbnth	0.0	
Minimum particle mixing coefficient	$D_{Pmin}$	3.0x10 <sup>-6</sup>	m <sup>2</sup> /d
Fraction POC in G1	fr <sub>poe1</sub>	0.65	
Reaction rate constant for GPOC1	k <sub>poe1</sub>	0.035	

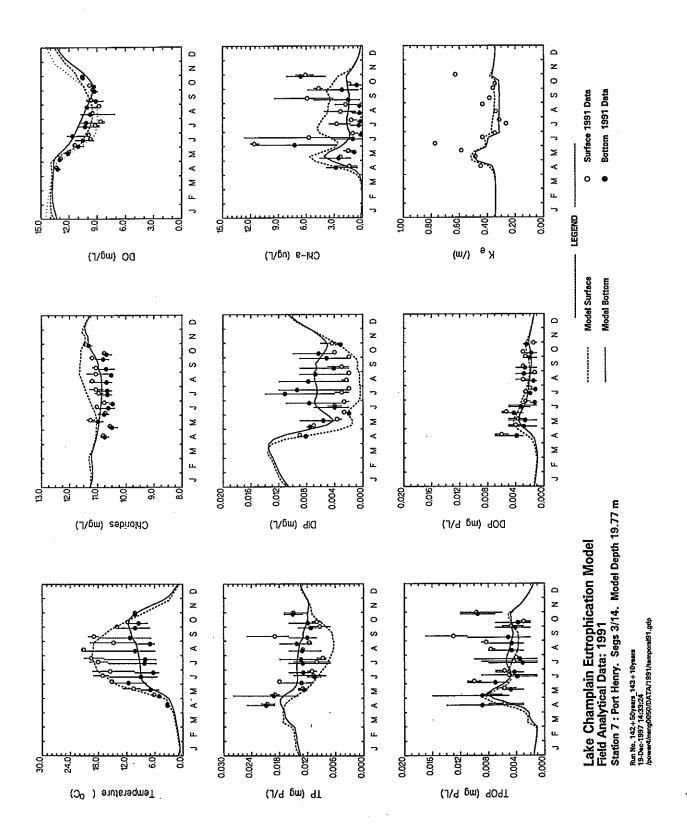
Table B-1. Sediment Model Coefficients

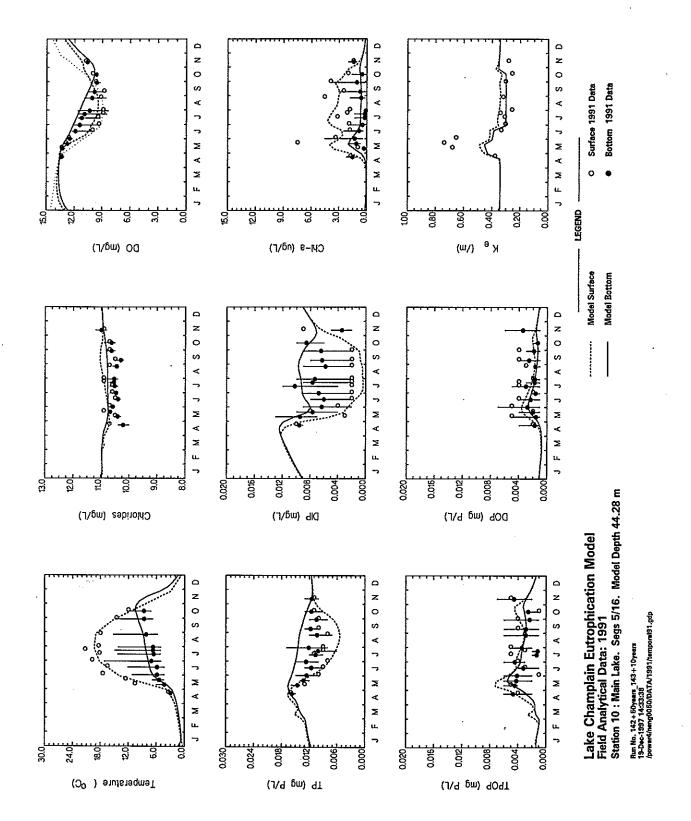
Description	Notation	Value	Units
Temperature coefficient	$ heta_{ m poc1}$	1.1	
Fraction POC in G2	$fr_{poc2}$	0.25	
Reaction rate constant for GPOC2	k <sub>poc2</sub>	0.0018	
Temperature coefficient	$\theta_{ m poc2}$	1.15	
Fraction POC in G3	$fr_{poc3}$	0.10	
Reaction rate constant for GPOC3	k <sub>poc3</sub>	1.5 x 10 <sup>-6</sup>	
Temperature coefficient	$ heta_{ m poe3}$	1.17	
Fraction POP in G1	fr <sub>pop1</sub>	0.65	
Reaction rate constant for GPOP1	k <sub>pop1</sub>	0.035	
Temperature coefficient	$\theta_{ m pop 1}$	1.10	
Fraction POP in G2	fr <sub>pop2</sub>	0.25	
Reaction rate constant for GPOP2	k <sub>pop2</sub>	0.0018	
Temperature coefficient	$\theta_{ m pop2}$	1.15	
Fraction POP in G3	fr <sub>pop3</sub>	0.1	
Reaction rate constant for GPOP3	k <sub>pop3</sub>	1.5 x 10 <sup>-6</sup>	
Temperature coefficient	$\theta_{ m pop3}$	1.17	

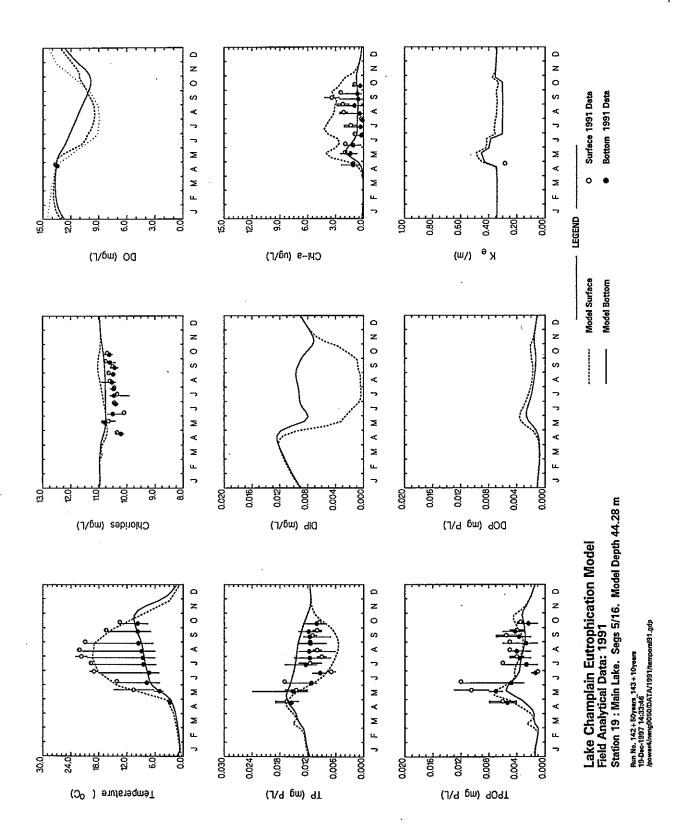
## **APPENDIX C**

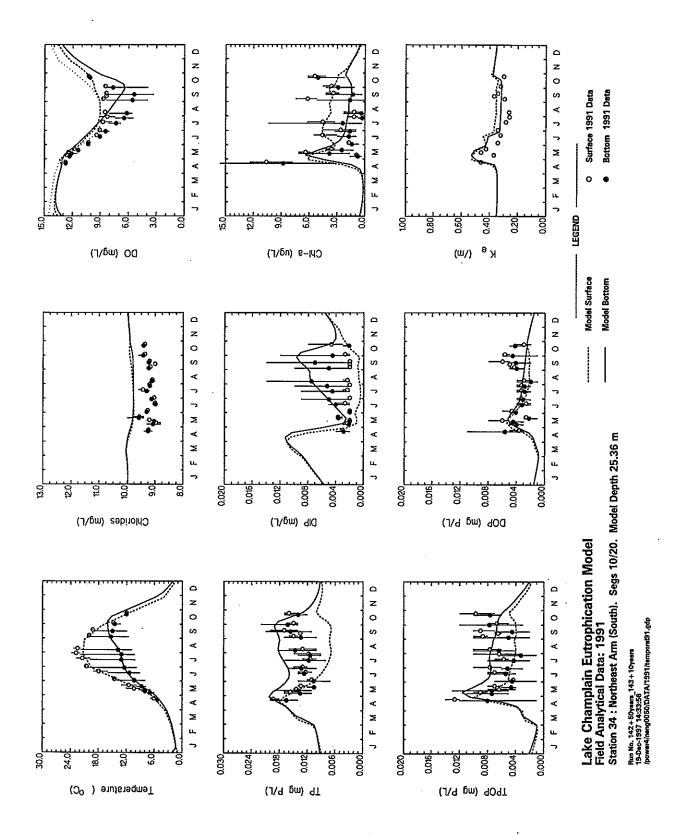
## **CALIBRATION FIGURES**

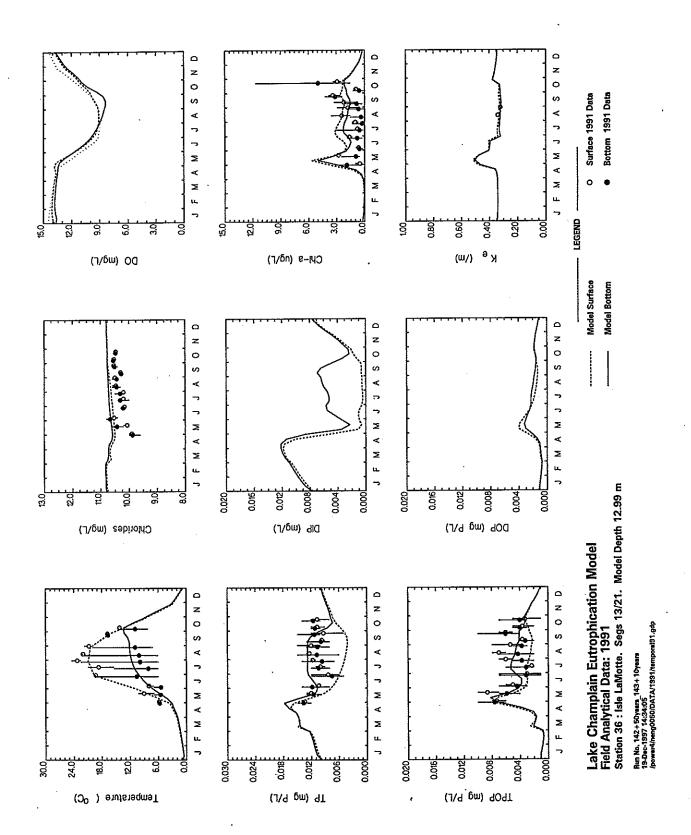
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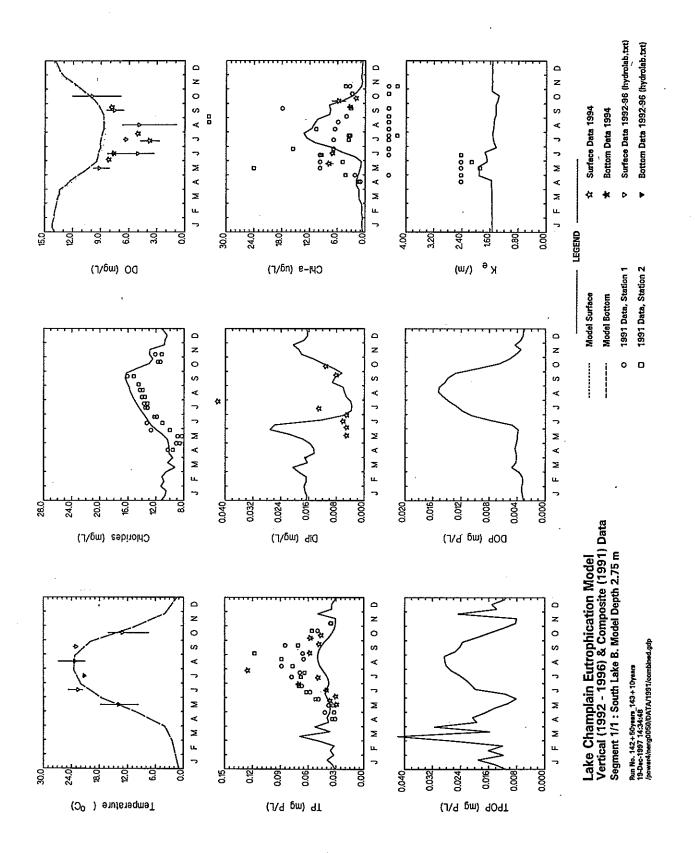


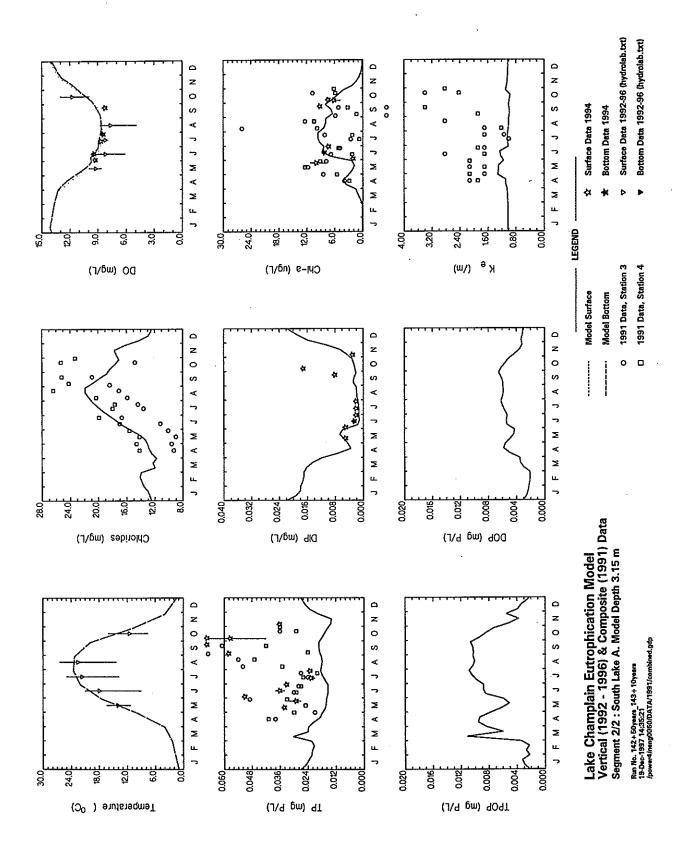


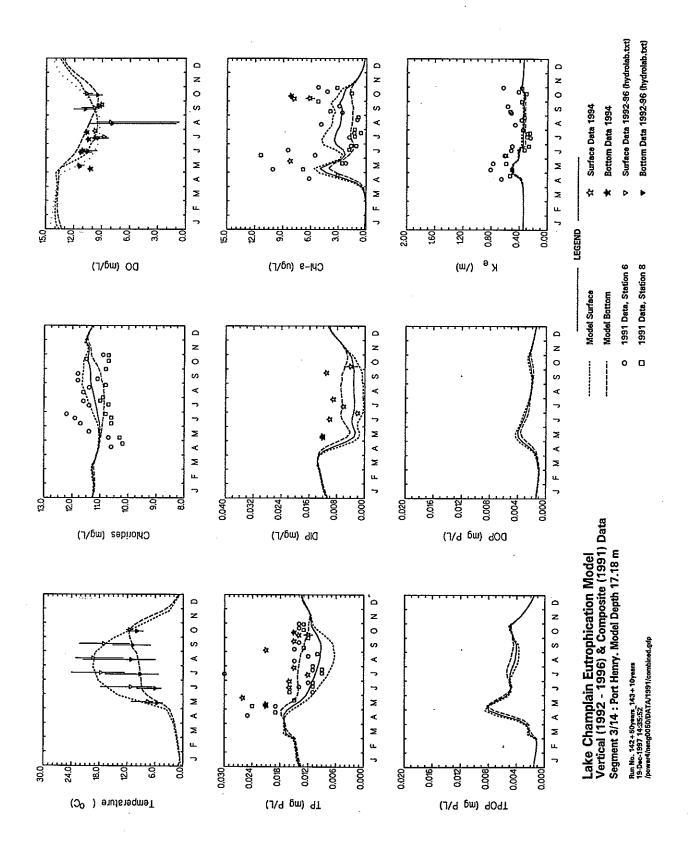


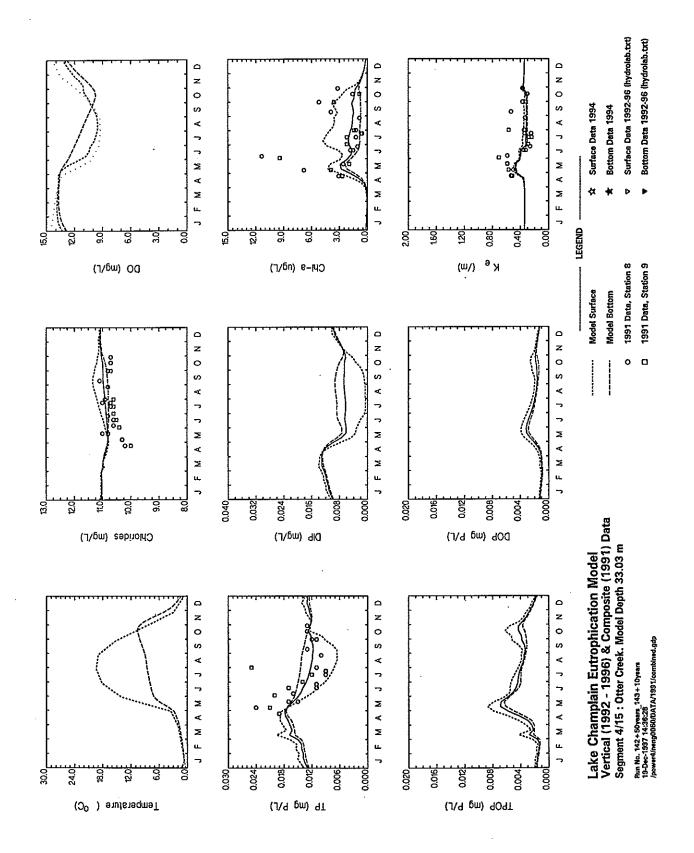


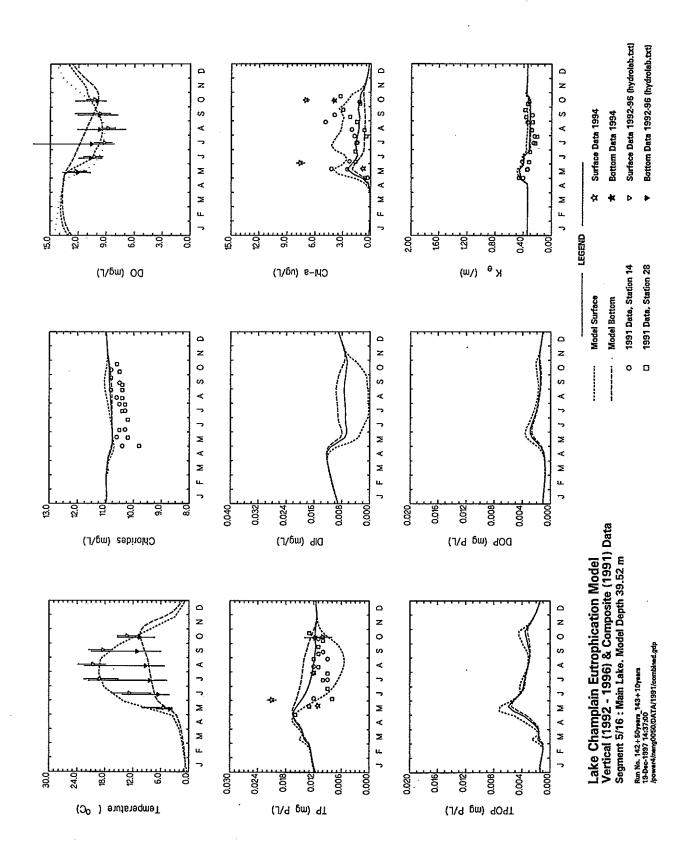


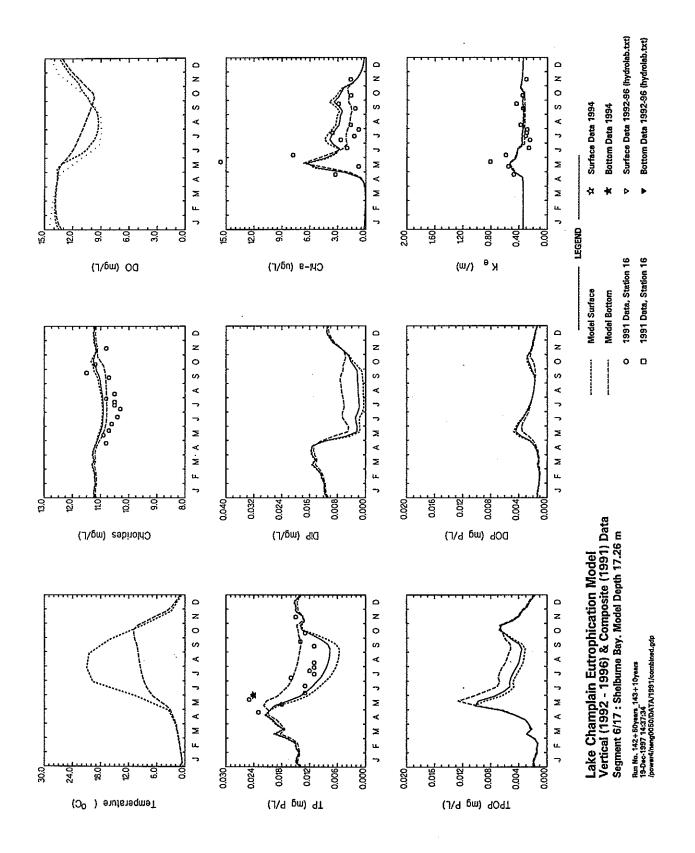


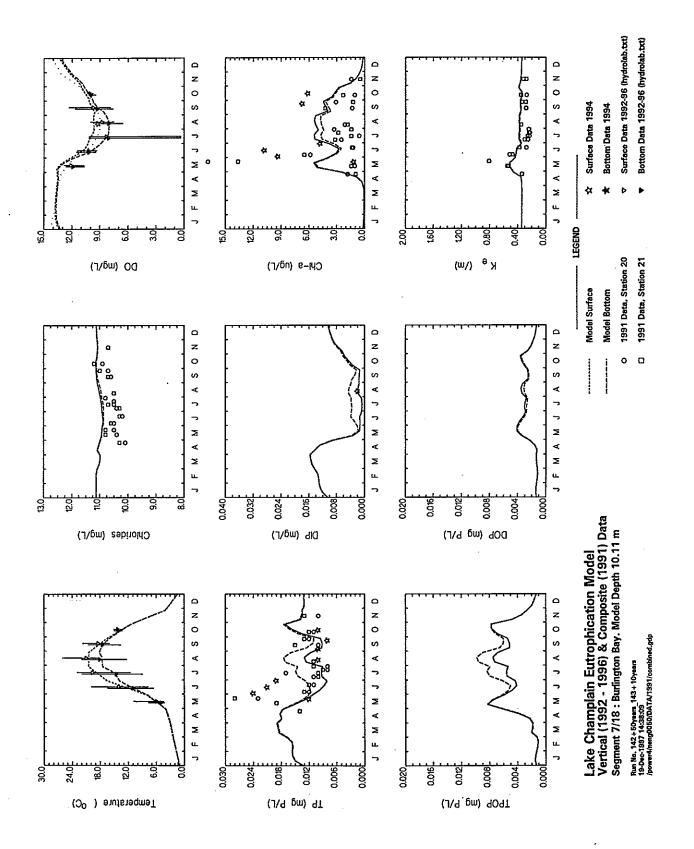


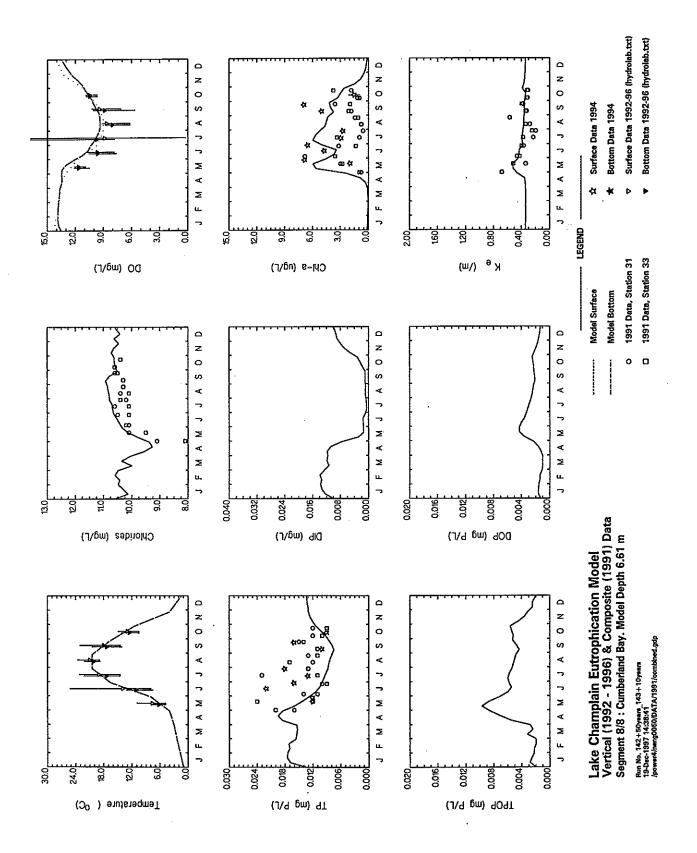


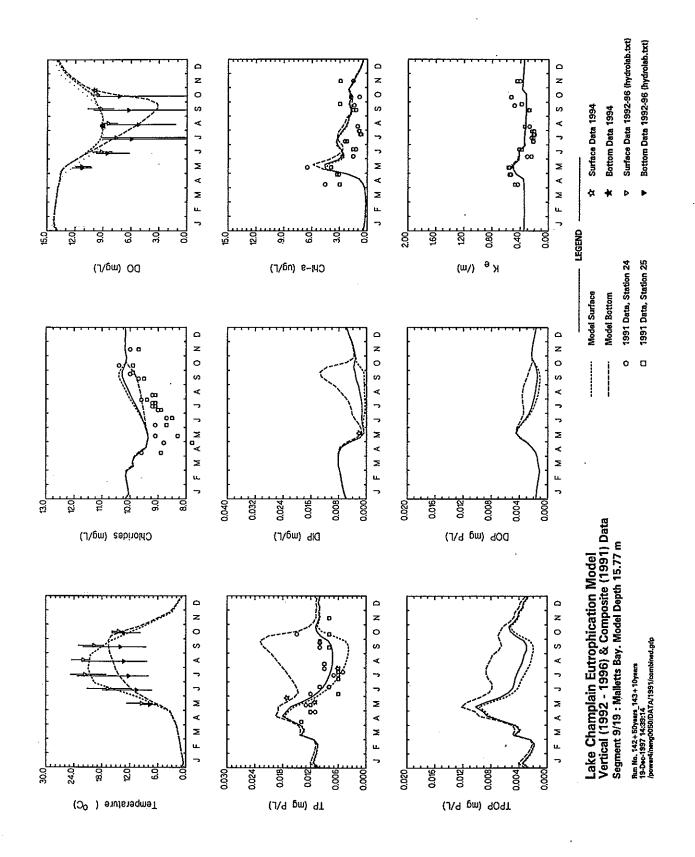


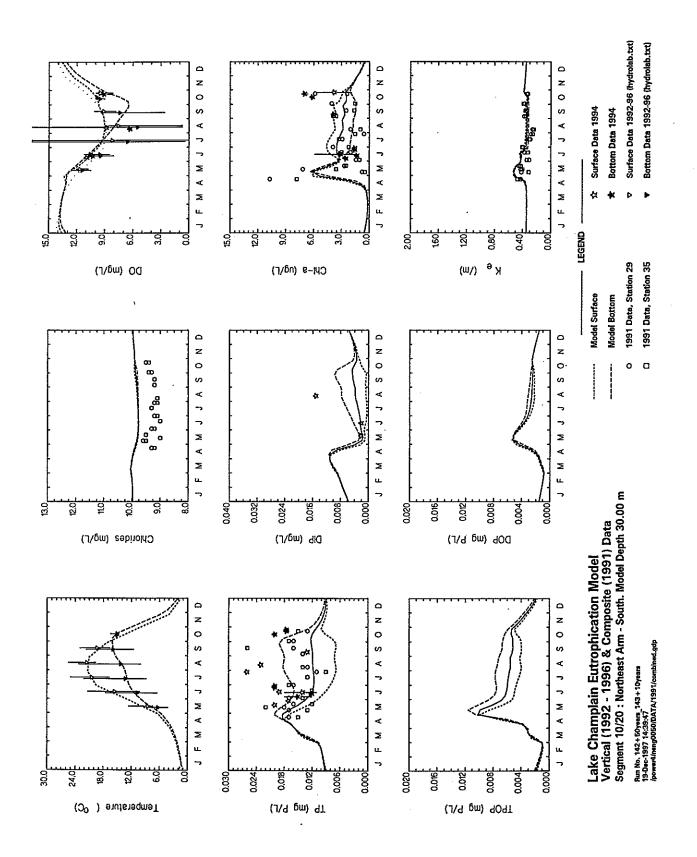


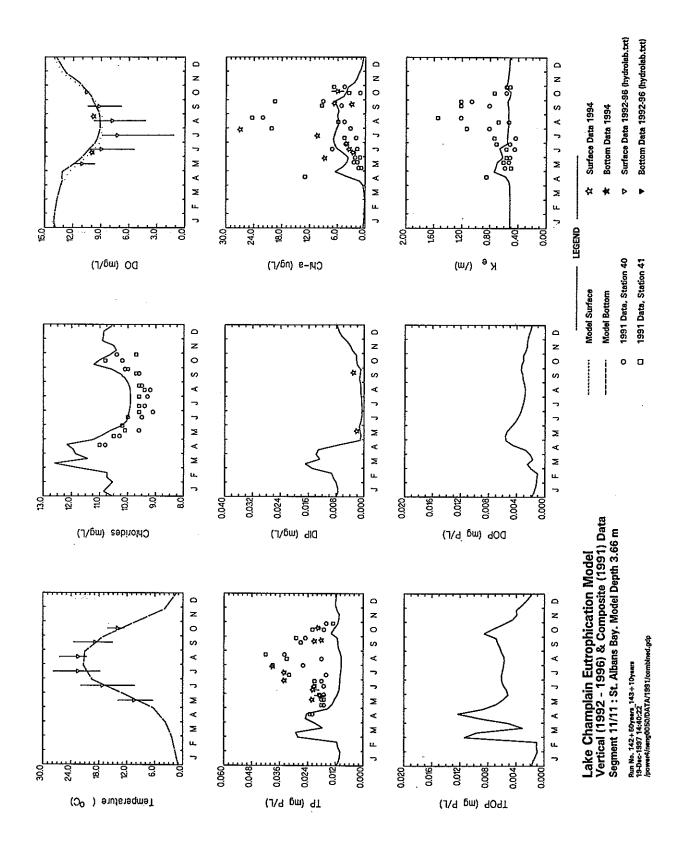


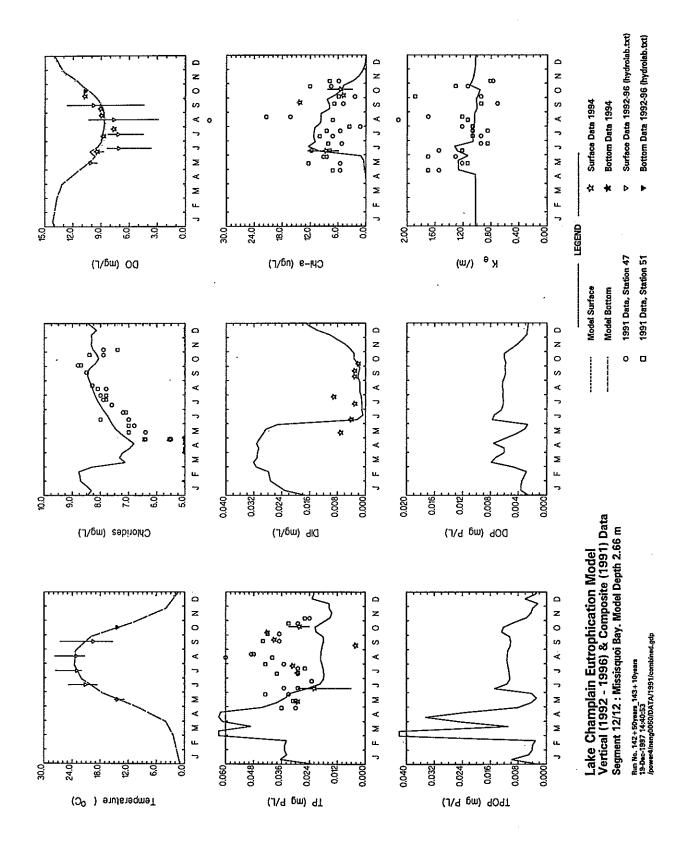


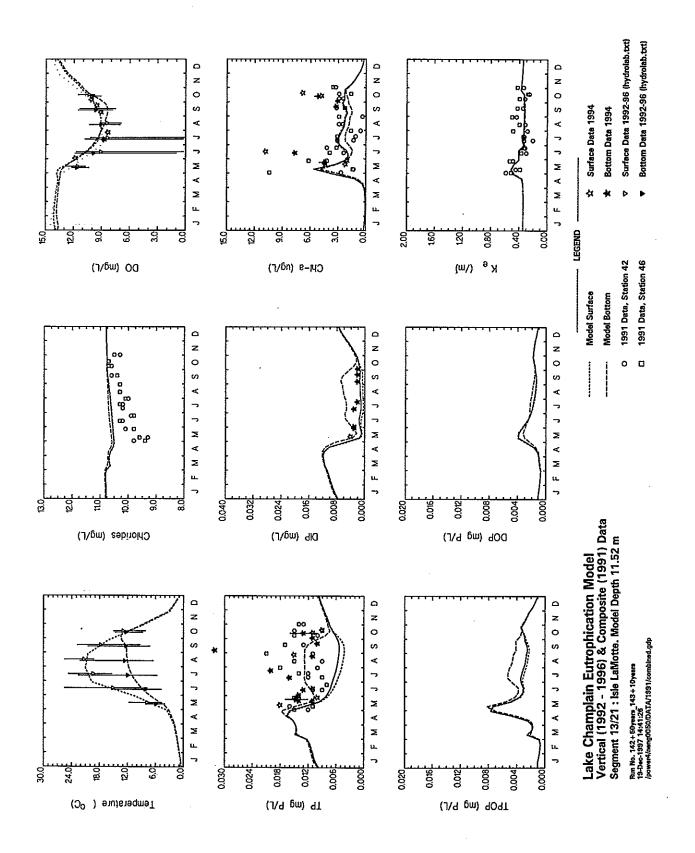


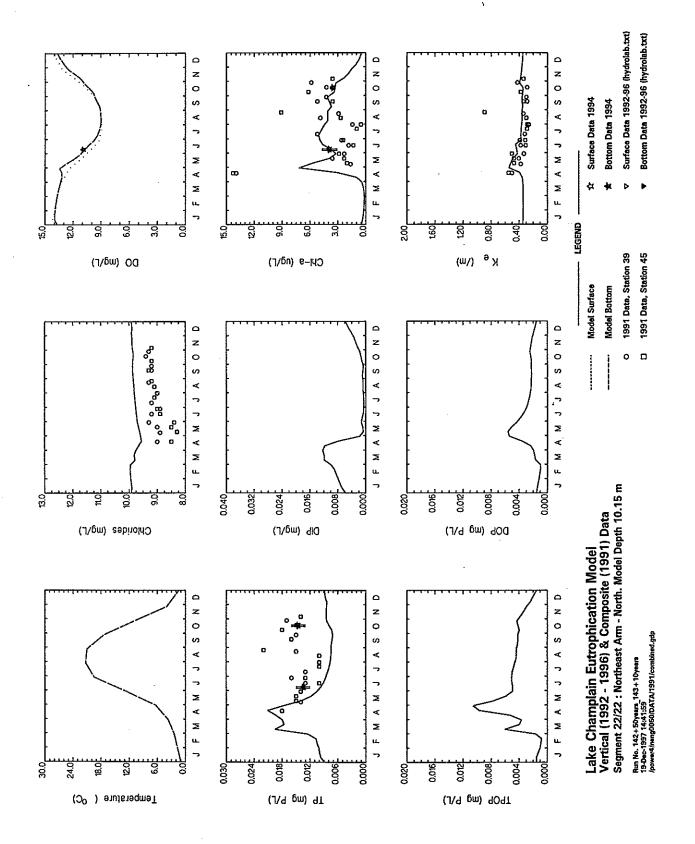




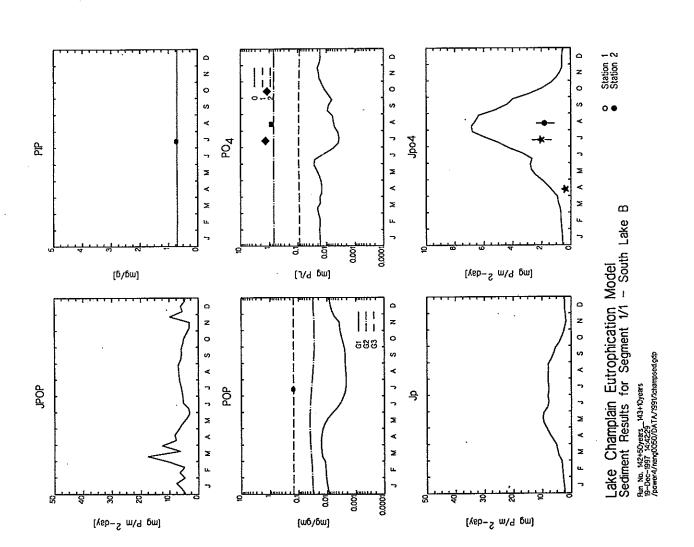


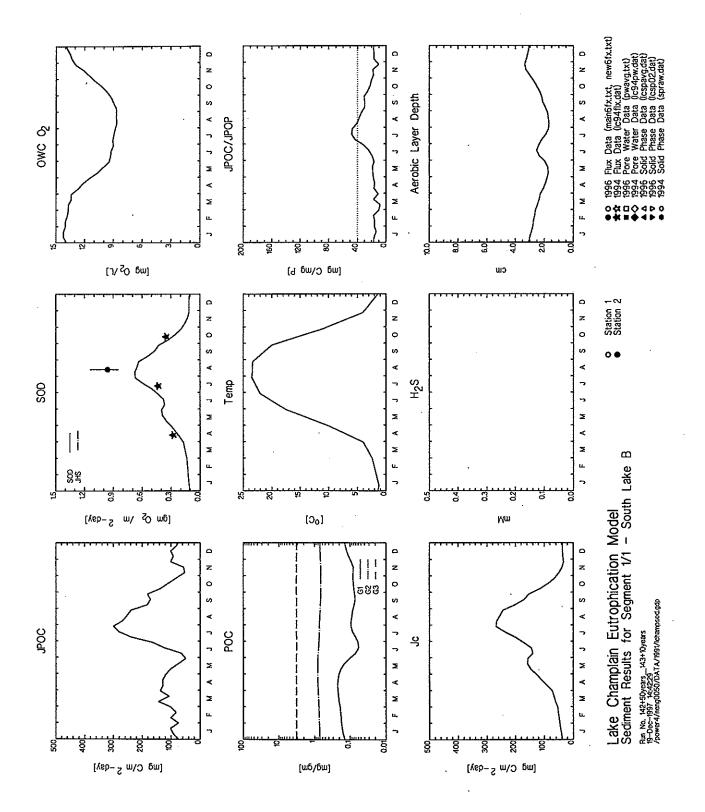




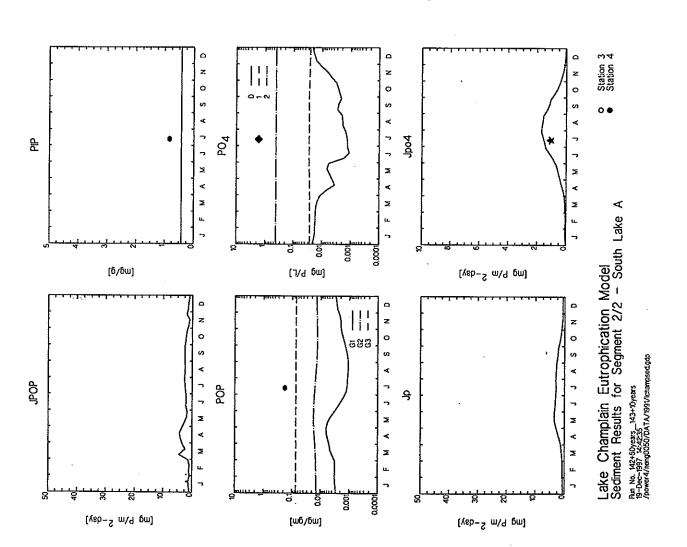


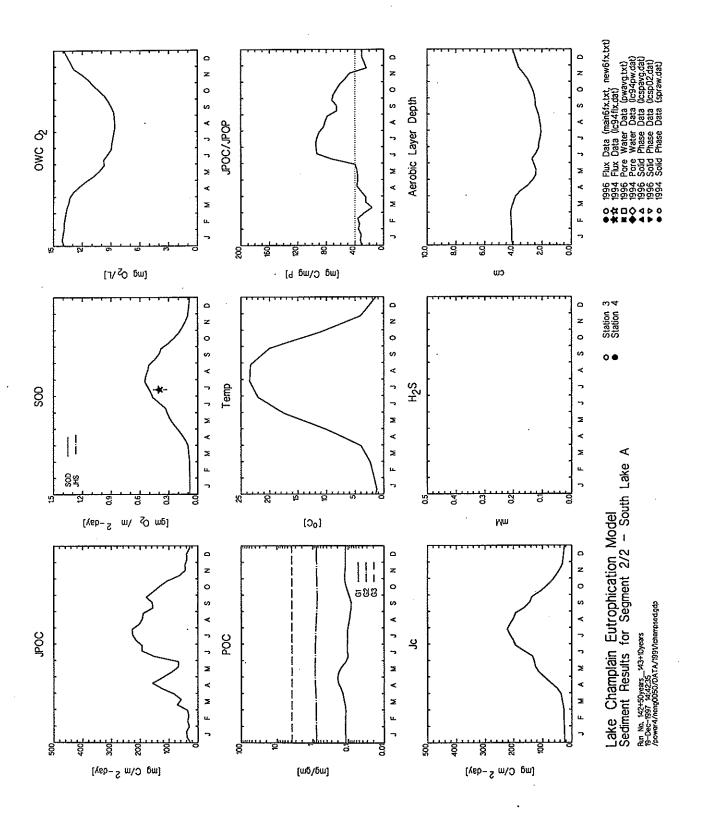




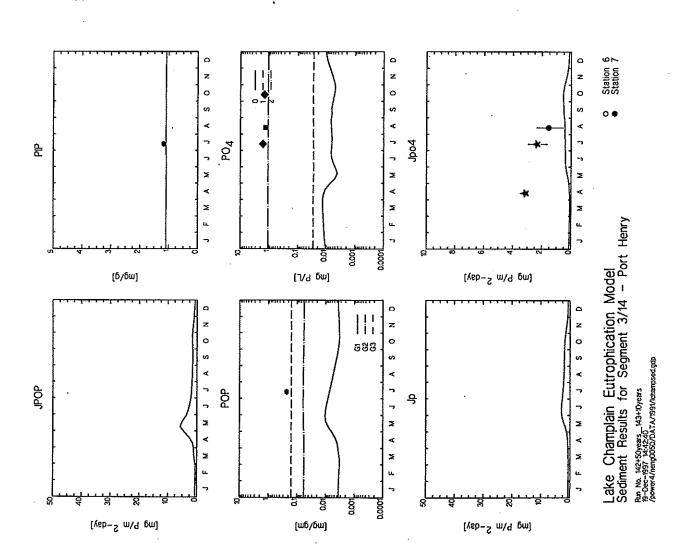


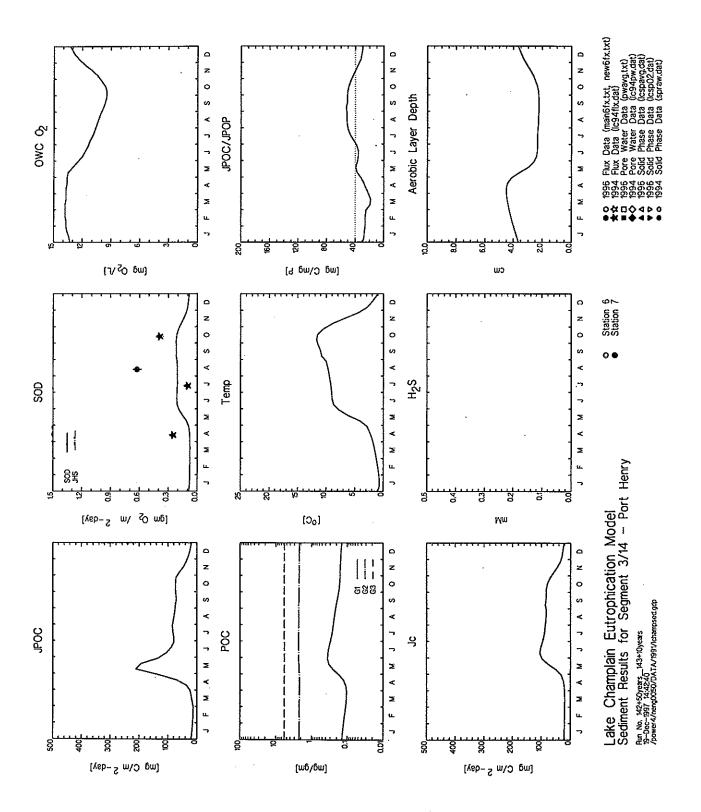




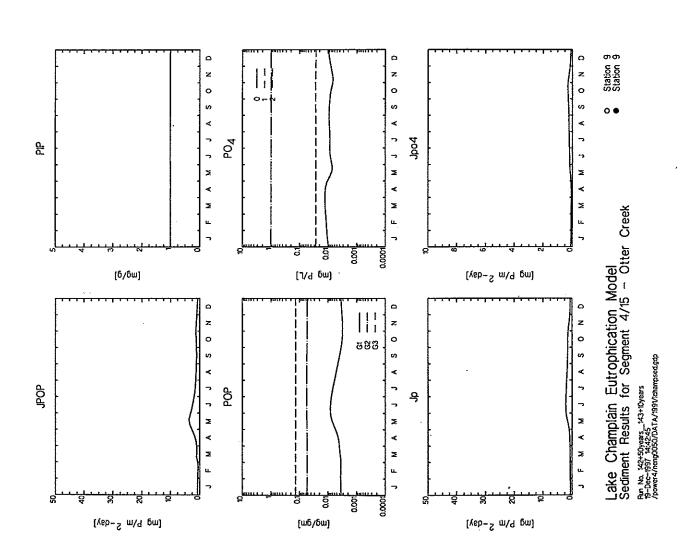


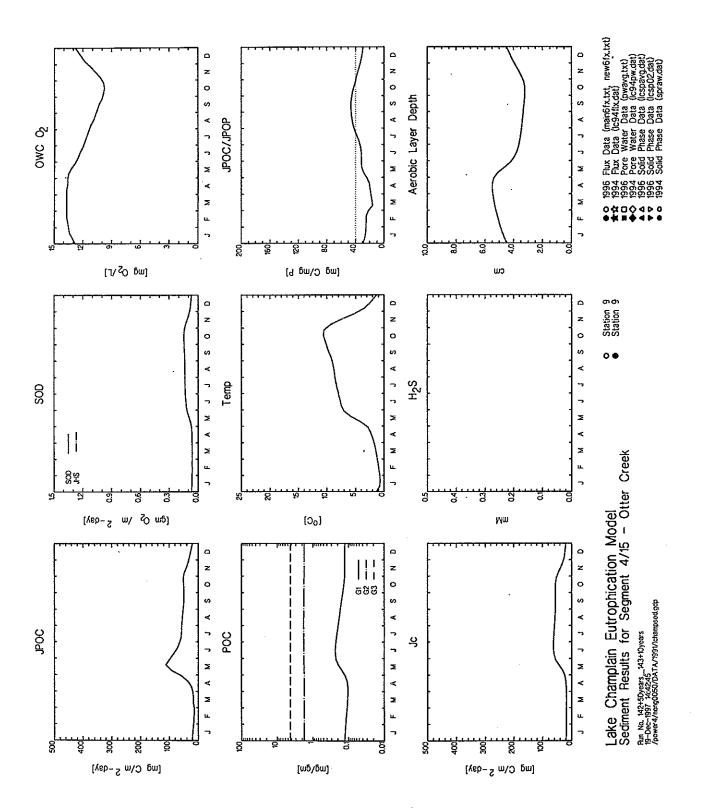




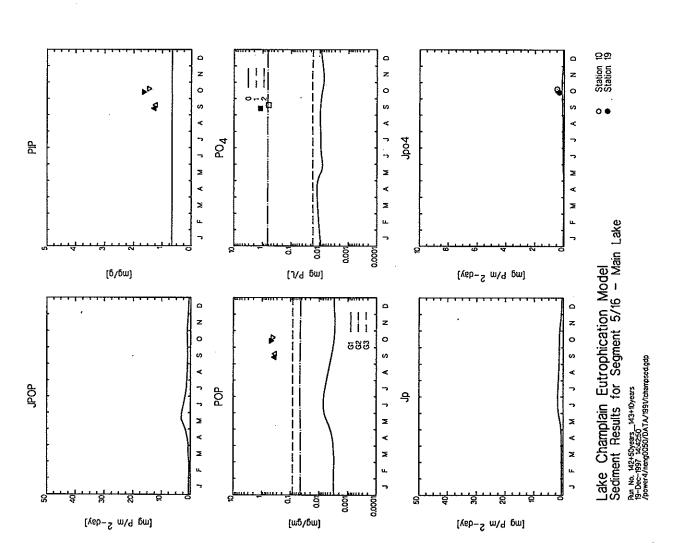


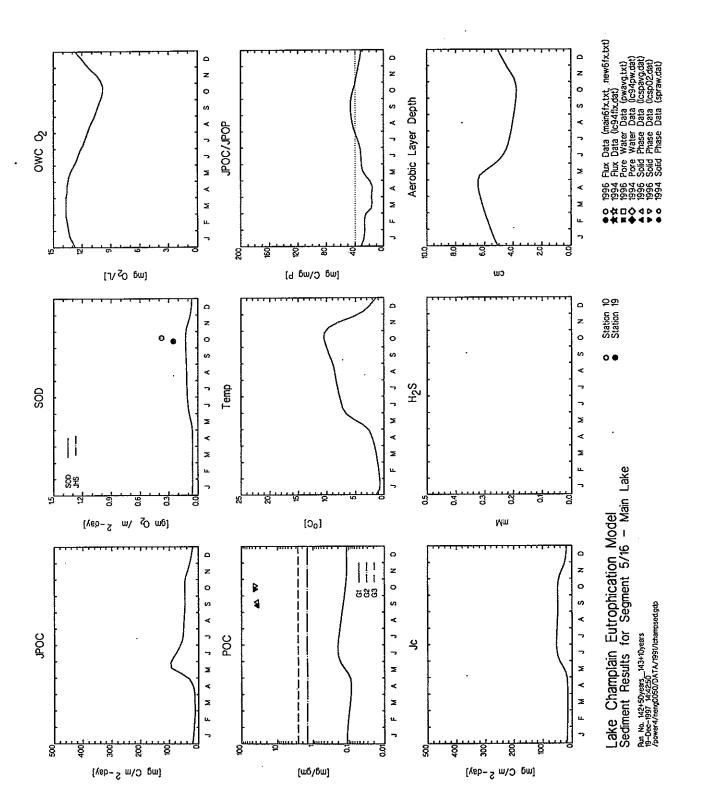




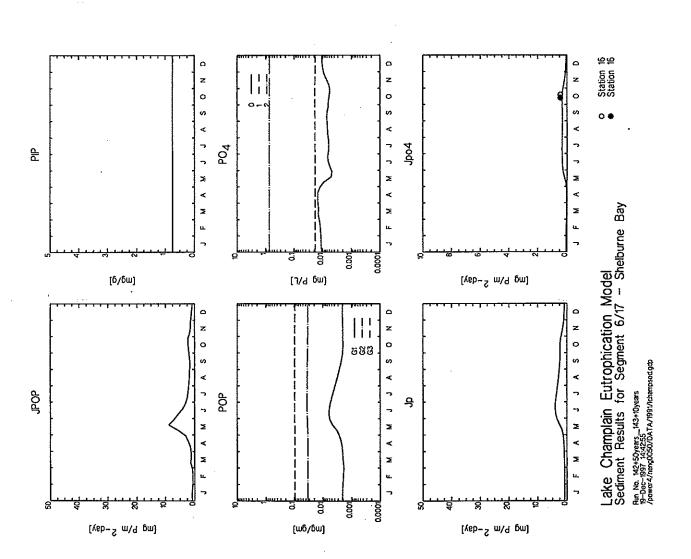


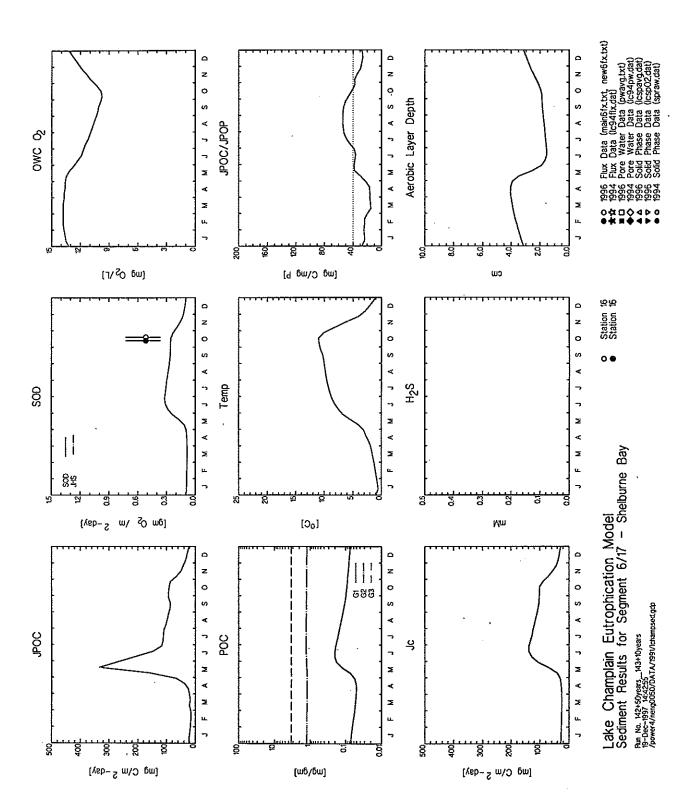




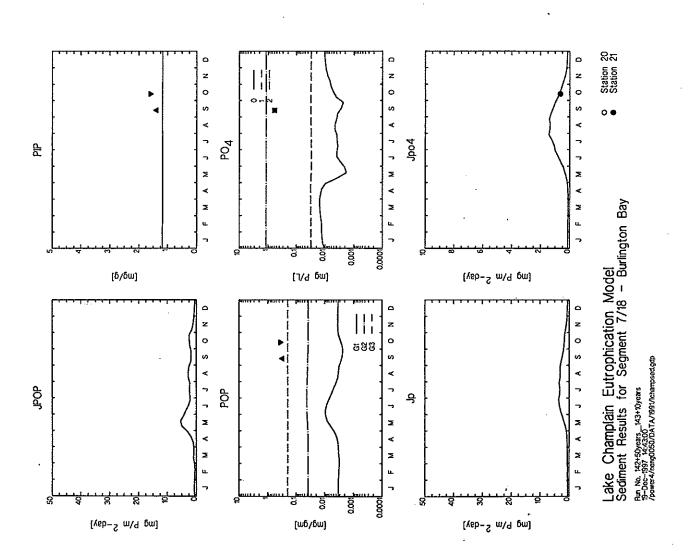


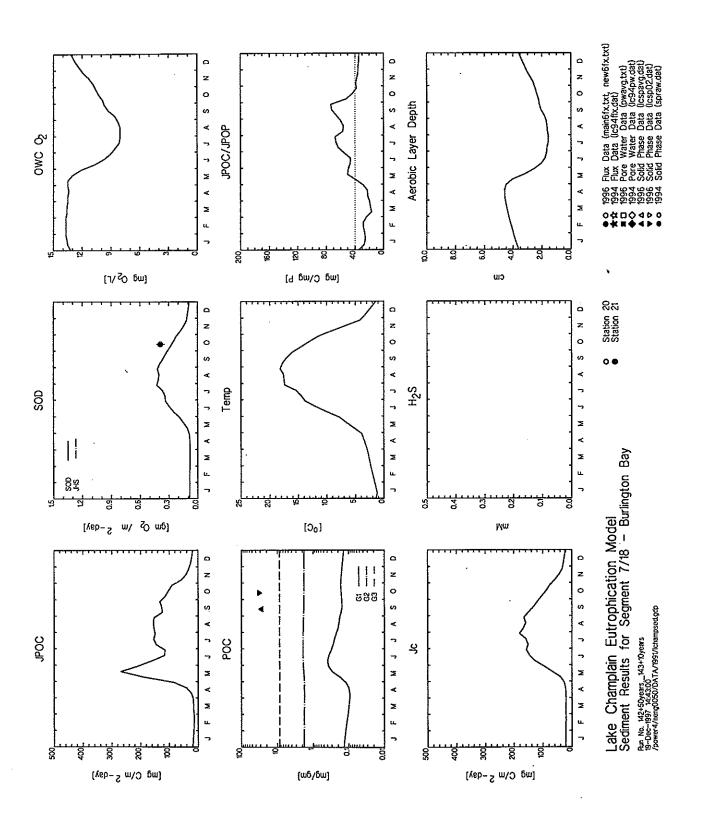




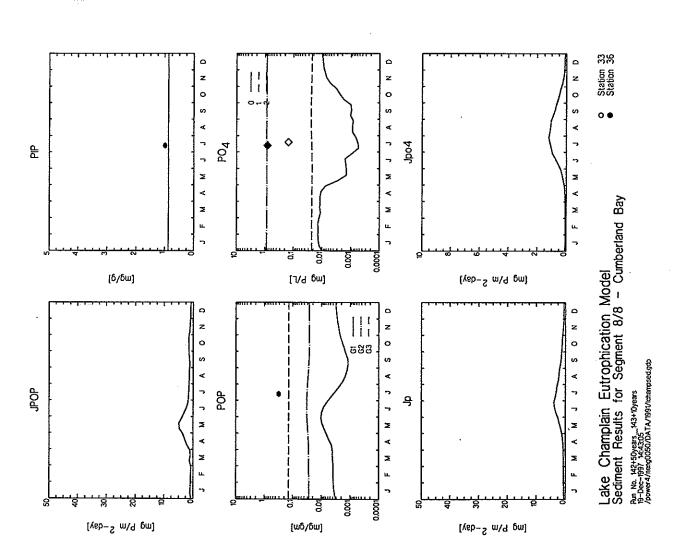


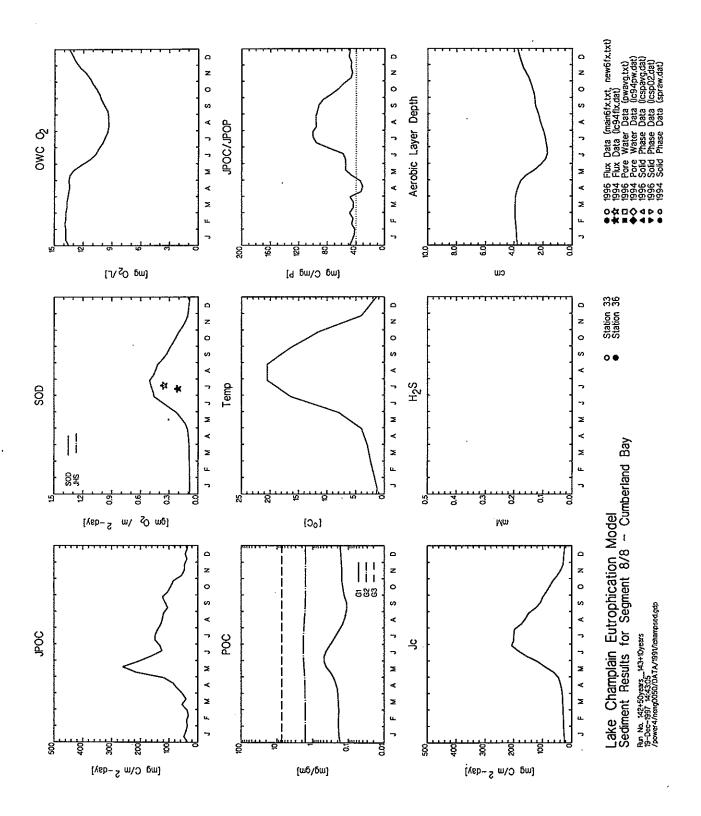




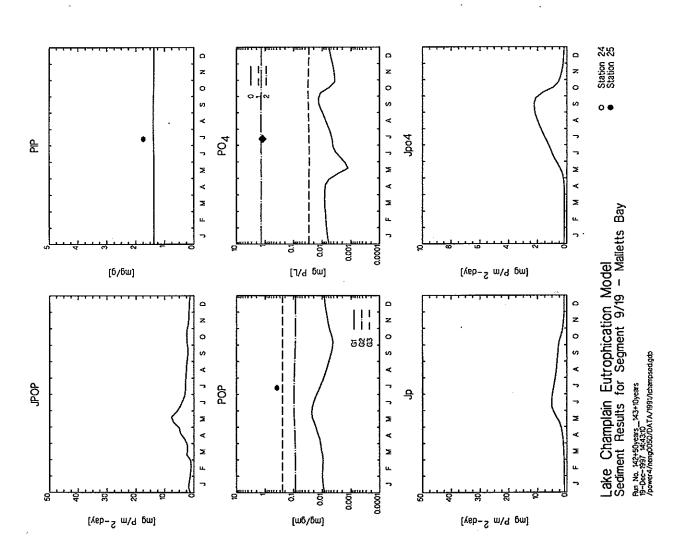


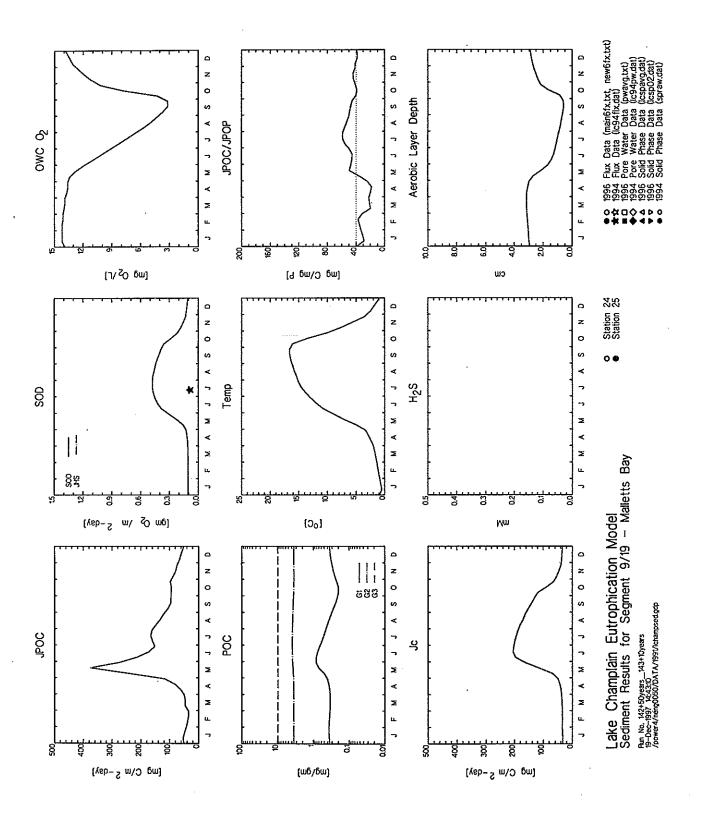




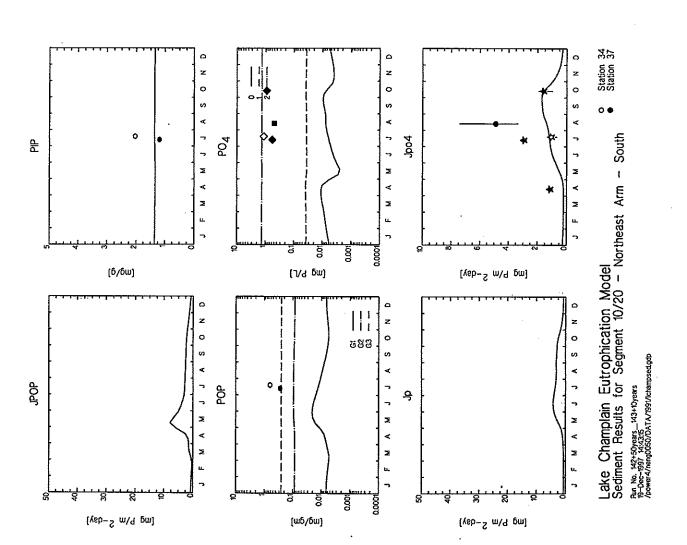


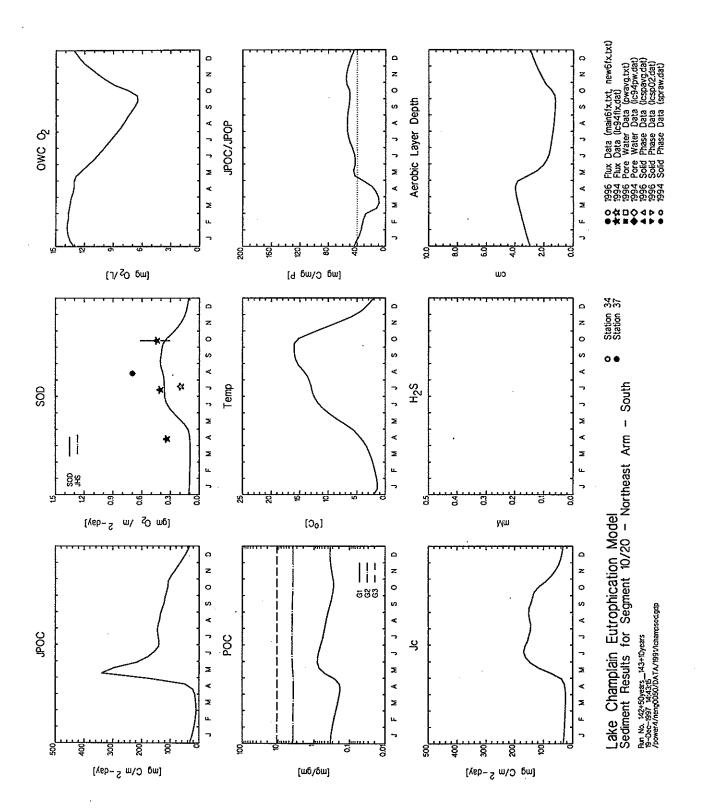




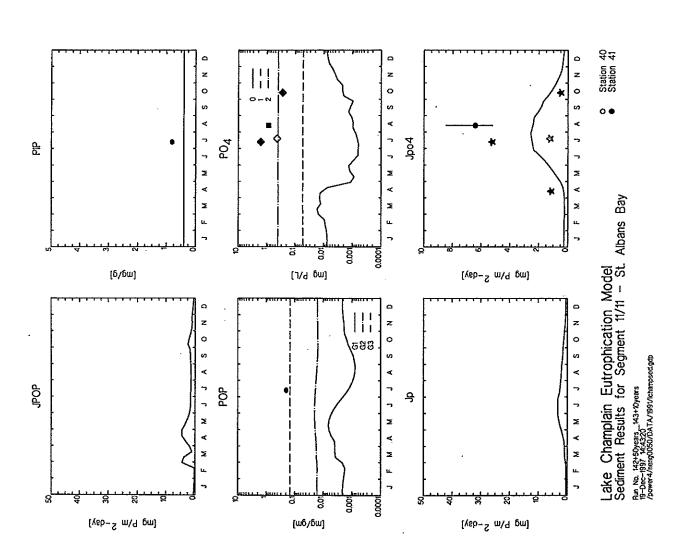


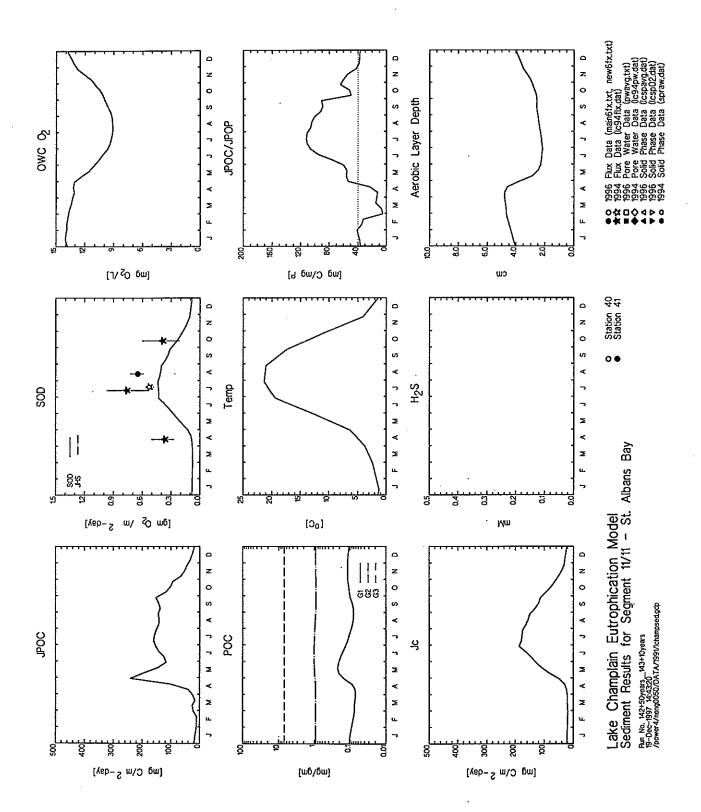




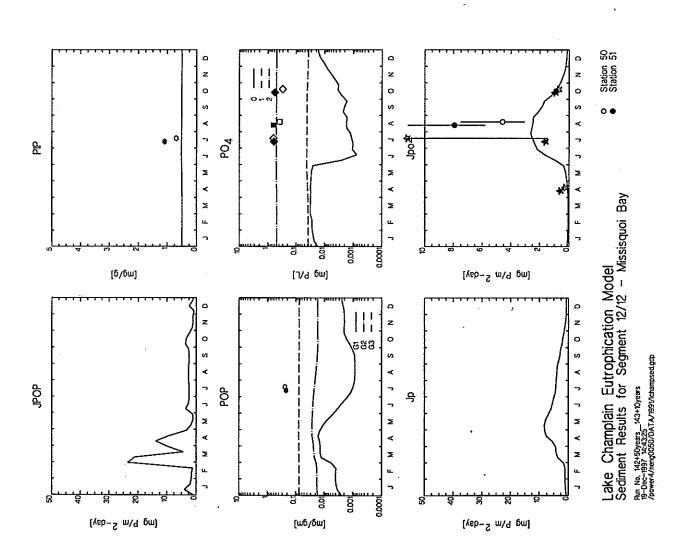


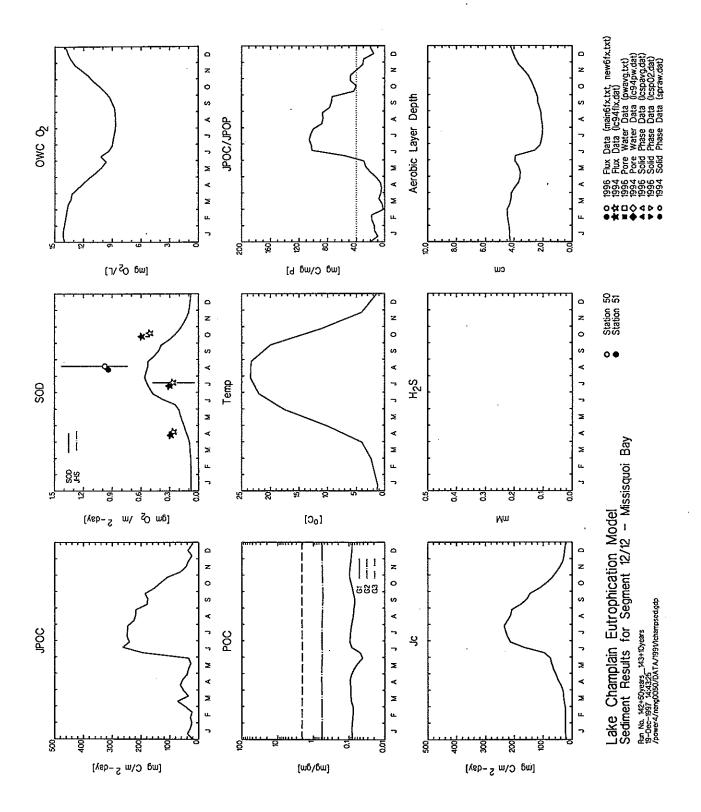




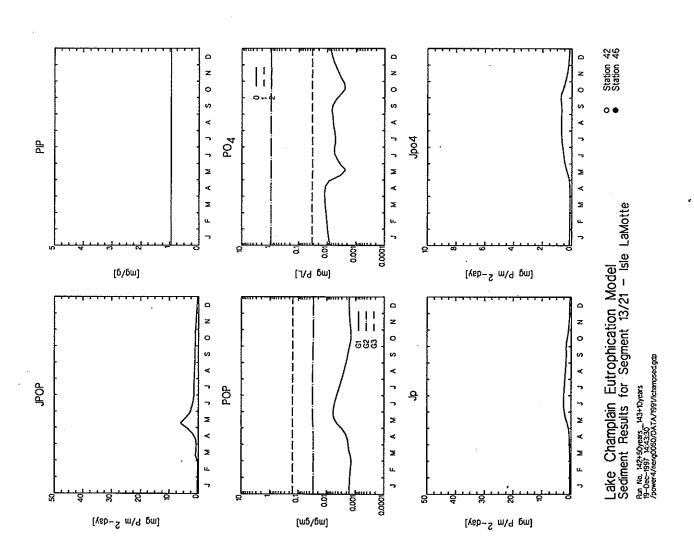


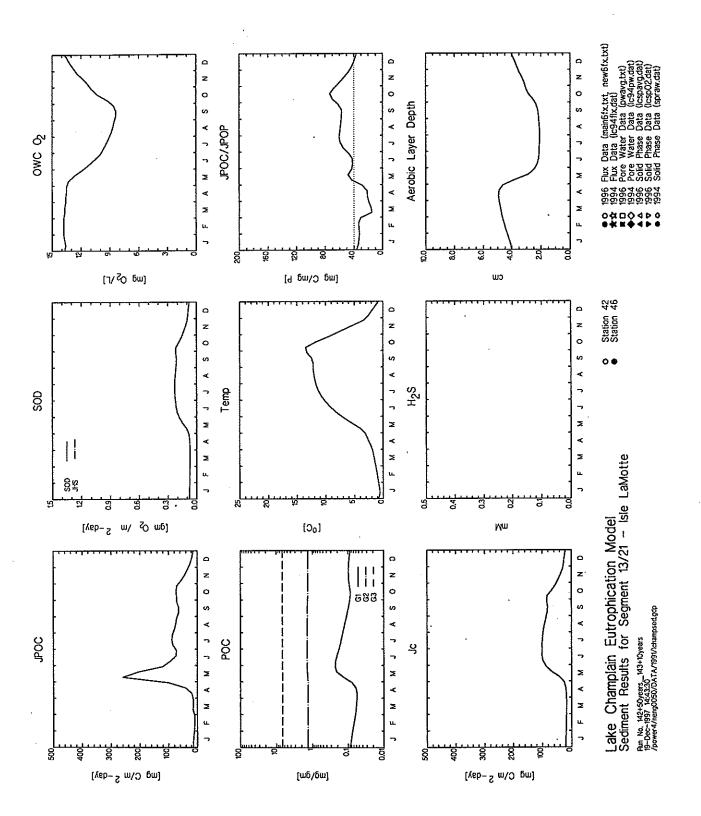




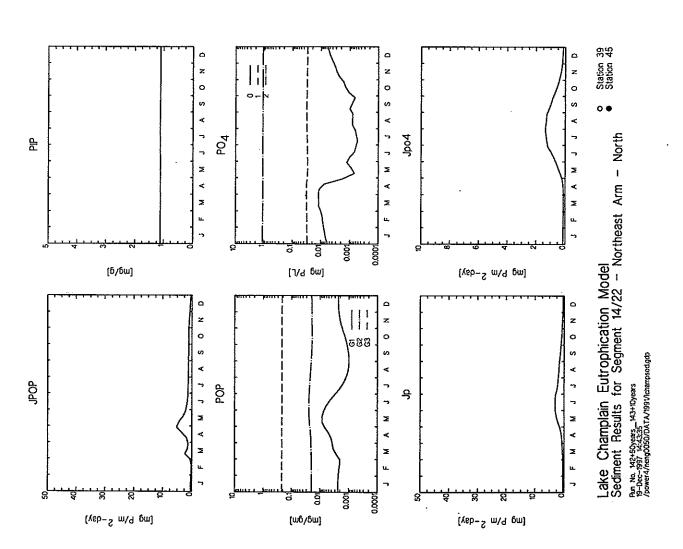


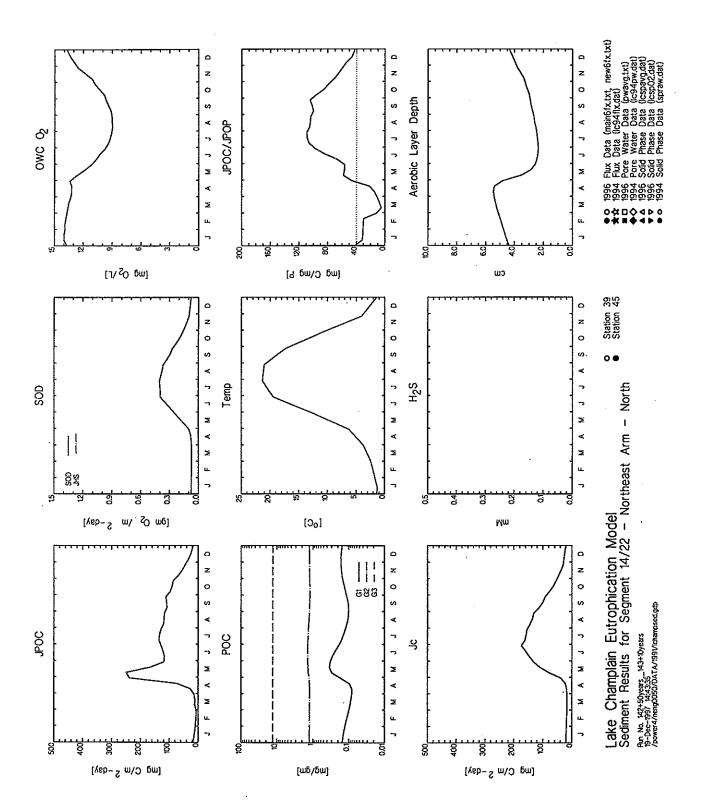








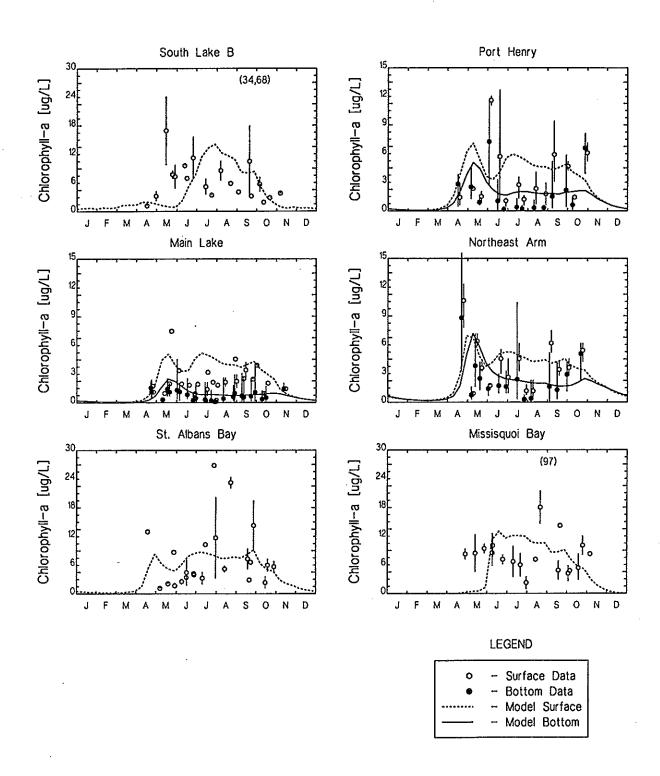




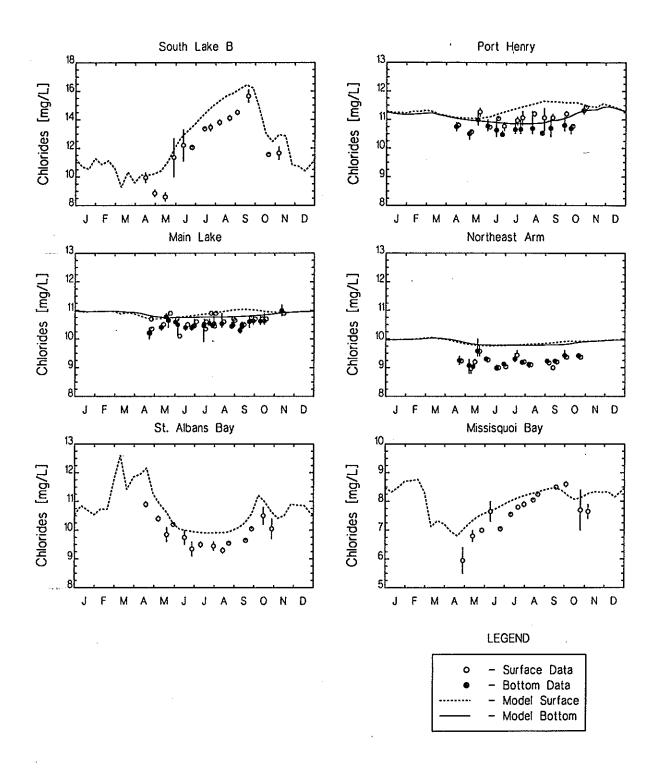
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## APPENDIX D HISTORICAL LOADING FIGURES

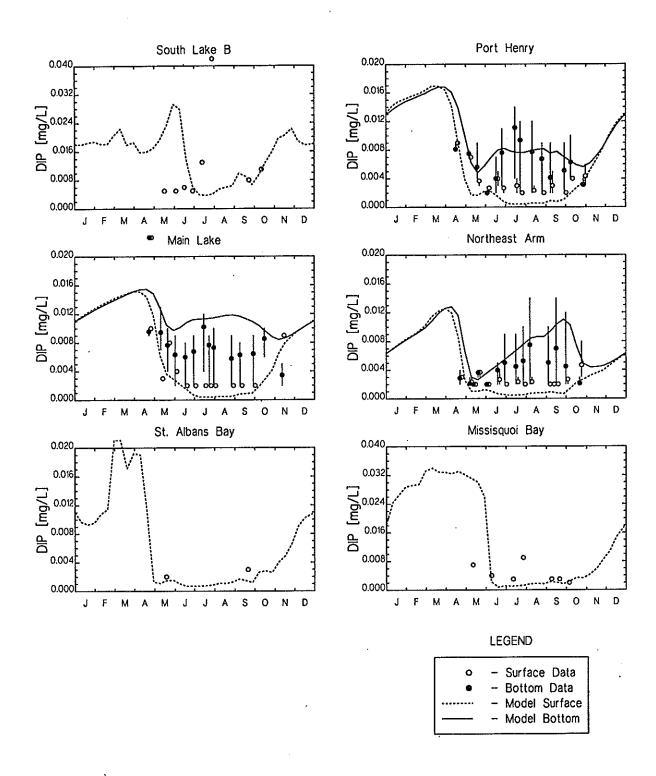




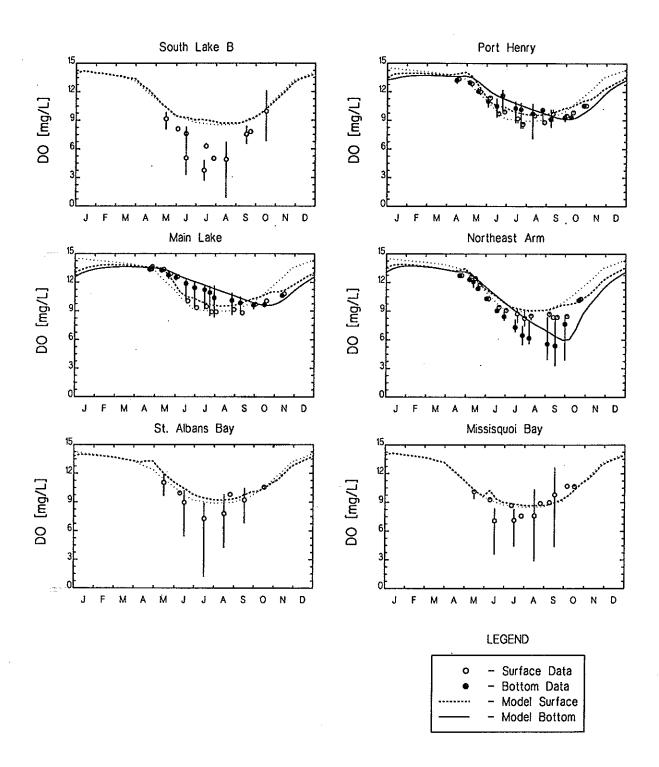
Water Column Chlorophyll-a



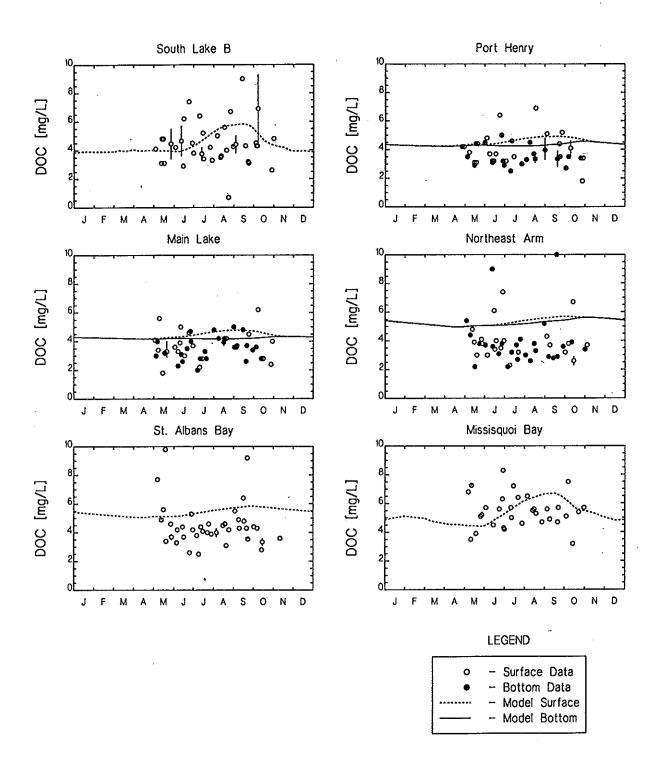
Water Column Chlorides



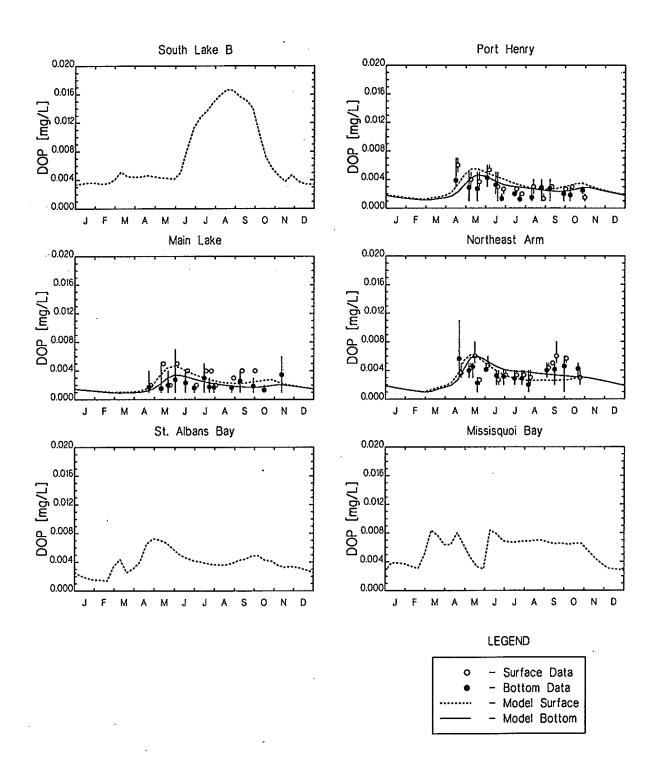
Water Column Ortho-Phosphorus



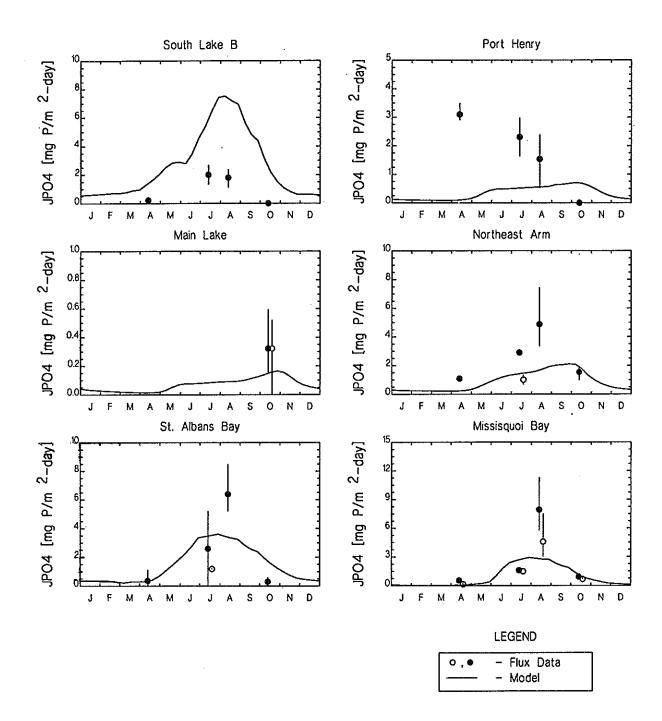
Water Column Dissolved Oxygen



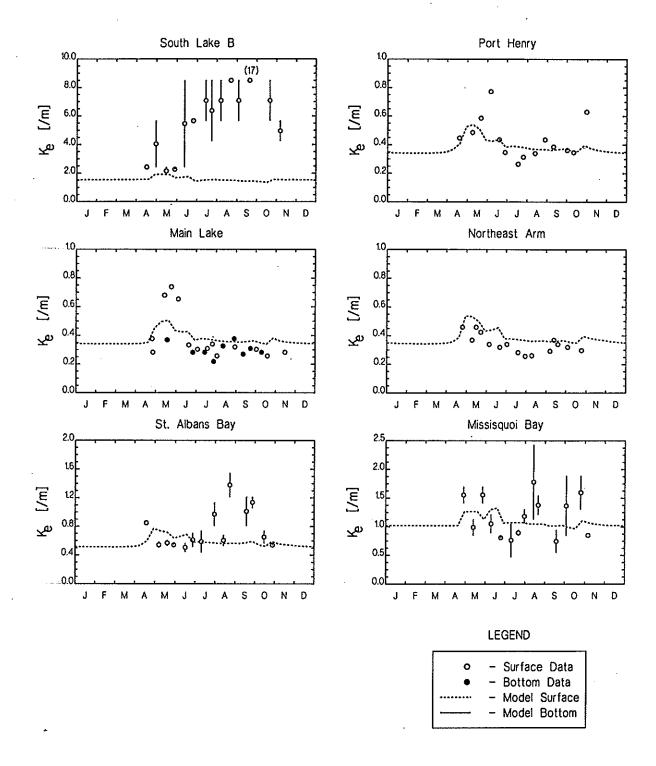
Water Column Dissolved Organic Carbon



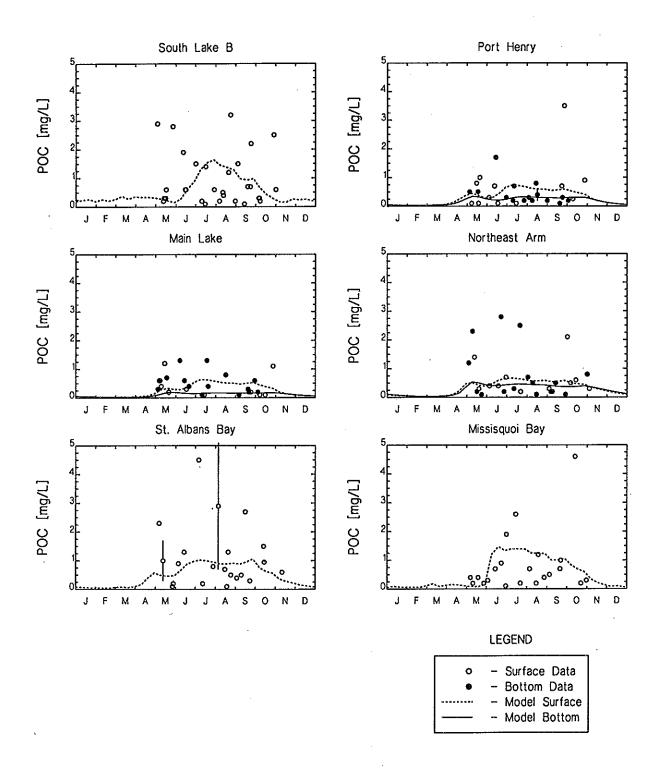
Water Column Dissolved Organic Phosphorus



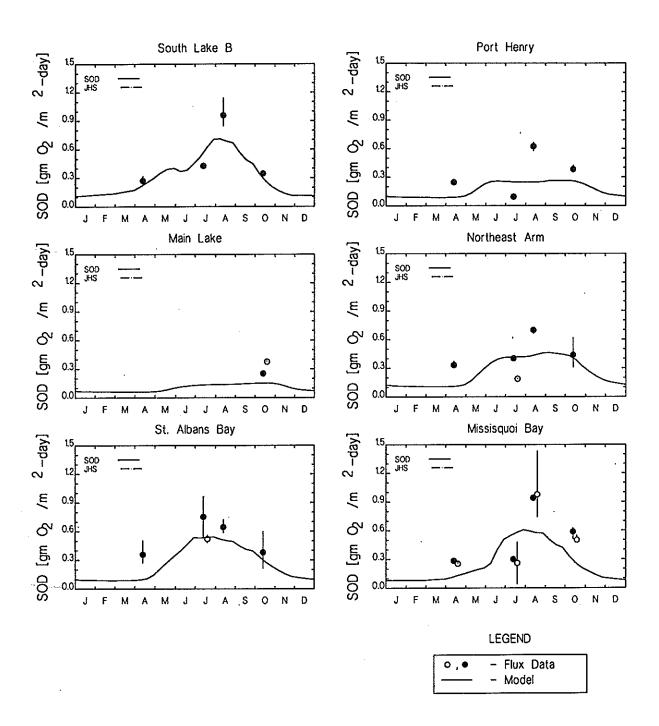
Sediment Phosphate Flux



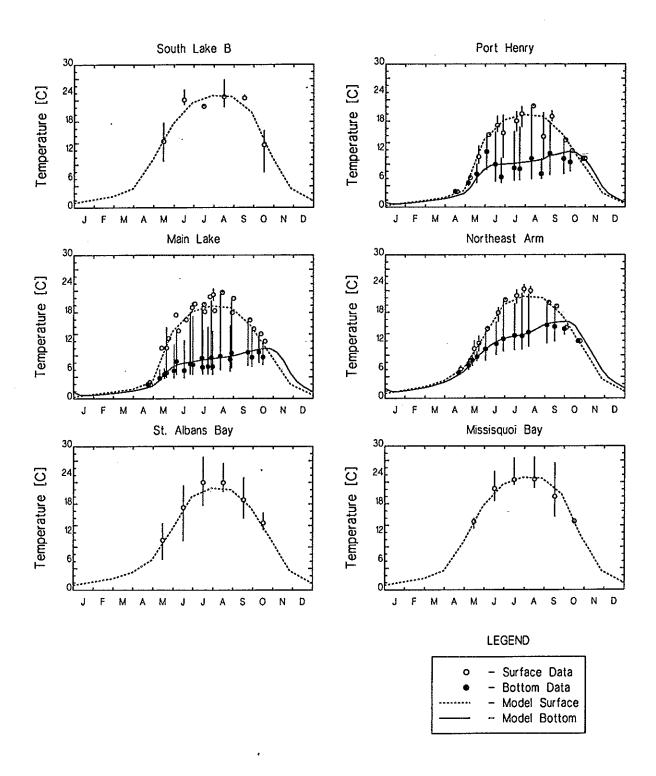
**Extinction Coefficient** 



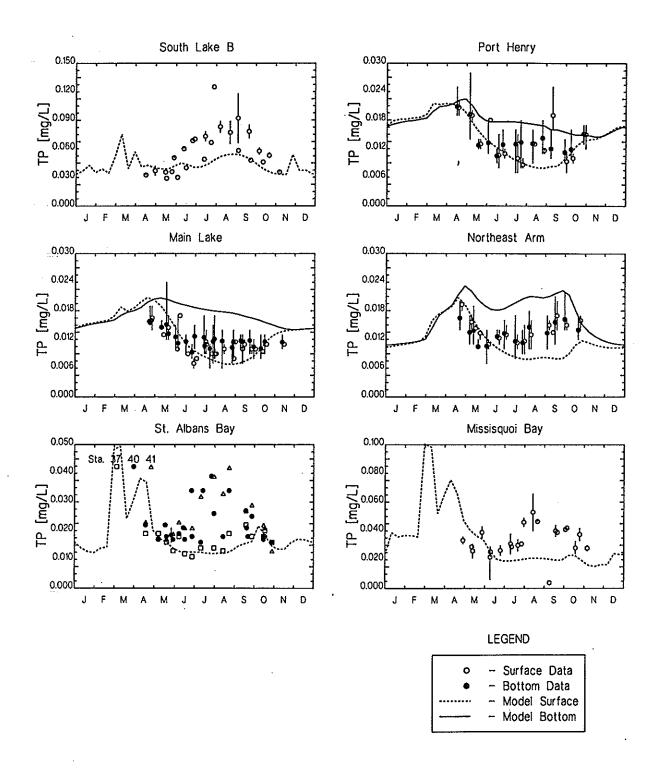
Water Column Particulate Organic Carbon



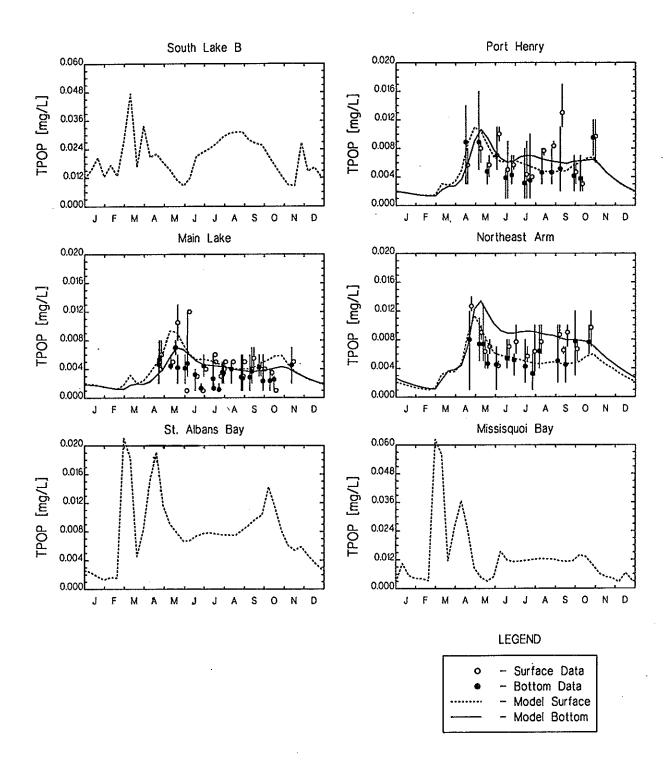
Sediment Oxygen Demand



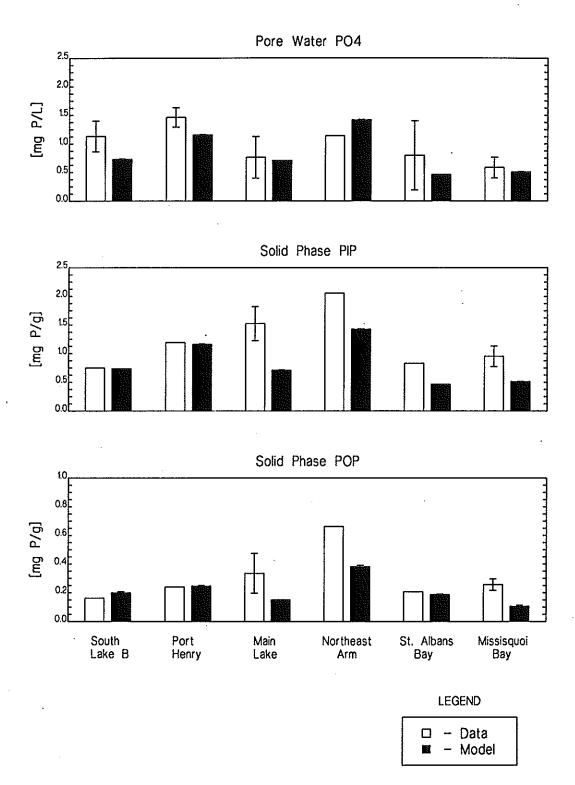
Water Column Temperature



Water Column Total Phosphorus



Water Column Particulate Organic Phosphorus



APPENDIX E
RESPONSE TO REVIEWERS' COMMENTS

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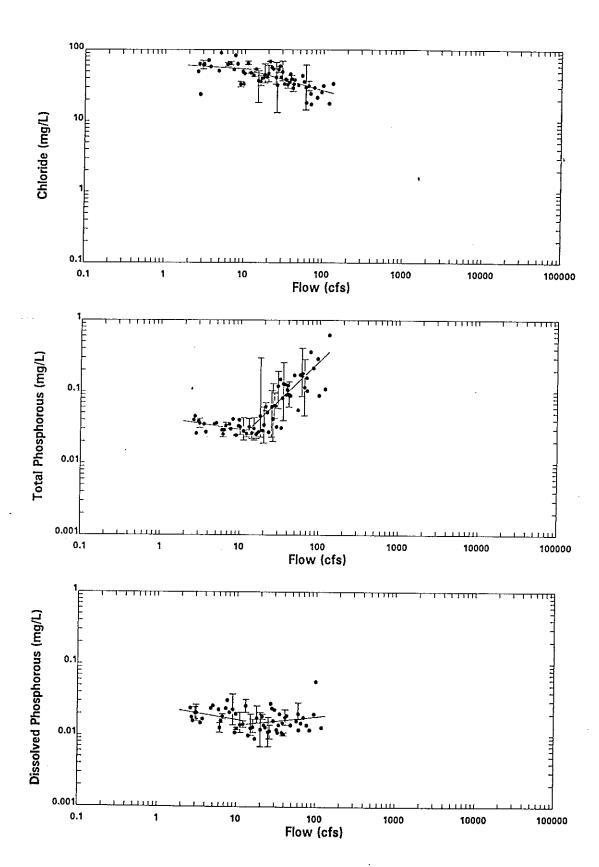
# APPENDIX E

# RESPONSE TO REVIEWERS' COMMENTS

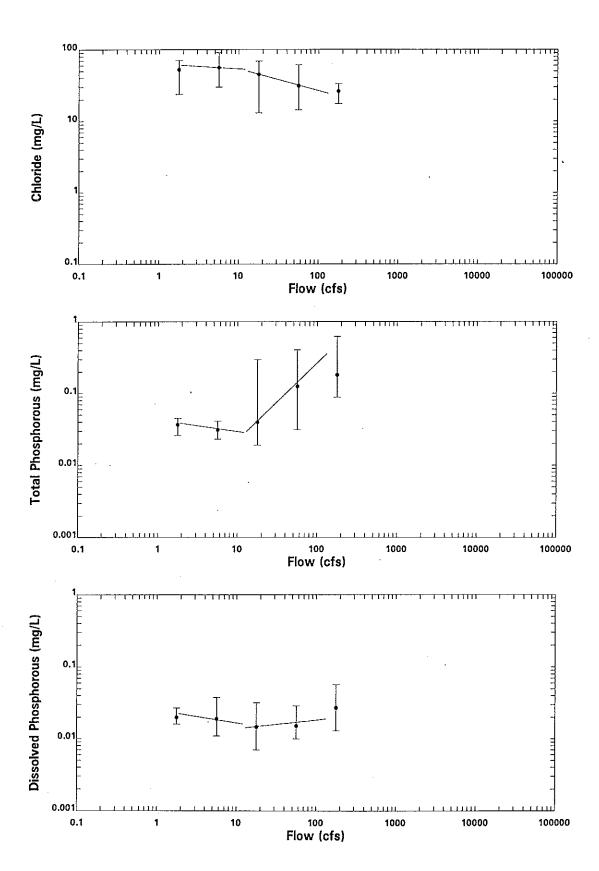
This Appendix was prepared in response to reviewers' comments on the draft report entitled "Benthic Phosphorus Cycling in Lake Champlain: Results of an Integrated Field Sampling/Water Quality Modeling Study" completed in February 1998. The reviewers' comments, as well as our response to them, are contained in this Appendix. Many of the reviewers' comments, particularly those of an editorial nature, have been addressed in the revised report. The remaining comments, especially those of a technical nature, are addressed in this Appendix. Rather than addressing each individual reviewer's comments on a point by point basis, the major comments will be addressed more broadly, as several reviewers touched upon similar points. We have divided our response to comments into the following categories: Loadings and Initial Conditions; Model Segmentation and Kinetics; Data; and the Calibration. Finally, we at HydroQual would like to thank the reviewers for their time spent in reviewing the draft report and for submitting comments. The result, we hope, is a better final report and product for our clients.

# **Loadings and Initial Conditions**

One reviewer commented on the concentration versus flow relationships developed for estimating tributary inputs. Since, for the period of interest, daily observations of phosphorus were not available for the tributaries, it was necessary to estimate phosphorus concentrations for those days for which data were not available. In addition, since the available budget did not allow us time to conduct an exhaustive data search of available tributary data, we relied heavily on a previous analysis of phosphorus inputs to the lake performed by Eric Smeltzer (VTDEC, 1997), which utilized concentration versus flow (C vs. Q) analysis. (We have also successfully used C vs. Q relationships for estimating pollutant inputs in other water quality studies.) The VTDEC used the C vs. Q technique using flow breakpoints based on the observed data. Guided by the flow breakpoints used by the VTDEC, HydroQual followed a procedure similar to that used by the VTDEC and developed its own C vs. Q coefficients. In an effort to improve the statistical reliability of the C vs. Q regression analysis, we binned the water quality data within fixed flow intervals (in log-space). The resulting C vs. Q relationships were used to develop time-variable loadings required as model inputs. Figure 1 shows C vs. Q relationships for the Indian River, using the unbinned data; (Figure 2 presents the binned data for comparison) there is clearly a



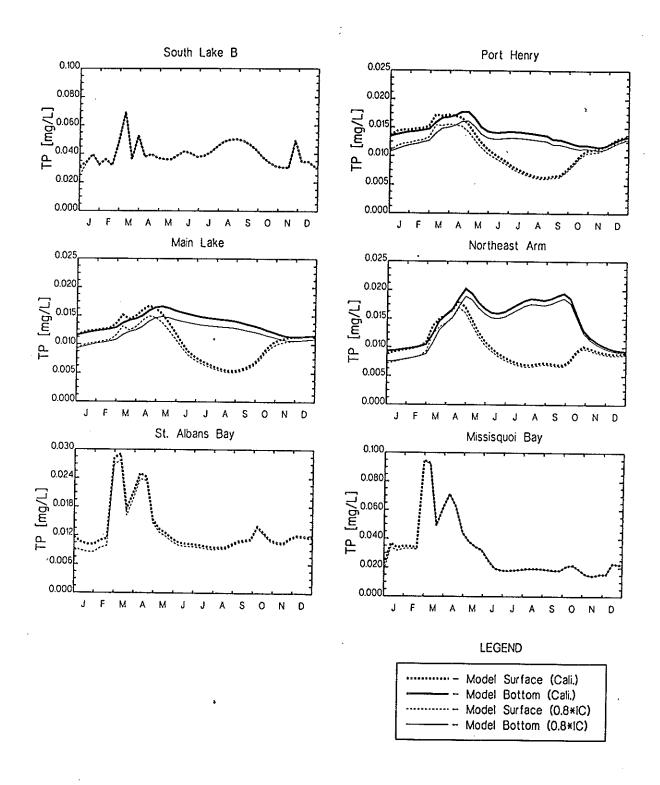
Indian River



Indian River

break in the C vs. Q relationship for the total phosphorus data. It is likely in the Indian River, as in many of these tributaries, that at a certain flow rate the bottom shear stress becomes large enough to resuspend sediment-bound phosphorus from the sediment bed. The majority of the resuspended phosphorus will be particulate in nature. However, the chloride and dissolved phosphorus data do not evidence such clear breaks. In the case of dissolved phosphorus and chloride, it appears that dilution is the dominant factor and, therefore, it was probably not necessary to include a breakpoint in the analysis. In addition, while it may not have been necessary to have breakpoints for all of the tributaries, it was done for consistency. Ultimately, the facts that the VTDEC and HydroQual loading estimates are within 10 percent of one another and that the water quality model compares favorably to the in-lake total phosphorus suggests that the estimates of the phosphorus loading to the lake are reasonable.

The initial conditions used in the model were another cause of concern to some reviewers. In the absence of observed data, running a water quality model to a periodic steady-state is often the best way to determine the initial conditions. For the sediments, there is really no other way to assign initial conditions other than running the model for a long period of time. Using data from sediment cores taken from the lake and interpolating between the points for the remainder of the lake would result in much larger uncertainties than using the model. This is in part due to the heterogeneous nature of the sediments. For the water column, no data were available with which to estimate initial conditions, given the fact that water column sampling is not conducted in the lake during the winter months. While it may have been feasible to estimate initial conditions via interpolating water column data between the last field survey of 1990 and the first field survey of 1991, it simplified running the model considerably by cycling the model to a periodic steady-state. However, to respond to the reviewer's comment, a sensitivity run was conducted to demonstrate that the model calculations are not strongly influenced by the choice of water column initial conditions. For the sensitivity run, initial conditions were decreased by 20 percent for all the phosphorus systems included in the model and then the model was run for one year. The results of this computation were compared to the calibration results (Figure 3). The dashed lines represent surface results and solid lines represent bottom results. The calibration results are represented by thicker lines. In places such as South Lake B and Missisquoi Bay, where the detention times are small due to small volumes and/or high flows, the choice of initial conditions does not appear to matter. In the Main Lake segment, which has the longest detention time, the model gets to within 94% of the original value within one year, after starting at 80% of



Water Column Total Phosphorus

the original concentration. The greatest errors caused by the initial conditions occur in chlorides because it is a conservative substance not subject to decay or settling.

An additional reason for cycling the model to a periodic steady-state concerned the sediment bed of the lake. Since Pb<sup>210</sup> dating of lake sediment cores indicated that sediment accretion rates were on the order of 0.1-0.5 cm/yr and since an active sediment layer of 10 cm is assumed in the lake, this means that the required time for the sediments to achieve a new equilibrium in response to changes in phosphorus loading is on the order of 20 to 100 years. Therefore, in order to ensure that there was no long-term mis-calibration of the model, resulting from the choices made in the sediment submodel coefficients, long-term model simulations were required. Ideally, one would like to utilize observed long-term point source and tributary loadings in performing these long-term simulations. However, primarily due to data limitations as well as budgetary limitations, it was not possible to generate a real 50-year history of phosphorus loadings to the lake. Instead the relatively simple approach described in the study documentation report was used.

# **Model Segmentation and Kinetics**

The choice of model segmentation was brought into question by some reviewers. The model segmentation used in this study was only slightly modified from work conducted by the VTDEC. To some degree, the segmentation used for a model is affected by the availability of data for a model calibration, the availability of detailed hydrodynamic information, with which to specify the transport of water quality constituents within the lake, and time and budget constraints. Time and budget constraints precluded the development and calibration of a hydrodynamic model of the lake. As a consequence, it was not possible to develop a more spatially refined horizontal or vertical segmentation of the lake, since the specification of the horizontal and vertical mixing coefficients and horizontal flows would have been speculative at best. In addition, our ability to include greater vertical segmentation was limited by the fact that in may areas of the lake only vertically composited data were taken. However, we decided it was appropriate to include vertical segmentation in the deeper areas of the lake for three reasons. First, the observed water quality data indicated strong vertical gradients in the deeper regions of the lake. Second, since phytoplankton primary productivity is strongly influenced by available light, treating the deeper portions of the lake as one completely mixed segment would have ignored the fact that a thermocline develops in the lake during the summer months, thus forming

a stable surface layer which assists in phytoplankton growth. Treating the deeper portions of the lake as one completely mixed segment would have precluded the growth of phytoplankton in those model segments. Third, since sediment phosphorus flux rates are strongly influenced by water column temperature, it is important to recognize that using bottom water column temperatures in the deeper portions of the lake would result in significantly different fluxes as compared to those generated using vertically averaged temperature data.

There were some comments expressed concerning the kinetic structure of the water column and sediment model utilized in this study. The first comment concerned the relatively simple nature of the water column kinetics utilized in this study which excluded state-variables for nitrogen and silica. This was, in part, in response to data availability and budget considerations. The data and loading information available for phosphorus in this study were much more extensive than the nitrogen and silica information available. While in-lake nitrogen and silica data existed to calibrate the model there were insufficient tributary and point source nitrogen and silica data to specify loading inputs. Hence, the model was simplified to exclude nitrogen and silica. While it is possible that nitrogen and/or silica could be limiting during certain times and in certain locations within Lake Champlain, based on the observed data it appears that phosphorus is the more limiting nutrient in Lake Champlain.

A second reviewer raised a concern about the application of a nitrogen-based estuarine sediment nutrient flux submodel to a freshwater system. While the sediment nutrient flux submodel employed in this study was originally developed and calibrated for the Chesapeake Bay system, the Chesapeake Bay model included phosphorus state-variables as well. As a matter of fact, the strong spatial gradients in dissolved oxygen within Chesapeake Bay provided a rigorous test of the sediment model's ability to reproduce observed phosphorus fluxes. While to date, the sediment model has primarily been applied in estuarine studies (Long Island Sound, New York Harbor, Jamaica Bay, New York, and the Massachusetts and Cape Cod Bays system to name a few) and has provided favorable comparisons to observed phosphorus flux, pore water and solid phase composition data for those water bodies, the model has also been applied to a number of freshwater systems including the Croton Reservoir, located near New York City; the Wanaque Reservoir, a water supply reservoir for Newark, New Jersey; and, Onondaga Lake, located near Syracuse, New York. The same framework was employed in each of these studies; the only difference between these studies was the choice of model coefficients, and, in particular, the values used for phosphorus partition coefficients in the sediments. The sediment nutrient flux

submodel has provided computations which compare favorably to the observed data for all of these systems.

Another point of concern was the use of the term "respiration" when describing the model kinetics. The term respiration in this modeling framework is an all-encompassing term which includes respiration and non-predatory death of phytoplankton. The use of this respiration term is common among eutrophication modelers. Since most water quality models do not account for variable internal nutrient stoichiometry (such as variable C:P stoichiometry) resulting from algal carbon loss associated with respiration and since it is imperative to maintain mass conservation, water quality modelers recycle an appropriate quantity of phosphorus (based on the C:P ratio of the algae) to the various organic and inorganic phosphorus pools as a consequence of "respiratory" losses. In this way the water quality model accounts for non-predatory algal detritus. In a similar vein, we are familiar with the fact that phytoplankton (as well as bacteria) produce extracellular phosphatase, under nutrient limiting conditions, in order to cleave orthophosphate from dissolved organic phosphorus. However, this process was not directly included in the model framework. We believe that the effects of phosphatase production are probably subsumed within the choice of phosphorus recycle rates and the variable C:P relationship, represented by Equation 2-10, employed in the model. We also acknowledge the role that bacteria play in nutrient uptake and in recycling organic nutrients. However, for Lake Champlain, a comprehensive bacterial biomass data set was not available for the period of interest, therefore, a direct calibration of bacteria was not possible. Since the kinetic reaction rates for bacterial growth, death, nutrient uptake, etc. are not known a priori their values would have to have been chosen based only on indirect evidence, that is, on how well the calculation as a whole reproduced the data for the other variables being considered. Without an equivalent increase in the data available for their estimation, these additional constants and dynamic equations would have significantly added to the available degrees of freedom in the model calibration. Thus our ability to uniquely specify a consistent set of kinetic constants would have diminished rapidly and, as a consequence, the resultant calculation would have been more speculative. Therefore, when constructing a water quality model, one only includes state-variables in a model framework if there is sufficient data with which to verify the variable of interest. In summary, while some of the intermediary steps of the phosphorus cycle are omitted, the overall process of phosphorus uptake by phytoplankton, the return of phosphorus to the organic pool and its subsequent hydrolysis and mineralization to inorganic phosphorus are properly represented in the model framework.

Settling and resuspension was another topic discussed by the reviewers. The model contains only a net deposition rate, and does not model the separate effects of settling and resuspension. To more explicitly calculate settling and resuspension would require the following: a more spatially detailed model segmentation; a hydrodynamic model that would compute bottom shear stress; and a sediment transport model. All of these requirements were well beyond the scope and budget of this project. However, the 'resuspension' sensitivity run performed as part of this study shows that resuspension may be important process to local phosphorus concentrations and, therefore, we would encourage further study of its effect in Lake Champlain.

The effect of bacteria and fish on dissolved oxygen was discussed by one reviewer. The effect of bacteria on dissolved oxygen is accounted for to some degree by the oxidation of organic carbon. Generally, it is believed that there are orders of magnitude difference between the biomass of phytoplankton and fish in a lake and, therefore, the effect of fish respiration on dissolved oxygen is thought to be small.

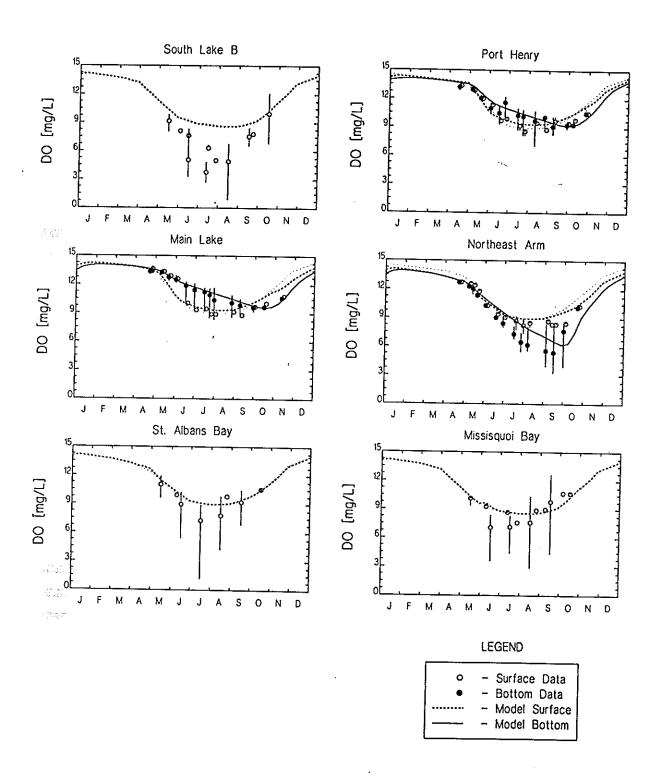
Two reviewers commented on the form of reaeration used in the model. A sensitivity run was performed using a reaeration equation reported in the WASP 4.0 manual:

$$k_a(T) = (-0.46W + 0.136W^2)\theta^{(T-20)}$$
H

where: W is the wind speed (m/s), H is the segment depth (m), and  $\theta$  is the temperature-correction coefficient. In this sensitivity run, the value of  $k_a$  was not permitted to drop below 1.6/H as specified in the WASP 4.0 manual. The results of this sensitivity for dissolved oxygen are presented in Figure 4. As can be seen the results do not vary significantly from the original calibration. However, it does seem appropriate to include the effects of wind on reaeration and, therefore, the model has been revised accordingly.

# Data

The issue of the difference between ortho-phosphate (OP) and soluble reactive phosphate (SRP) was brought up by one reviewer. The data were reported as OP, so we were not inclined to differ from what was reported. Technically the data should be reported as SRP. In general,



Water Column Dissolved Oxygen

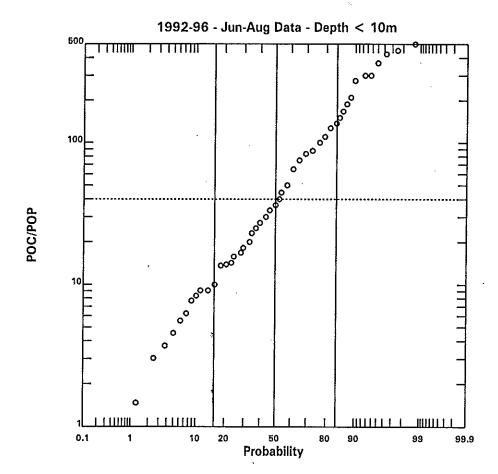
the water quality modeling community does not differentiate between OP and SRP for modeling purposes, since SRP is assumed to be readily available for phytoplankton uptake.

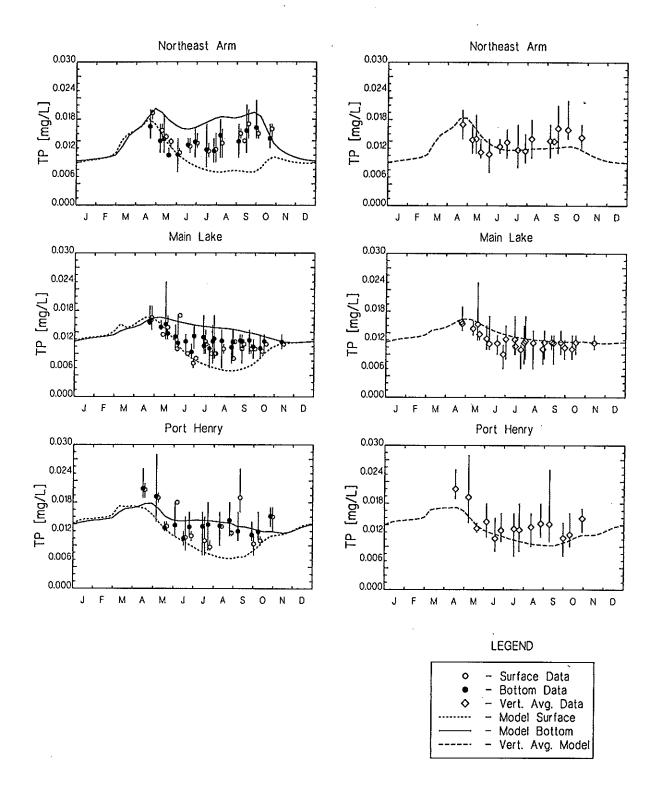
The Redfield ratio and the data used to determine it was discussed by one reviewer. The Redfield ratio for carbon and phosphorus is approximately 40 to 1 (on a weight basis). It is known, however, that phytoplankton can modify their C:P ratio depending on available nutrients. There were limited data available to establish a C:P ratio. Concentrations of POC were estimated from TOC and DOC data and POP concentrations were estimated from TP and DP data. The assumption was made that the concentrations of POP and POC observed in the lake were largely associated with phytoplankton biomass and detritus and not other sources of organic matter. Figure 5 shows the available data yielded a median C:P ratio of nearly 40 to 1. The range of data may be indicative of the error associated with the estimated concentrations. The degree to which this ratio was allowed to change in the model was established through calibration.

#### Calibration

One reviewer took issue with the statement that the model reproduced the measured TP concentrations at the deep stations in the lake fairly well. Figure 6 presents the calibration of TP at the three deep stations along with a model versus data comparison of vertically averaged, volume weighted model output and data for the same three stations. While it appears from the left-hand panels that the model reproduces the approximate magnitude of the observed TP data, the model predicts more stratification than is indicated by the data. Hence, the reviewer raised a legitimate question as to whether the model could be considered "reasonably calibrated." However, as can be seen from the panels on the right which compare volume weighted data concentrations versus volume weighted model computations, the total phosphorus at each sampling location is predicted "fairly well" by the model.

However, we do acknowledge that the model calibration does have weaknesses. It is disappointing that after considerable effort the model cannot produce low dissolved oxygen levels observed in locations of critical importance in Lake Champlain. These dissolved oxygen levels have an important impact on the phosphorus cycle in the lake. More research needs to be conducted to explain the phenomena occurring in areas such as South Lake, Missisquoi Bay and St. Albans Bay.





Water Column Total Phosphorus

Despite the model's shortcomings, the inclusion of an interactive sediment submodel provides a vastly improved tool for management use. The model as it currently exists can provide an initial screening of management alternatives. More detailed management decisions may require further research and model development.

Thank you for the opportunity to review the Lake Champlain Benthic Phosphorus Cycling Study work performed by HydroQual, Inc. And the University of Maryland. My time for this review is limited so I cannot conduct an exhaustive review of either report. My comments, at this point, are general and based on my overall assessment as compared to similar studies on the Great Lakes.

First I will attempt to comment using the review questions which you provided.

1. Were the field and laboratory studies conducted in a scientifically sound manner, and are the conclusions of the University of Maryland report supported by the data analysis and results?

#### Response:

The work appears credible and sound. The researchers appear to have captured contemporary approaches to their work and have included appropriate references to similar efforts by others. I would have to agree with the authors' conclusion on page IX-1 that the "....program ...has provided a first order understanding of sediment phosphorus burial and recycling fluxes." Many issues and uncertainties remain, however.

The conclusions are reasonable for the specific sampling stations and experimental chambers. However, with work like this it always remains a matter of judgement as to how to extrapolate the results in space and time. Sediment researchers tend to bias their work by sampling in the deepest areas where deposition is at a maximum. Without further bathymetric information it's impossible for me to tell whether this was the case for this work. For the Great Lakes researchers have gone to great pains in mapping sediment characteristics around the lake. With this information it is possible to at least tell where any particular sample might be representative. With current acoustic technology it would be relatively easy to roughly map surficial sediment types in Lake Champaign. The authors seem to acknowledge the problem of extrapolation on page VIII-4. This also may explain the difference between model and experimental results.

In this regard, the question remains as to the optimal sampling design for this kind of work. The report does not explain why sampling stations were selected nor the "data quality objective" in quantitative terms. I assume that a quality assurance plan was prepared for this work which explains all of this. If so reviewers should be provided with a copy. I agree with the Hydroqual report conclusions that additional sampling would be useful. Any additional sampling plan should be designed with regard to the modeling requirements.

Another question I have has to do with the impact of physical resuspension due to shear stress. How much of the P recycling is due to resuspension of sediments and desorption or mineralization of these resuspended P laden particles? Was this even considered to be a factor? In this regard, how does meteorology (winds) affect the resuspension of sediments in the lake? W. Lick, University of California, has shown that the majority of sediment movement in the Great Lakes is due to a few major events spaced over a long time frame. One major event (1 in 50 years) can resuspend and move more material than a great number of smaller events (1 in 2 years).

2. Were the results of the field and laboratory work used appropriately by HydroQual, Inc. To develop and calibrate the sediment sub-model for Lake Champlain?

I am interpreting this question to include whether I agree with the modeling framework.

# Response:

First of all I would consider the modeling framework for this work to also be a "first order" attempt at modeling the bio-chemical processes in the lake. I say this because the model could include more physical, biological, and chemical resolution. For example, more phytoplankton types could be modeled and silica and nitrogen could be included as a possible limiting nutrients. I assume that someone has determined that theese are not limiting in Lake Champlain at the present time. The question would be whether they might become limiting under some future scenario. Silica can be limiting for diatoms in Lake Michigan. However, it did not seem to be within the scope of the workplan to do more than what is described here. In that regard for the funds available, I think the modeling work is excellent and represents a first order calculation.

Concerning use of the generated data:

Sedimentation rates were incorporated appropriately (Page 3-15) It looks like the data were used correctly in providing calibration comparison.

3. a. Does the coupled water quality and sediment model provide us with an enhanced ability to predict the response of Lake Champlain to phosphorus loading reductions, taking into consideration the effects of benthic phosphorus cycling?

Response: Yes. It's better but not yet good enough.

b. Should environmental agencies and researchers use the model for this purpose?

Not yet and not without additional data and model refinement. However, if decisions are being made anyway, then this model, with proper qualifications, would be better than no model at all. The primary purpose of the model is to estimate the lag time the sediments contribute to the time to equilibrium. Two estimates--by Martin and Hydroqual, page 3-56--appear to be fairly close except when the calculation was redone using the with the resuspension formulation. So for 90% Reduction at takes 27 to 50 years. Is this close enough for management decisions? If not, then there needs to be more work in defining loads, refining spatial resolution of the model, and refining the spatial definition of sediment characteristics.

4 Is the model software sufficiently well documented and readily useable by agency staff and researchers in the Lake Champlain Basin for the purpose of simulating the effects of changing phosphorus loads to the Lake?

Response: I was able to run the model, and with additional information provided by Jim Fitzpatrick, I was able to plot the model output. Given the training course and the availability of Hydroqual to answer detailed questions, I think someone with a scientific background should be able to run the model. How well any person is able to interpret the results is another matter. Anyone can run a model. It's another matter as to the correct application and interpretation. I do not think the model is ready to just plug in new loading scenarios and get projected phosphorus and phytoplankton concentrations. But I do think this model can provide the basis for further study and understanding. The model results should not substitute for common sense, scientific insight, etc.; but rather should be used to enhance the process. I get the feeling from the Hydroqual report that the model is not ready to just "turn over" for management utility.

Whether or not the model can be used for management decision making is up to the managers. Given the uncertainties pointed out by the authors and the lack of resolution and the inability to calibrate to several state variables adequately in several lake segments, I personally would not use the results to make quantitative decisions.

I have read the report ...... Benthic Phosphorus Cycling in Lake Champlain. As you are aware the topic is one that I am a non-expert in and I feel a little uncomfortable in

making any review of these documents ... but here goes.

(1) I found the HydroQual report to be well written and I had little difficulty following their logic and model development. I did find it somewhat tedious following their presentation of model results but there is soooooo much in the report and so many runs to describe that it would be very difficult making everything as clear and concise as I might wish. On the other hand I found Horn Point Lab Report, especially Chapters III, VII, and VII, to be less than helpful for me to understand the meaning of the approaches they took and the inter-relationships among all the parameters they measured. I believe a better discussion is needed in this regard.

(2) The Horn Point Lab report conclusion that in eutrophic portions of the lake about 50% of the sedimented P is recycled back to the overlying water is quite significant from a management standpoint. Their overall Lake Champlain estimate should also be useful. Their conclusion that bivalves may have a profound effect on P recycling is interesting. Does this occur largely in the more shallow (and eutrophic) areas of Lake

Champlain, am I right?

(3) The HydroQual report develops the model nicely and I have no problems with the fundamental basis for their model. They do, however, point out in their conclusions that their model "cannot reproduce the low dissolved oxygen observed in South Lake B, Missisquoi Bay and St. Albans Bay". They also point out that the model appears to be sensitive to partition coefficients assigned for P. Overall the model problems seem to be most severe in the same areas in which P recycling is the greatest and where immediate

management concerns may be the greatest.

Clearly more research needs to be done to understand these recycling processes in eutrophic areas where low DOs and ORPs probably substantially influence partition coefficients, where wind suspension of sediment may be the greatest, and where bivalve activity may also be substantial. Model flexibility and applicability to the more shallow areas of Lake Champlain would obviously be enhanced considerably with the incorporation of additional low DO, resuspension, and bivalve process information. As it is, I believe the model is useful, certainly for helping in making strategic management decisions, and, with caution, in making management decisions for individual embayments.

You specifically asked me to look at the model which I interpreted as trying to run the model. As you know I am primarily a Mac person and I feel inadequate in the PC world. Even so, we attempted to run the model on a relatively powerful PC with a

pentium processor and Windows 95. We were not completely successful even though a considerable amount of time was spent trying. We could operate the model only by entering commands through the DOS window. Because of personal time constraints I finally was forced to give up. We did not discuss our problems with the developers although they did provide their name and number and an invitation to contact them if there were difficulties.

The instructions provided through the various Readme files of the diskettes are minimal and were totally inadequate for a novice, like me, to access the model. There are few clear instructions as to how to begin or how to view the model outputs. We did finally get the model to run (for a 10 year period not the 50 to 60 years mentioned in the Readme file) using the example files supplied but we were never able to view any output. It took between 2 to 3 minutes for the computer to finish the computations for each year. There is an eighty some page users guide buried in the Diskette 2 files but with no table of contents making it time-consuming to find anything. The guide has not been updated for "GDP98", whatever that is. The users guide is for GDP release 5.40, I presume some version of the GDP model previous to the Lake Champlain work? I found no mention of the "GDP" model in the Lake Champlain report documents. I again presume it is the generic name of the model used to generate the results in the report. In the second and third paragraphs of the users guide it is stated that GDP models "lack the friendliness" of spreadsheets or databases and it may be more efficient in many circumstances for a user to change the GDP command file and then submit it to one of HydoQuals UNIX systems for running. Clearly the model is not user friendly nor interactive, not even when running it on the files supplied on the diskettes, let alone when trying to change parameters and input data to test scenarios other than the one presented in the report. Substantial familiarity with the model is needed before one would change the GDP command file and data input files to reflect changes in model inputs.

I cannot see how anyone in VTANR or NYDEC or elsewhere could run the model without considerable training or self-study beforehand. It appears to me, as it stands from the submitted materials I reviewed, that the primary value of the model is the outputs it generated and their description in the submitted reports. The meaning to management programs of the outputs in the report can be assessed but, without additional contracting with HydroQual or without substantial training for agency personnel there appears to me to be little likelihood that the model will be used in the future to generate output for other alternative scenarios. The one day of training to be provided by HydroQual that you mention in your letter is ABSOLUTELY essential but so is

additional model documentation.

I am sorry that I could not take the time to become sufficiently familiar with the model to fully test its capabilities. The theoretical basis for the model seems competent to me but the utility of the resulting model to local scientists and managers is limited for the reasons cited above.

I hope these comment are helpful.

Review of Draft Report "Benthic phosphorus cycling in Lake Champlain: results of an integrated field sampling/water quality modeling study," prepared by HydroQual, Inc.

The report provides information on a water quality modeling study conducted on Lake Champlain using data provided primarily by previous studies on the lake. The date were supplemented with studies conducted by Horn Point Environmental Laboratory of the University of Maryland to support the sediment component of the model. The water quality model includes a sediment submodel for carbon and phosphorus dynamics that is based upon prior work in the estuarine environment for carbon and nitrogen dynamics. The report focuses on specifics of the model components and the calibration of the overall model. Selected sensitivity studies for dissolved oxygen and wind resuspension are presented to elaborate on possible explanations for deficiencies in the model calibration.

Basic questions proposed to reviewers:

1. Were the field and laboratory studies conducted in a scientifically sound manner, and are the conclusions of the University of Maryland report supported by the data analysis and results?

I did not review the University of Maryland report, but the discussion in the HydroQual report indicates that the field studies may not have been conducted in a manner that provides the appropriate quality of data required by the modeling study. Quoting from pg 3-40 of the HydroQual report:

"Two of the highest phosphate fluxes (25.6 and 44.7 mg P/m²-day) observed in this study are found in Missisquoi Bay. These high fluxes have been attributed to benthic organisms collected in the sediment cores. It is believed that these organisms are stressed during the sediment incubations and artificially increased the rate of exchange between the sediment and overlying water (Cornwell, private communication). Therefore, these two values are omitted from the analysis and Figure 3-19. "

and

"During the 1994 sediment sampling study, phosphate fluxes were measured using cores whose overlying water had been raised to dissolved oxygen saturation rather than using ambient *in-situ* conditions. It is believed, that in areas that experience hypoxia such as South Lake B and St. Albans Bay, the summertime phosphate flux measurements may have over-estimated the actual in lake fluxes, due to re-aeration of the cores prior to incubation."

2. Were the results of the field and laboratory work used appropriately by HydroQual, Inc. to develop and calibrate the sediment sub-model for Lake Champlain?

Not having reviewed the University of Maryland report, I can not directly answer this question. However, I can say from the discussion in the water quality report that HydroQual attempted to use the data as best as they could within the difficulties noted above in response to question 1.

3. Does the coupled water quality and sediment model provide us with an enhanced ability to predict the response of Lake Champlain to phosphorus loading reductions, taking into consideration the effects of benthic phosphorus cycling? Should environmental agencies and researchers use the model for this purpose?

The coupled model is an improvement over a model that includes the sediment component through a specified boundary condition. However, enough questions are raised by HydroQual in the report to discourage use of the existing model, as is, for phosphorus loading reduction scenarios. The lack of fit of dissolved oxygen and other parameters in the shallower segments brings into questions the utility of the model for use in management alternatives that are focused on improvements in these shallower segments.

4. Is the model software sufficiently well documented and readily useable by agency staff and researchers in the Lake Champlain Basin for the purpose of simulating the effects of changing phosphorus loads to the lake? However, the comments to questions 3 are applicable.

I was able to get the software loaded on my PC and was able to get it to run. I did not try to make modifications to the software. A one-day training session for interested users of the software would be beneficial. However, until deficiencies in the model are addressed, the software should not be widely distributed.

# Major comments:

The sediment model framework discussed in this report was developed in estuarine areas for nitrogen dynamics with detailed vertical and horizontal spatial segmentation, and utilized a multi-dimensional hydrodynamic model for computing transport and dispersion coefficients. No explicit rational was provided in the report of why this framework would be expected to be directly applicable in a freshwater system to describe phosphorus dynamics with coarse vertical and horizontal spatial segmentation, and with transport inferred from chloride distributions. In fact, no references are provided for this framework having been applied to phosphorus dynamics in freshwater systems. The lack of detailed spatial segmentation and the use of chlorides to infer transport are probably the result of the funds available to conduct this project. But a rationale of why something developed for nitrogen should work for phosphorus should be given.

The model fit appears to be worse in shallow, single-layer segments. This could result from the sediment model "requiring" vertical layers since the flux at the sediment-water interface is driven by the water column conditions just above this interface, not vertically averaged values that result from a single layer segment. The large variability in dissolved oxygen data as shown in Figure 3-17 for the single layer segments could possibly indicate that vertical stratification exists in those segments, but was not appropriately accounted for in the model segmentation. Multiple layers would be necessary if these shallow segments experience hypoxia just above the sediment-water interface.

Why would one expect the periodic steady-state results of the model to compare with a

given set of annual field data? On what basis would one expect a given year of field data to be in a periodic steady-state with a constant annual loading? The report notes that loads are changing from year to year, so periodic steady-state does not appear to be supported. Since this is a major assumption used to conduct the modeling simulations, some rational should be given to support it. Also, sensitivity to this assumption or implication of errors in this assumption should be provided.

# Specific comments:

Pg. 2-6, 1st full ¶: The sediment submodel was developed for N dynamics in estuarine waters. No discussion is given for applicability to P dynamics in fresh water.

Pg. 2-11, 1<sup>st</sup> ¶ of §2.2.4: Where did the data for determining Redfield ratio for Lake Champlain come from? What were the calculated ratios?

Pg. 2-15, equation 2-12: Why isn't the reaeration coefficient a function of wind speed?

Pg. 2-18, the equations for  $J_{GPOC,1}$ ,  $J_{GPOC,2}$ , and  $J_{GPOC,3}$ : something is wrong with these definitions as the dimensions don't seem to match; J's are fluxes, f's are unitless, and POC is concentration.

Pg. 2-19, equation 2-17: the first and third term on the RHS of the equation can not both have the same sign, unless one of the K's is negative; one term represents vertical mass transfer into the segment and the other transfer out of the segment. Have I missed something with the conventions that are used to display the equations?

Pg. 2-19, equation 2-18: why is the fourth term, sedimentation out of the cell, based on total concentration, not particulate concentration as is comparable term in equation 2-17?

Pg. 2-21: C<sub>d0</sub> is not defined.

Pg. 2-22, equation 2-19: "SOD =" should be added for clarification.

Pg. 2-26, 2<sup>nd</sup> sentence of § 2.3.3.6: "can longer" should be "can no longer".

Pg. 2-27, 1<sup>st</sup> full ¶:  $\kappa_{M.HS.02}$  should be  $K_{M.HS.02}$ .

Pg. 2-28, equation 2-32:  $k_{M.HS,O2}$  should be  $K_{M.HS,O2}$ .

Pg. 2-28, equation 2-33: Is  $\pi_1$  suppose to go to zero as  $\Delta \pi$  goes to zero?

Pg. 2-28, definitions at bottom of page: is  $\Delta \pi = \pi_2 - \pi_1$ ? If yes, then equation 2-33 is incorrect.

Pg. 3-4, Table 3-1: where did these numbers come from?

Pg. 3-4, 1st sentence of § 3.2.2: a number should be substituted for "majority".

- Pg. 3-9, Table 3-4: where did these numbers come from?
- Pg. 3-10, 1st full ¶: the determination of lower layer depth is confusing, and possibly wrong. For example, the volume using surface area and average depth (§ 1.1) is 25.764 km³. Summing the volumes using the method described (Table 3-6) gives 24.324, which is low by about 5%.
- Pg. 3-11, Table 3-6: the depth for segment 18 is ridiculously low. This should be made a single layer segment or the depth of the upper layer should be decreased.
- Pp. 3-10 to 3-12, § 3.4.1: data used to derive temperature functions should be referenced.
- Pg. 3-14, § 3.4.6: reference to Table 3-8 is incorrect table.
- Pg. 3-14, § 3.4.7: what were the measured values used to calculate the partition coefficients.
- Pg. 3-15, Table 3-7: column heading "Sedimentation Rate" was referred to as accretion rate in text.
- Pg. 3-16, Figure 3-34: do numbers used as plot symbols represent segment numbers?
- Pg. 3-18, 1st full ¶: are the results presented in the rest of the report from the last year of model simulation?
- Pg. 3-18, § 3.5.1: it is not true that the model is able to reproduce the observed stratification between top and bottom data at Northeast Arm.
- Pg. 3-21, Table 3-9: what is h in the units hm<sup>3</sup>?
- Pg. 3-21, §3.5.2, 1<sup>st</sup> ¶: What is the difference between bulk vertical dispersion and the vertical dispersion coefficients? What is the significance of this difference that they both need to be presented in Figure 3-7?
- Pg. 3-24, § 3.5.3: why does the model calculate negative values?
- Pg. 3-24, § 3.5.3.1,  $2^{nd}$  ¶: there is a switch in the discussion between station numbers.
- Pg. 3-25, Figure 3-9 (and others later on): comparison of the information would be easier if plots for the same figure were plotted with the same vertical scale.
- Pg. 3-26, § 3.5.3.2: starting here I note numerous occasions where the word "data" is treated as singular.
- Pg. 3-27, Figure 3-10: no explanation is given for the exceptionally high values that the model

generates in the early spring, which are not supported by data.

- Pg. 3-28, Figure 3-11: no explanation is given for the spiking in values that the model generates in the early spring for the single layer segments.
- Pg. 3-30, Figure 3-12: no explanation is given for the exceptional high levels in July to September for South Lake B (single layer segment).
- Pg. 3-32, § 3.5.5: for some reason, the light extinction due to the elevated chlorophyl concentration levels does not show up in Figure 3-14. In fact in Figure 3-14, the deviations from the base light extinction do not correspond with the bumps in the Figure 3-13. What is driving the light extinction?
- Pg. 3-41, Figure 3-19: no-explanation is given for the difference between open and filled circles.
- Pg. 3-42, Figure 3-20: no explanation is given for the difference between open and filled circles.
- Pg. 3-43, 3<sup>rd</sup> ¶, § 3.6: The opening sentence is the conclusion that can not be understood until the reader gets through the next 3 paragraphs.
- Pg. 3-47, Figure 3-22: the extremely elevated levels for July to September in South Lake B (single layer segment) is not explained.
- Pg. 3-49, Figure 3-24: the shapes of the modeled curves for South Lake B and Missisquoi Bay (single layer segments) disagree with the shapes inferred from the data.
- Pg. 3-56, top  $\P$ : another plausible explanation is that Lake Champlain in 1991 is not in periodic steady-state with the loads.

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# REVIEW OF THE FINAL REPORT: "BENTHIC PHOSPHORUS CYCLING IN LAKE CHAMPLAIN" HYDROQUAL- UNIVERSITY OF MARYLAND

The purpose of this project as stated in the RFP was to study P dynamics in selected areas of Lake Champlain (basically South Lake, Missisquoi Bay and St. Albans Bay) to enhance the predictive value of water quality models. In particular, internal P fluxes were to be quantified and mass balance modeling undertaken to determine the importance of the internal loading mechanisms to overall P dynamics. The internal P fluxes deemed essential for quantification were: chemically and biologically mediated sediment release, sedimentation, and physical resuspension of sediments.

The HydroQual-UM team approached the project through laboratory and field measures of P flux from sediments and of parameters potentially affecting flux rates, 210Pb dating of sediments to determine sedimentation rates, experiments in which net P release/adsorption from suspended sediments was measured, and modification of a model originally developed for Chesapeake Bay to meet Lake Champlain conditions. Much of the modeling done and many of the field and laboratory measures as well were peripheral to the main goals of the project. However, my impression was that this work was done "on top of" the meeting of basic requirements, rather than in place of them. I believe the Management Conference has gotten its money's worth on this project. Had there not been a pre-existing model or had the research team been less experienced or less "set-up" to process sediment samples, much less would have come out of the project.

Being a biogeochemist and a microbiologist, I am more qualified to assess the University of Maryland portion of the study than the modeling effort. I was somewhat disappointed with what I saw of the model in that I didn't consider the P cycle depicted very accurate. There are a number of problems with models, one being that important processes might not be included or that their nature is not properly described; another being that grossly incorrect values might be used in their parameterization. All of these problems could exist for this model. On the other hand, models can suggest hypotheses for testing and help define research and management priorities. Thus I believe this model may be useful for Basin researchers and managers- provided that we are aware of its shortcomings and willing to amend it. I felt that the field and lab work was appropriate to the project goals, and carried out with care.

We were asked to consider certain questions while examining the reports. Below are my responses to the questions asked (plus a couple more that I've inserted):

Regarding the Univ. of Maryland effort:

1. Were the objectives of the RFP (proposal) effectively addressed by the field and laboratory methods used?

Sediment fluxes: This group used three different methods to estimate P flux from sediments: pore-water profiles, core incubations, and in-situ chambers. Analyses were done in several lake regions and the results of the different methods compared,. I felt the effort here was commendable, and the data likely to be useful for managers and aquatic biogeochemists alike.

The P data were supplemented with measurements of ammonium, nitrate, DO, Fe, Mn and methane in core profiles and of their flux from the sediment surface, as well as

information on solid phase chemistry. These data provided clues about the importance of different processes in the sediments that might affect P chemistry, and information for the modeling effort. They should also prove valuable to researchers interested in other aspects of the lake's biogeochemistry (e.g., N and S cycling, and methane production).

Sedimentation: 210pb profiles were measured to estimate sedimentation rates. This is a fairly standard method of sediment aging, and the researchers seem informed about its proper use. Confirmation of the estimates with data obtained through 137Cs dating would have been desirable. Instead profiles of elements such as Pb were used for confirmation. Was this because a gamma counter was not available? Sedimentation rates might have been measured with sediment traps as well. However, sediment traps do not work well in shallow bays, as sediments in traps may be resuspended during turbulence. Therefore, I believe that the researchers chose a reasonable approach to addressing the issue of sedimentation.

Resuspension of Sediments: This was the internal process that received the least attention, although it is undoubtedly important in shallow bays such as the areas of concern, and can be important in deep waters during internal seiches (and Lake Champlain has a strong seiche). The research team looked some at the adsorption/ desorption dynamics of sediments brought into suspension, and this information may be useful to others analyzing P dynamics in the lake. What is missing is some estimation of how much sediment is brought into suspension in the lake regions of interest. Perhaps another project could address this issue?

Mass Balance: The researchers provided an estimate of the fraction of deposited P returned to solution in the shallow areas of most concern, as well as in the Main Lake. This I believe is what the Conference asked for. It would also be interesting to assess internal loading as a proportion of total loading (ie., returned P/ (returned + input P), as this is what is particularly important to phytoplankton.

2. Were the field and laboratory studies conducted in a scientifically sound manner?

All of the methods used were standard fare, and appear to have been carried out skillfully.

3. Were the conclusions of the report supported by the data analysis and results?

I felt the researchers' did a good job of interpreting their results, of pointing out problems, and attempting to explain oddities. A few of their analyses would benefit from statistical tests for significance (detailed below).

Specific to the modeling effort were the following questions:

1. Is the model realistic and appropriate for Lake Champlain? Does it provide managers with enhanced ability to predict the response of Lake Champlain to P loading reductions?

My impression was that some processes in the lake were not well described by the modeling. The frequent references to P release through "algae respiration" and the lack of discussion of P release through decomposition in the water column, were disturbing. Many of the values inputed into the model were not obtained through field measurements on Lake Champlain, but from the literature or best guesses (sometimes cycling the model to equilibirum conditions). This situation of inadequate data to appropriately fit a model to

a particular lake is common. The major benefit of a model may be to prompt researchers to measure some of the parameters.

I think the model should be used to predict the outcome of alternative P management schemes, but with caution. I wouldn't base multi-million dollar projects on the model outcome.

2. Does the model take full advantage the field and laboratory results of the Univ. of Maryland?

I had some difficulty assessing this, but I believe that it did. There are references to the field work values in the discussion on model initial conditions.

3. Is the model software well documented and readily useable by agency staff and researchers?

I did not try to run the software as my computer is a MacIntosh.

General comment: While these reports were generally well-written, there are still many mispelled, repeated or omitted words, and some grammatical errors. They should be carefully edited prior to publication. I have done some editing on my versions, and could send them to the authors (or editor) if doing so would be useful (most required changes are obvious, however).

Some Specific Comments: Univ. Maryland Report:

- 1. p. vii. Here and elsewhere sedimentation rates have the units g.m2/y. It is not clear what the mass term refers to: wet weight of the particles? dry weight? Weight as C? Weight as Pb?
- 2. p. I-1. Background: Plants may also enhance P fluxes by "mining" P from porewater and releasing it to the water column, or they may decrease fluxes by oxidizing reduced sediments through root release of O2. As there are many plants in the shallow bays of Lake Champlain that concern us, it would have been useful to study their role in P cycling. Perhaps in a future study? Here I am only suggesting that plants might be mentioned.

There are a number of lakes with anaerobic hypolimnia that release little P; the ELA lakes are examples.

- 3. p. I-2. The authors refer to questions asked by the original RFP, but don't state what they were.
- 4. Table II-2. I don't like the question marks in the colum headings. They give the impression that the authors are uncertain what they measured. And it isn't obvious that "x" means that something was measured. I'd indicate what "x" means in the table heading and leave out the "?"s.
- 5. II-4. Filter pore size should be in  $\mu m$ .

- 6. Table II-3. "NBS, AAS, TCD, FID" need to be defined, at least the first time they are mentioned.
- 7. III-1. Last para. Another possiblity for poor release of NH4 at Station II could be bacterial growth limitation by N. Bacteria decomposing organic matter take up released nutrients required for their growth. If N limits growth, they deplete their surroundings of N. Bacterial limitation by P is a more common situation in lakes, however.
- 8. Fig III-5. Don't bother with the A and B designation; "bivalve" and "no bivalve" is sufficient. Keep the "bivalve" value to the left.
- 9. Figure III-6. Are both 41's supposed to be black?
- 10. The comparisons of SRP fluxes in the presence and absence of bivalves, of fluxes in incubated cores vs. in in-situ chambers, and of ambient vs resuspension nutrient releases should be accompanied by statistical tests for significance.
- 11. IV-2. Pore water Mn. Pore water concentrations are said to "increase rapidly at most sediment sites", but it is unclear in what direction the increase is occuring. Probably "with depth" or "downcore". I saw this problem in a couple other places in the report as well.
- 12. V-2. para. 2. The stoichiometric relationships used to predict fluxes should be stated. However, I'm not too certain where the comparison between expected and measured rates is made. Fig V-5 shows only measured rates, I think.
- 13. Fig VI-8. Is #4 really significant? To me, it looks worse than several insignificant ones.
- 14. p. VII-2. What impact does mobile <sup>210</sup>Po have on age estimation? Does up-moving Po leave the sediments and diffuse into the water, or is it reabsorbed onto surface sediments?
- 15.p. VII-6. I am curious as to what these mass-based sedimentation rates amount to as far as sediment depth is concerned.
- 16. p. VIII-4. Point #3. Errors are not only inherent in the sediment estimates, but also in the mass balance estimates.

# HydrQual Report:

1. p. 2.2 para. 1. "Phosphorus is returned from the phytoplankton biomass to the dissolved and particulate organic P pools and to PO4 through endogenous respiration". Likewise Fig. 2-1 shows P recycled from algae to dissolved P via "algae respiration". This is an inaccurate description of the biology of the system. Respiration is the oxidation of matter to form (in eucaryotes) H20 and CO2. Phosphorus is not an endproduct of respiration. P may leak from algae, or be exuded, or phytoplankton may die and decompose. The main two mechanisms for P recycling from algae to PO4 are zooplankton excretion (included in the model) and decomposition of algal-derived detritus (not included). This misguided idea of algae producing P through their respiration is found in several places in the report.

- 2. p. 2.2 para. 2. Additional organic C sources are terrestrial runoff, and the byproducts of all living organisms (including fish and zooplankton grazing on organisms other than algae). For the latter, one might say "biological production", rather than "primary production and zooplankton grazing".
- 3. p. 2.2. para. 3. Fig 2.3. Oxygen losses include animal respiration as well. Sometimes there is more zooplankton + fish biomass in the lake than there is algal biomass.
- 4. p. 2.2.3. How was the summer phytoplankton assemblage chosen? Dinoflagellates and greens are not typically the summer dominants in Lake Champlain. Cryptophytes and blue green algae are generally more important. Little is known about winter assemblages in the lake. Diatoms may be common, but I would bet that cryptophytes dominate.
- 5. p. 2-8. para 1. Light extinction is as much due to absorption by water molecules as to absorption by particles.
- 6. p. 2-9 last para. Respiration decreases the biomass of individuals, but does not eliminate these individuals. I wouldn't say that it contributes to the "death rate".
- 7. p. 2-10. The sinking rates given are appropriate for diatoms, but high for other phytoplankton species.
- 8. p. 2-12. para. 2. The authors should understand that bacteria take up phosphate from the water to meet growth needs. Their net effect is not always P recycling into solution, but can be P depletion. Currie has authored many papers on P competition between bacteria and algae.
- 9. p. 2-14 para. 2. Phytoplankton (and also bacteria) produce extracellular phosphatases that cleave phosphate from DOP. It is not true that DOP and PP must be mineralized before the P is available to algae. We have measured alkaline phosphatase activity in Lake Champlain and it is considerable in those regions of the lake where P limitation occurs.
- 10. p.2-14 para. 3. Detrital organic carbon is not always produced as a result of predation. Algae can die without being eaten.
- 11. p. 2-15 para 1. Isn't reaeration a function of wind speed as well as temperature (the thickness of the stagnant boundary layer)?
- 12. p. 2-15. para. 2. Salinity is not an issue in Lake Champlain.
- 13. p. 2-15. para. 3. Animal respiration also depletes DO
- 14. p. 3-1. para. 3. Orthophosphate should be SRP. We don't know how much of the SRP in Lake Champlain is orthophosphate. In most lakes, the two fractions are not equivalent.
- 15. p. 3-24. para. 3. I don't know that I would agree that the model reproduced measured TP concentrations at deep stations in the lake "fairly well". The model lines in the figure do not run through the data.

- 16. p. 3-26. para. 2. Does the model really predict "nutrient limitation", or only nutrient depletion? The data shown are for nutrient concentrations. There is no evidence that nutrient limitation assays were done.
- 17. p. 3-35. para. 3. "soluble ferrous iron...does not sorb phosphate as strongly". Isn't adsorption a phenomenon involving charges on a solid surface? A dissolved substance I would expect not to be capable of adsorbing P at all.
- "As algae respire, in the bottom water of the lake oxygen is consumed..." The main process removing DO in bottom waters is decomposition. Why not include this process? It occurs on the sediment surface, as acknowledged by references to SOD, but also in the water column.
- 18. p. 3-38, also p 3-44. Model difficulty in computing DO depletion may be related to lack of input on animal respiration, decomposition in the water column and bacterial (or abiotic) oxidation of reduced compounds leaving the sediments. Not just nitrification, but also methane oxidation, sulfide oxidation, Fe and Mn oxidation deplete water column DO. Perhaps there processes are included in SOD? I wasn't certain.

#### Executive Summary

1. The executive summary provides a good, succinct description of a large, complicated project. However, given the problems encountered in model development and application (as well as the text that describes model calibrations and alternatives) it would be useful to include references to specific report sections to improve a reader's ability to directly "navigate" to critical information in the report without needing to re-read entire sections. For example, the development of the total external phosphorous budget is itself a significant project result regardless of the success of model calibrations and could be noted/referenced in the executive summary.

#### Section 1 - Introduction

1. The section is provides a good "big picture" overview of why this study was conducted. However, one worthwhile element to add would be a "little picture" description of subsequent report sections. For example, a Section 1.4 could be added to ease the transition from the big picture of why the study was undertaken to the little picture details of model theory and development. The second to last sentence of Section 1.3 (page 1-4) could become the first sentence of the new section. At present, the transition between sections is very abrupt.

# Section 2 - Model Theory

- The eutrophication and diagenesis kinetics described are very detailed and complex. However, this
  complexity may have exceeded the data available for model parameterization. One issue not
  addressed in the report is whether a simpler model would have more adequately reproduced field
  observations. Would a simpler model be more appropriate given this data set? This is an
  important consideration especially given the difficulties encountered during model calibration.
- 2. In Section 2.3.3.2 there is an assumption that benthic biomass is proportional to the labile carbon in the sediment. Is this reasonable? What set of observations leads to this conclusion? More detail and development to demonstrate the appropriateness of this important assumption should be presented.
- 3. The model, apart from all other details and complexities, does not expressly include a process for nitrogenous oxygen demand. Is this reasonable? Given the large internal reservoir and external inputs of phosphorous, is some information available to evaluate whether the system is at times nitrogen rather than phosphorous limited? Could nitrogen limitations exist in phosphorous-rich, well-mixed, near shore regions of the lake? (Does this model represent enough of the essential behavior of the physical system?)
- 4. Particle transport across the bottom boundary of the model network is described by a net sedimentation velocity. However, unless I misunderstand, the model does not apparently have a means to specify/compute separate settling and resuspension velocities/fluxes. This may be a major limitation.

In systems subject to periodic sediment disturbances such as storms or high flow events, net sedimentation rates may not provide much insight into particle transport. Sedimentation rates

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computed from sediment core geochronology data are difficult to interpret. A critical assumption of typical geochronology models is a constant well-mixed sediment layer thickness. Mixed layer depths vary as a function organism densities, temperature, dissolved oxygen concentrations, and hydrodynamic disturbances (mixing attributable to resuspension/deposition), etc. Also, for waterbodies with a large watersheds, radionuclide profiles can often be smeared by the different delivery times for materials from outlying areas to reach a final depositional zone when compared to material from nearby areas. Variation in these factors contribute to uncertainty in computed sedimentation rates. Sediment trap data are often just as difficult to interpret (although for different reasons).

Perhaps more importantly, at least from my perspective, net sedimentation is not itself a distinct process. It is better conceptualized as the consequence of two more fundamental processes: deposition and erosion. Both deposition and erosion are strongly influenced by fluid shear forces. Even with detailed descriptions of particle characteristics in the water column and sediments, it is still necessary to have some description of system hydrodynamics. The useful but simple chloride calibration describes only the bulk movements of water. No real insight into water velocities and corresponding fluid shear stresses is gained. Wind generated waves are a further complication. As a result of currents and wind waves, near shore areas can behave in a dramatically different manner than deeper, presumably more quiescent regions of the lake.

It may therefore be necessary to reconsider whether the present model, for all its detail and complexity in some aspects, provides an appropriate representation of the Lake Champlain system. Given the complex hydrodynamics expected within the lake, it may be necessary to construct a 2-dimensional (or perhaps even 3-dimensional) hydrodynamic model to describe the fine-scale movements of water, fluid shear, and the shear stress exerted at the sediment-water interface. Deposition and erosion fluxes could then be directly estimated/calibrated and net sedimentation fluxes computed by difference. Any net sedimentation observations could then be used as an independent means to confirm model performance by comparison to computed sedimentation. While this approach is labor intensive (and you also need to consider whether adequate information exists to develop a hydrodynamic model), it is "doable". (To my understanding, this would also make the Lake Champlain model more closely resemble the Chesapeake Bay model...)

5. Sediment initial conditions remain an significant unknown (Section 2.3.6). Although an attempt is made to make the best of an undesirable situation, a more detailed and complete discussion of the importance of initial conditions is necessary. The present approach to assign initial conditions is, at a minimum, recursive and potentially circular. Initial conditions are computed in a manner that depends on model parameterization. Subsequent parameterization efforts depend on the initial conditions that are computed from initial parameter values.

The real and serious limitation here is that the "loop" on the mass balance/budget is not closed. Subsequent model "failures" at the calibration stage may be more a reflection of the inability to construct global phosphorus and solids budgets rather than "poor" calibration. This may be the weakest aspect of the study.

# Section 3 - Model Calibration

1. The flow-concentration relationships presented in Section 3.2.2 are potentially problematic and may be inappropriate. Consider the relationships presented in Figure 3-2. Even in log-log space, there is little basis (in my opinion) for dividing the data into low flow and high flow strata. Given the large standard deviations, there is no strong apparent "break points" in the relationships for each parameter. Whether stratified or not, are the regression results meaningful? How much variability (expressed as r² values) is described by the regressions? Are these relationships statistically significant (expressed as p values)?

From my perspective as an outside reader, Section 3.2.2 raised a red flag. The model chassis (eutrophication kinetics) may be state-of-the-science but the engine (external forcing functions and initial conditions) is potentially little more than screening-level. (Have we put the Pinto engine into the Ferrari body? If so, do we expect performance more like the Pinto or the Ferrari?)

- 2. The chlorophyll and organic carbon calibrations appear weak. As noted in Section 3.5.7, this may contribute to DO calibration weakness. From my perspective, this makes me wonder if these calibration weaknesses are the symptoms of inadequate knowledge regarding external material inputs and initial conditions...
- 3. The uncertainty in critical model forcing functions (and initial conditions) and process parameters is unexplored. Given the screening-level nature of information to define forcing functions and initial conditions, uncertainty in computed loads, etc. may be very large. These uncertainties may be so large that the 95% confidence intervals of the present model predictions (assuming zero additional parameter uncertainty is introduced during calibrations) may bracket the full range of observations. If so, then all subsequent discussion of model calibration weakness may be misdirected.

Errors cannot be attributed to model calibration until the uncertainty in forcing functions and initial conditions is quantified. Further, errors cannot be attributed to second-tier processes (such as nitrification) until uncertainty in the model calibration itself is quantified.

(Although is looks like a Ferrari, it seems to drive like a Pinto...)

4. Section 3.9 should be expanded and reorganized to become separate "Conclusions and Recommendations" section.

# Recommended Revisions to Report Structure

To make this report a bit more "user friendly", I recommend revisions to report structure. Consider the following outline structure:

Executive Summary

- 1. Introduction
  - 1.1 Physical Description of the Lake
  - 1.2 History of Nutrient Management

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- 1.3 Study Purpose
- 1.4 Scope of Model Development and Application
- 2. Model Theory
  - 2.1 Introduction
  - 2.2 Eutrophication Kinetics Submodel
  - 2.3 Sediment Submodel
- 3. Numerical Representation of the Physical System
  - 2.1 Model Segmentation
  - 2.2 Estimation of External Pollutant Loads (P, TSS, etc.)
  - 2.3 Estimation of Internal Pollutant Reservoirs (Initial Conditions)
  - 3.3 Exogenous Inputs (Temperature, Solar Radiation, etc.)
  - 3.4 Other Boundary Conditions
- .4. Model Calibration/Parameterization
  - 4.1 Overview of the Model Calibration Process (how is the model calibrated)
  - 4.2 Model Calibration Quality Criteria (how you know the calibration is acceptable)
  - 4.3 Calibration Data
  - 4.4 Calibration Results (Chloride, Temperature, P, Chl-a, OC, DO)
  - 4.5 Parameter Sensitivity Analysis
- 5. Interpretation and Discussion of Model Results
  - 5.1 Phosphorous Budget (including time to equilibrium)
  - 5.2 Other Pollutant Budgets
  - 5.3 Uncertainty in Model Results
  - 5.4 Discussion
- 6. Conclusions and Recommendations
  - 6.1 Conclusions
  - 6.2 Recommendations

Thank you for the opportunity to finish my review of the HydroQual Benthic P modeling reports. As a caveat, while I have done a fair amount of modeling in the past, I would not be considered a modeling expert on par with the authors of this study. That said, I will proceed.

# Benthic P Cycling in Champlain (2/6/98 draft)

#### General comments:

The report is thorough and well written. It is a shame, overall, that the model does not work well at low dissolved oxygen and high P concentrations, and that the model underestimates sediment phosphorus. These are the conditions we should be most interested in as far as P contribution to the lake. I question whether the model is modeling benthic P cycling or just making up for the acknowledged deficiencies through the use of calibration coefficients.

I agree with the authors that this study produced a good deal of useful information on Lake Champlain sediments.

# Specific comments:

It is not clear on page 3-3 whether sediment measurements were taken in-situ or from cores taken back to the laboratory in Maryland. Measuring oxygen demand and pore water composition are best measured in the field, although perhaps this was not possible at deep stations. Measuring sediment nutrient flux is never easy and the core method is used fairly frequently. (This method question answered in Cornwell & Owens).

#### Benthic P Cycling in Champlain (Cornwell & Owens)

Not sure if this was provided to review or as background material (can't seem to find your cover letter), but I reviewed it anyway since these methodologic studies are of particular interest to me. It would be interesting to know how much sediment surface disturbance occurred during collection with box core and resampling with core tubes.

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