Lake Champlain Basin Program

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Development of a Phosphorus Mass Balance Model for Missisquoi Bay

March 30, 2012

Prepared for:
Lake Champlain Basin Program

Under Contract to:
New England Interstate Water Pollution Control Commission
NEI Job Code: 989-003-006
Project Code: L-2010-034

Prepared at:
Ann Arbor

by Limnotech

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1. EXECUTIVE SUMMARY

Missisquoi Bay has a long history of excessive nutrient loading and eutrophication. Efforts to deal with these issues began in the 1970s with phosphorus detergent bans and states requiring enhanced phosphorus removal from point source dischargers within the watershed. Over the last several years Missisquoi Bay has suffered from an increased recurrence of nuisance cyanobacteria blooms that have produced toxins and severely limited use of the bay for drinking water supply and recreation.

While it is clear that the external load of phosphorus to Missisquoi Bay is high, the relative contribution of external and internal loads of available phosphorus to creating and sustaining late summer cyanobacteria blooms is not clear. The primary objective of this project is to develop a fine-scale, time-variable linked hydrodynamic–water quality model that captures the major cycling pathways of phosphorus in Missisquoi Bay as they relate to future management of the system and its watershed. The Missisquoi Bay Phosphorus Model, termed MBPHOS, uses available atmospheric, hydrologic, and nutrient monitoring data to simulate the transport of phosphorus from the major tributaries, deposition and release from the sediment bed, and export through the bay, and out into the Northeast Arm of Lake Champlain.

Development of the model consisted of several major components including the selection of an appropriate model framework, site-specific configuration to Missisquoi Bay, development of boundary conditions and other external forcings, and then modification of model coefficients to achieve an acceptable fit with monitoring data. The details of model development are discussed in Section 3. Monitoring data from 2006 to 2010 were used during the model calibration process. After calibration the MBPOS model was evaluated against monitoring data collected from 2001 to 2005. This period served to independently verify model calibration and confirm the models ability to accurately simulate water quality conditions in Missisquoi Bay. To support the calibration of the sediment digenesis model a field effort was designed to measure P release rates under anoxic and oxic conditions.

A model grid was designed to cover all of Missisquoi Bay with enough detail to simulate the impacts of the major tributaries on the nearshore portions of the Bay. In addition, the model grid was developed to accurately represent key bathymetric features in the system while minimizing the time required for running multi-year model simulations. An open model boundary is located at the southern edge of the model grid at the Highway 78 bridge causeway. The total number of grid cells used in the model grid is 1,486.

The data sources utilized in this project originated from a range of sources including samples collected by the Miner Institute as part of this project, routine tributary and lake monitoring data from the VT DEC, daily water level, tributary flow, and load estimates from the USGS, daily tributary flow estimates from the Quebec Ministry of Environment, and atmospheric data from NOAA sponsored weather stations. Data were either downloaded from the internet where available or obtained directly from a contact at each agency.

The atmospheric and tributary datasets were used to generate model boundary conditions while the datasets collected in 2010 by the Miner Institute in the bay and from the long-term data collected by VT DEC in the bay were used in the calibration and confirmation of the model (Section 5 and 6). Tributary loads of total phosphorus, dissolved phosphorus, and total

suspended solids were obtained from the USGS for the Missisquoi and Pike Rivers. Rock River TP, DTP, and TSS concentrations were estimated from concentrations/flow regressions using monitoring data from 2006 to 2010 and daily average flow data.

The model calibration approach was to focus first on the hydrodynamic model and then on the water quality model. The water quality calibration focused primarily on model-observation comparisons of total phosphorus data over several spatial and temporal scales. Model to data comparisons are made for 2010, which includes high temporal and spatial comparisons, and 2006 to 2010, which is the calibration period, and 2001 to 2005, which is the confirmation time period. The June through September summer average TP concentration for both of the long term VT DEC stations and the model predicted bay-wide surface average concentrations is shown below in Figure 1-1. The 10-year summer average surface TP concentration at the VT DEC station is 48.7 ug/L, which is within 2% of the 10-year average model predicted concentration of 49.5 ug/L. The year to year variation in the median relative error is very reasonable at 7%, and even the average relative error is 12%. These statistics demonstrate that the model is well calibrated to the season average TP concentration.

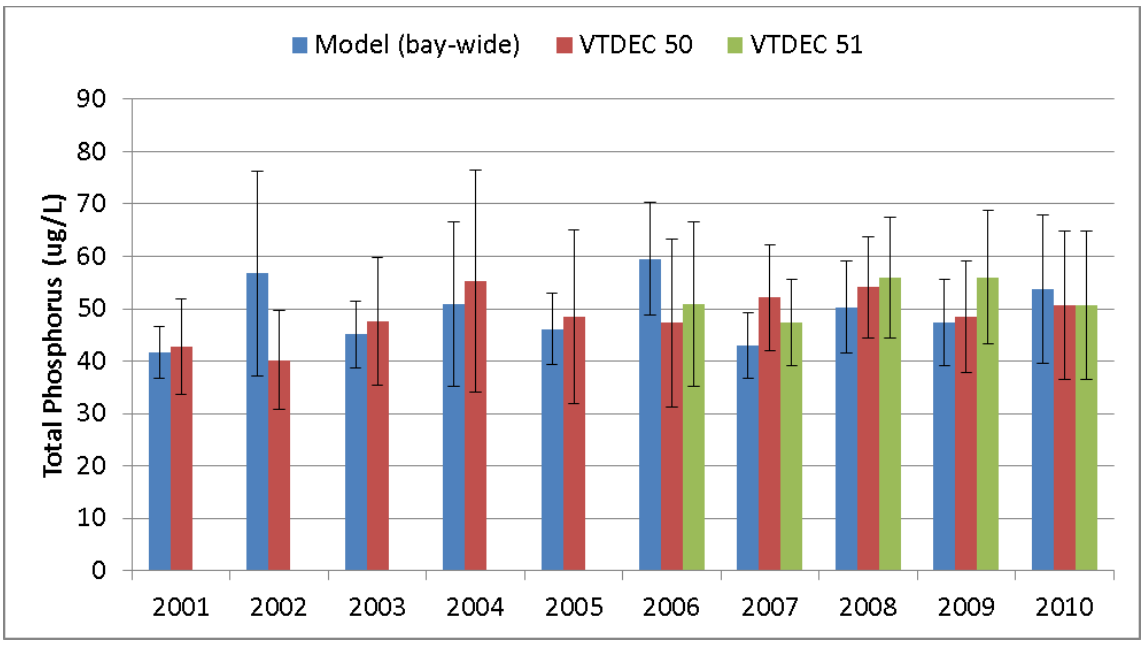

Figure 1-1. Comparison of measured and model predicted summer average TP concentrations.

One of the powerful features of the water quality model is the ability to develop a mass balance model of the major pathways of phosphorus movement within the bay. Figure 1-2 shows the average phosphorus mass balance from 2001 to 2010 on an annual and summer basis. Over the ten year period sediment flux averages 20% and 43% of the total P inputs during the whole year and summer period, respectively.

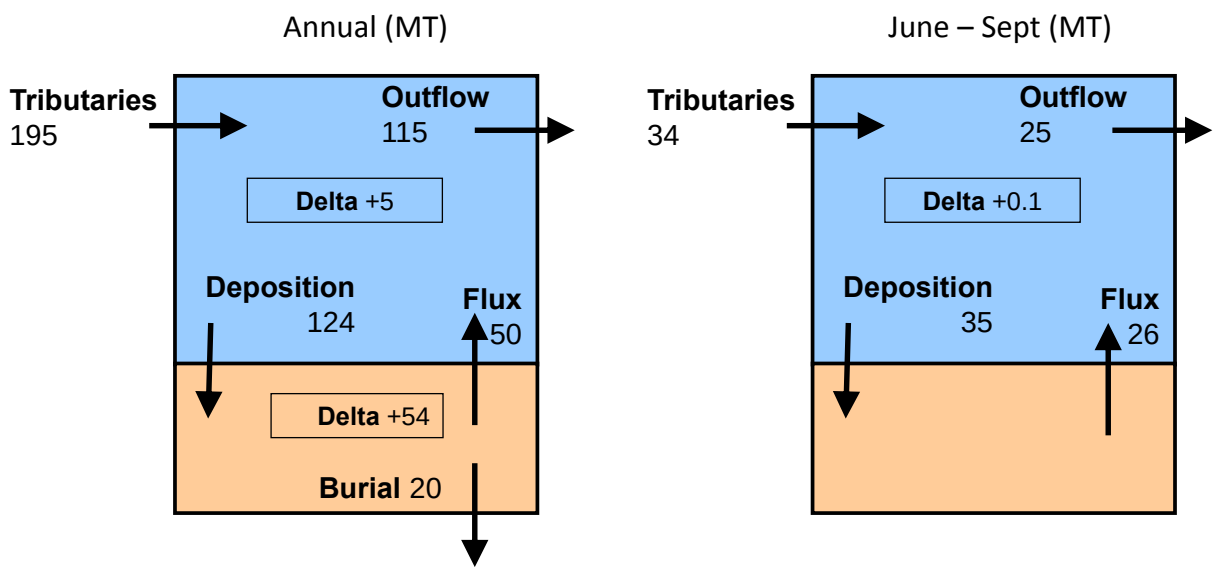

Figure 1-2. Average total phosphorus (metric tons) mass balance for 2001 to 2010.

A diagnostic simulation done with the calibrated model shows that the bay-wide average water column TP concentration from June to September decreases from 54 ug/L to 31 ug/L (a 43% decrease) when fluxes of TP from the sediment are eliminated. The calibrated model was also run in a forecasting scenario mode to project the summer average TP concentration under a range of tributary TP load reductions. For each run, total phosphorus concentrations were reduced for all of the tributaries in equal proportions for every day of the year. Inorganic solids concentrations were not reduced for any of the scenarios. A plot of the June to September average water column TP concentration for the first ten years of the load reduction scenarios is shown in Figure 1-3 for each of the load reduction scenarios.

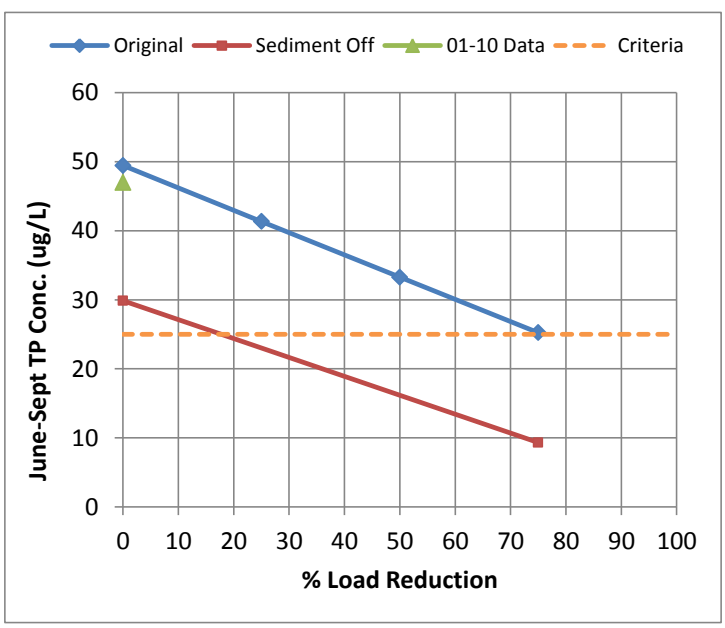

Figure 1-3. Average summer TP concentration for first 10 years of load reduction scenario run with and without sediment feedback.

A closer look into the mass balance information obtained from the water quality model shows that the diffusive flux of phosphorus from the sediments averages approximately 31 MT/yr across the whole bay from 2001 to 2010. Resuspension of bottom sediments in the shallower parts of the bay contributes an additional 19 MT/yr. Resuspension rates are highest in the spring and late summer and fall when wind speeds are higher. The combined impact is the delivery of an additional 50 MT/yr of phosphorus to the water column per year. The timing of each of these sediment flux components is different as the diffusive fluxes are highest in the summer and the resuspension fluxes are higher in the fall. The average June to September diffusive flux is approximately 18 MT, while the resuspension flux is 8 MT for a total of 26 MT.

The results of the model application provided useful insights into the phosphorus cycle in Missisquoi Bay. The mass balance results showed that the flux of phosphorus from the sediments to the water column is and will continue to be an important component of the P load to Missisquoi Bay and shouldn't be ignored in the selection of load reduction alternatives.

2. INTRODUCTION

This report describes the development, calibration/confirmation, and application of a linked-hydrodynamic-water quality model for Missisquoi Bay, Lake Champlain. The model, called MBPHOS, was developed as a tool to quantify the external and internal loads of phosphorus (P) to the bay. A mass balance understanding of phosphorus within Missisquoi Bay will help resource managers make informed management decisions.

2.1 PROJECT LOCATION

Missisquoi Bay is a protected embayment situated on the north end of Lake Champlain (Figure 2-1). The majority of Missisquoi Bay resides on the Canadian side of the border with the United States. However, the largest tributary, the Missisquoi River, enters the bay on the U.S. side. The old Highway 78 bridge causeway defines the southern edge of the bay, which limits hydraulic exchange between the bay and the Northeast Arm of Lake Champlain to a narrow gap only several hundred feet across. Burlington, VT is located approximately 35 miles south and Montreal, QC is located 35 miles to the northwest. Characteristics of the bay and watershed were summarized in Levine et. al. (2011) and are reproduced below in Table 2-1.

Table 2-1. Characteristics of Missisquoi Bay and watershed (Levine et al, 2011).

Water Body		Watershed	
Surface Area (km^2)	77.5	Area (km^2)	3105
Mean Depth (m)	2.8	% Forest	62
Max Depth (m)	4	% Agriculture	25
Volume (km^3)	0.22	% urban	5

The major tributaries of Missisquoi Bay include the Missisquoi, Pike, and Rock Rivers. A map of the major watersheds surrounding Missisquoi Bay is shown in Figure 2-2. A summary of the land use and watershed areas for each major tributary are shown below in Table 2-2.

Table 2-2. Land use characteristics of Missisquoi Bay watershed (Hegman et al., 1999)

Watershed	Area (km^2)	Area	Forest	Agriculture	Urban	Other
Missisquoi	2,240	72%	70%	17%	5%	9%
Pike	667	21%	43%	45%	5%	7%
Rock	147	5%	40%	26%	5%	29%
Direct	51	2%	21%	56%	13%	10%
Total	**3,105**	100%	**62%**	**24%**	**5%**	**9%**

2.2 BACKGROUND

Missisquoi Bay has a long history of excessive nutrient loading and eutrophication. Efforts to deal with these issues began in the 1970s with phosphorus detergent bans and states requiring enhanced phosphorus removal from point source dischargers within the watershed. Over the last several years Missisquoi Bay has suffered from an increased recurrence of nuisance cyanobacteria blooms that have produced toxins and severely limited use of the bay for drinking water supply and recreation (LCRC Workshop, April 9, 2005). While phosphorus (P) concentrations in the bay have been historically high, the quantitative relationship between water quality and the recent appearance of harmful algal blooms is yet to be established.

In 1991, the State of Vermont adopted numeric total phosphorus criteria of 0.025 mg/L (VT DEC and NYDEC, 2002). Since the 1991 standards were adopted, P concentrations in Missisquoi Bay have consistently been in violation of the criteria (Smeltzer et al., 2009). Monitoring data from the Vermont Department of Environmental Conservation (VT DEC) show that P concentrations in the last five years (2006 to 2010) are at the highest levels since routine compliance monitoring began in 1990, with annual average concentrations above 0.050 mg/L. A Total Maximum Daily Load (TMDL) analysis has been developed for phosphorus in Lake Champlain that assigned a target P load to Missisquoi Bay of 97.2 metric tons per year (MT/yr), which represents a decrease in present day loads of 35% to 75% (VT DEC and NY DEC, 2002).

The increased recurrence in cyanobacteria blooms and phosphorus concentrations in recent years is not isolated to Lake Champlain/Missisquoi Bay. Researchers in Saginaw Bay, Lake Huron (Bierman et al., 2005); Maumee Bay, Lake Erie (Bridgeman and Penamon, 2010); Lake Ontario (Makarewicz et al., 2009); and Green Bay, Lake Michigan (Qualls et al., 2007) have documented a recent increase in cyanobacteria blooms and P concentrations, often associated with colonization of Dreissenids (zebra and quagga mussels). A nutrient model of the Saginaw Bay ecosystem coauthored by the primary investigator for this project (Bierman et al., 2005) showed that zebra mussels have the capability to filter massive amounts of particulate phosphorus from the water column during spring blooms and mediate the release of excess phosphorus in forms that are readily available for uptake by *Microcystis* during the late summer. The combination of the warm waters in late summer, the additional phosphorus recycling at that time of the year, and a documented selective rejection of cyanobacteria by filter-feeding Dreissenids (Vanderploeg et al., 2009) has been hypothesized as the cause of the recurrence of *Microcystis* blooms in Saginaw Bay. Recent research in Lake Champlain suggests that zebra mussels could be increasing the amount of available phosphorus (Miller and Watzin, 2007). Data from VT DEC also suggest that mussel veliger densities have increased by several orders of magnitude in recent years in Missisquoi Bay (LCBP, 2010).

A recent study of sediment phosphorus cycling by Smith (2008) in Missisquoi Bay concluded that a significant portion (30-40%) of sediment phosphorus is closely associated with iron hydroxides, which are susceptible to reduction in anoxic conditions. The reduction of iron releases sorbed phosphorus into the sediment porewater, creating a significant gradient across the sediment-water interface and resulting in enhanced diffusion of phosphorus into the water column. The author goes on to state that the loss of reactive phosphorus from the sediment could have contributed to an estimated water column P increase on the order of thousands of μg/L, which could have sustained the algal bloom for an extended period of time. While Smith did not document dissolved oxygen concentrations, profile data from VT DEC do show evidence of low dissolved oxygen in water near the sediments during the cyanobacteria bloom in August of 2008. Smith concludes that is not possible to distinguish if the sediment release caused the cyanobacteria bloom or if the release of P (and low DO) was a result of the large influx of organic material produced by the bloom, thus producing a positive feedback process. This latter process was observed in the tidal-fresh portion of the Potomac River during late summer algal blooms (LimnoTech, 1983).

2.2.1 Previous Modeling Studies

Modeling efforts to date on Missisquoi Bay have concluded that phosphorus cycling within the bay is dominated by different mechanisms than those within the main body of Lake Champlain. Contribution of phosphorus from the sediments to the water column likely play a much larger

role in phosphorus cycling in the bay versus the open lake due to the bay's low average depth and large watershed are to water surface area ratio. As part of the Lake Champlain Diagnostic-Feasibility Study in 1997 (VT DEC and NYSDEC, 1997), the authors concluded that, "additional research on the internal phosphorus dynamics of the bay would be particularly desirable in order to confirm and enhance the model's predictive capabilities for this lake segment." The BATHTUB model used in this study treated Missisquoi Bay as a completely mixed reactor with only one vertical layer and no internal load of phosphorus. A fine-scale hydrodynamic and simplified phosphorus model of Missisquoi Bay concluded that sediments must be acting as a source for phosphorus because tributary total phosphorus (TP) loads were not large enough to explain TP concentrations measured in the lake (Menhelsohn et al., 1997). A third model of Lake Champlain that also treated Missisquoi Bay as a completely mixed system concluded that "the model has difficulty reproducing the observed water column phosphorus concentration in areas of the lake where low dissolved oxygen is also observed" (Cornwell and Owens, 1999). Data collected as part of this study in Missisquoi Bay concluded that over half of the phosphorus that reaches the sediment is recycled back into the water column, whereas in other parts of Lake Champlain this percentage was only 11%.

The Levine et al 2001 paper also estimated sedimentation accumulation rates (SAR) from a sediment core collected in the center of Missisquoi Bay. The authors suggest that SAR remained fairly steady between the early 19th and throughout the 20th century; however, there was a steep increase in SAR in the 1990s when SAR increased from 0.6 kg/m^2/yr to over 1.4 kg/m^2/y. Table 2-3 below summarizes these results. Assuming an average sediment bulk density of 0.8 kg/L, this would convert to between 0.75 mm/yr and 1.75 mm/yr. A corresponding increase in sediment TP concentrations was also observed during this time period. Sediment TP increased from approximately 1.0 mg/g dry weight to over 1.5 mg/g dry weight. Sediment concentrations of total nitrogen and organic carbon also increased nearly two fold during the same time period. The authors attribute the increase in sediment nutrient concentrations to increased agricultural activity. The SAR and TP concentration were combined to estimate a TP mass deposition rate flux and rate for each period. The results of this calculation are shown in Table 2-4.

Table 2-3. Historical sediment deposition characteristics (Levine et al, 2011).

	Year	Sediment Rate	Sediment Mass	Deposition Rate
Era	**Range**	**kg/m^2/yr**	**MT/yr**	**mm/yr**
Pre Settlement	1600-1750	0.17	13,175	0.21
Max Deforestation	1850-1900	0.68	52,700	0.85
Pre-Modern	1940-1960	0.85	65,875	1.06
Modern	1990-2007	1.44	111,600	1.80

Table 2-4. Historical phosphorus deposition characteristics (Levine et al, 2011).

	Year	Sediment P Concentration	P Mass Deposition Flux	P Mass Deposition Rate
Era	**Range**	**mg/g dwt**	**g/m2/yr**	**MT/yr**
Pre Settlement	1600-1750	1.04	-	-
Max Deforestation	1850-1900	1	0.67	52
Pre-Modern	1940-1960	1.29	1.09	85
Modern	1990-2007	1.69	2.46	191

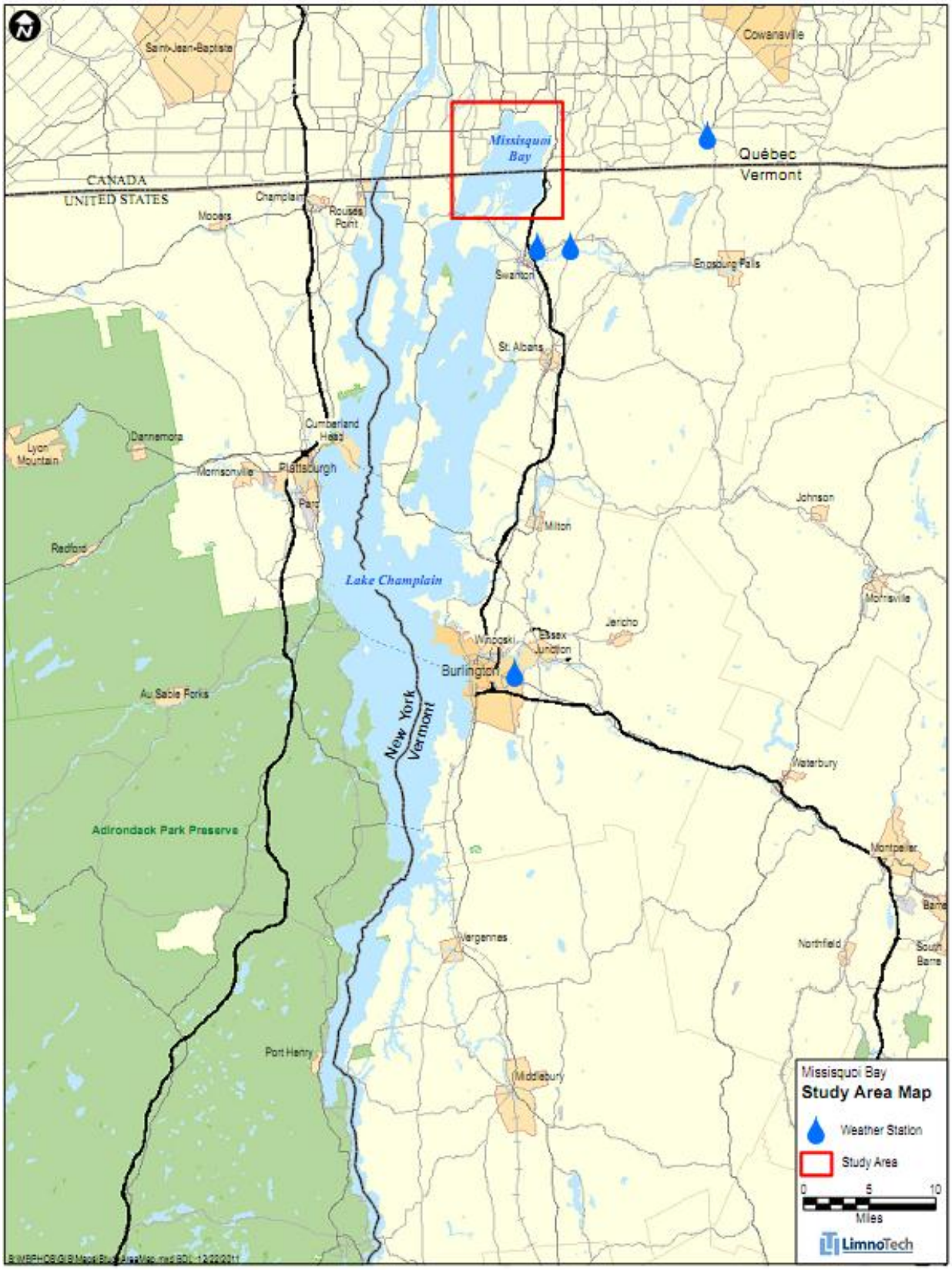

Figure 2-1. Study location map of Lake Champlain and Missisquoi Bay.

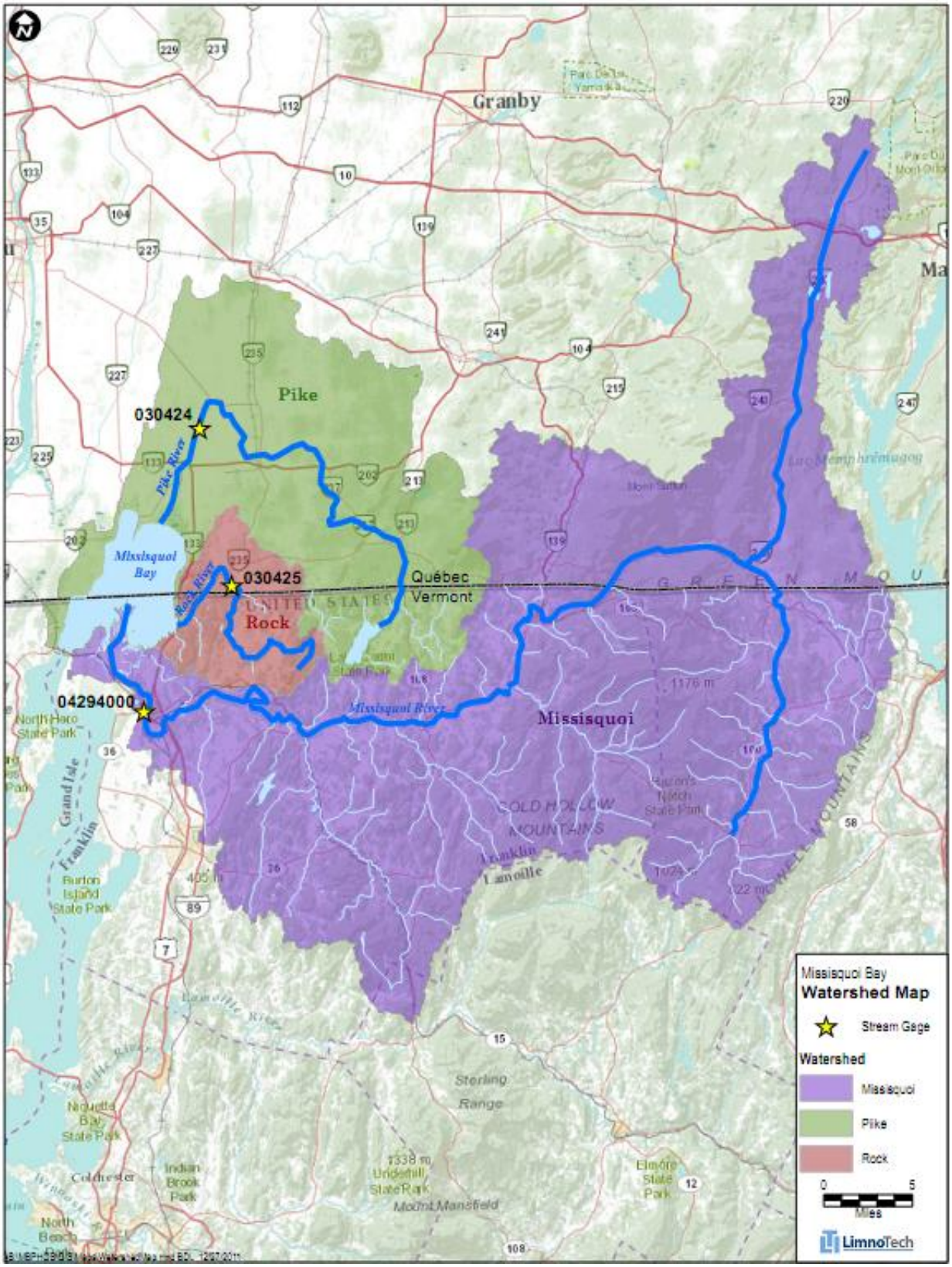

Figure 2-2. Map of Missisquoi Bay watersheds and stream gages.

2.3 PROBLEM SPECIFICATION

While it is clear that the external load of phosphorus to Missisquoi Bay is high, the relative contribution of external and internal loads of available phosphorus to creating and sustaining late summer cyanobacteria blooms is not clear. Previous experience with phosphorus-eutrophication problems, along with other well-documented studies in the literature (e.g., Shagawa Lake, Minnesota (Larson and Mercier, 1976; Larson et al., 1975; Chapra, 1997), Lake Pepin in the upper Mississippi River (James, 2007; LimnoTech, 2009), and Lake Okeechobee (LimnoTech, 1999), has indicated that the relative importance of internal loading from sediments is inversely related to the overflow rate (mean depth/hydraulic retention time) of a system. In other words, longer hydraulic retention times in shallow lakes make them especially vulnerable to sediment-water interactions (i.e., internal phosphorus load) in determining the response to a reduction of external loads. The Lake Champlain Diagnostic-Feasibility Study (VT DEC and NYDEC, 1997) estimated annual average hydraulic retention times of 80 to 100 days for Missisquoi Bay based on an analysis of chloride concentrations in 1991 and 1992. However, during the summer low-flow period, the retention time can be on the order 200 days. Therefore, with a mean depth of 2.5 meters during the summer period, Missisquoi Bay has an overflow rate of approximately 4.5 m/yr. This overflow rate is quite low, and it suggests the importance of understanding the role of internal sediment feedback as it relates to the recovery of Missisquoi Bay.

2.4 STUDY GOALS AND OBJECTIVES

The primary objective of this project is to develop a fine-scale, time-variable linked hydrodynamic–water quality model that captures the major cycling pathways of phosphorus in Missisquoi Bay as they relate to future management of the system and its watershed. In the application phase of the project the model will quantify the impact of bottom sediments on the phosphorus mass balance of the bay to predict the expected recovery time of the lake sediments in response to external load reductions that could potentially be implemented in the watershed. A final objective is to provide recommendations for future refinements of the model, including the development of a full eutrophication/ecosystem model, and to identify datasets that are needed to support such a model.

2.5 APPROACH

To address the primary objective of this project, a linked, three-dimensional hydrodynamic-phosphorus mass balance model was applied to Missisquoi Bay. The Missisquoi Bay Phosphorus Model, termed MBPHOS, uses available atmospheric, hydrologic, and nutrient monitoring data to simulate the transport of phosphorus from the major tributaries, deposition and release from the sediment bed, and export through the bay, and out into the Northeast Arm of Lake Champlain.

Not only will this modeling framework address the objectives stated above, it is easily expanded into a full eutrophication model with the capability to simulate phytoplankton, benthic algae, zooplankton, and benthic filter feeders (zebra and quagga mussels). This modeling framework also overcomes the limitations of previous models of Missisquoi Bay because it can dynamically simulate the deposition and subsequent release of phosphorus back to the water column.

2.5.1 Model Approach

Separate, but linked hydrodynamic and water quality models were chosen to simulate the fate and transport of phosphorus from the major tributaries, through Missisquoi Bay, and out into the Northeast Arm of Lake Champlain.

The hydrodynamic model used in this study is based on a LimnoTech-modified version of the EPA-supported *Environmental Fluid Dynamics Code* (EFDC) model. EFDC simulates tributary inflows, water circulation within the bay, outflows at the causeway, and it also contains a thermal sub model to simulate temperature distribution within the bay. The water quality model is based on a LimnoTech-modified version of the *Row-Column AESOP* (RCA) model, a public-domain model developed originally by HydroQual, Inc. (HydroQual, 2004). In addition, LimnoTech has created a custom graphical user interface for these models that provides pre- and post-processing capabilities and can be used to visualize model output and observational data in a variety of ways.

Both the hydrodynamic and phosphorus mass balance models that make up the proposed modeling framework were adapted from public domain models by LimnoTech in previous projects. The combined modified versions of the models, termed the Advanced Aquatic Ecosystem Model (A2EM) have been applied in Lake Pepin (Mississippi River), Saginaw Bay (Lake Huron), and Maumee Bay (Lake Erie) (LimnoTech, 2009; Bierman et al., 2005; DePinto et al., 2009a; DePinto et al., 2009b; Verhamme et al., 2009). Hence, the model framework developed for this project would be available for use by the Lake Champlain Basin Program for future development and use on the Missisquoi Bay system.

As stated in the project goals and objectives the primary purpose of this project is to develop a mass balance model of internal and external loads of phosphorus to Missisquoi Bay. To meet this objective the model must be able to simulate the release of phosphorus from the sediment back into the water column. The magnitude of this flux could be estimated by subtracting the TP load required to match monitoring data from the tributary load included in the MBPHOS model. However, in order to understand the long term change in this flux over time due to changes in tributary loads a more complex mechanistic model is required that can dynamically respond to changes in external TP loads. To meet this requirement, the sediment diagenesis sub model contained within RCA was used. The diagenesis model simulates the mineralization of organic phosphorus to inorganic phosphorus and provides mechanisms to release dissolved and particulate phosphorus back into the water column based on diffusion rates and resuspension rates, respectively.

2.5.2 Model Development and Evaluation

The development and evaluation of the MBPHOS model followed the steps that are outlined in the "Draft Guidance on the Development, Evaluation, and Application of Regulatory Environmental Models", which was prepared by The Council for Regulatory Environmental Modeling (CREM, 2003). Although the model developed for this project is not being directly used in a regulatory setting, the results from the model will be used to inform management decisions and to inform an update to the phosphorus TMDL for Lake Champlain. As such, the selection of an appropriate model framework and evaluation criteria followed the Draft Guidance.

Development of the model consisted of several major components including the selection of an appropriate model framework, site-specific configuration to Missisquoi Bay, development of

boundary conditions and other external forcings, and then modification of model coefficients to achieve an acceptable fit with monitoring data. The details of model development are discussed in Section 3. Monitoring data from 2006 to 2010 were used during the model calibration process. After calibration the MBPOS model was evaluated against monitoring data collected from 2001 to 2005. This period served to independently verify model calibration and confirm the models ability to accurately simulate water quality conditions in Missisquoi Bay.

A data gap identified during the proposal phase of this project was a lack of sediment release data for Missisquoi Bay sediments. Previous studies only characterized the potential for P release (Smith, 2010) and historical sediment P concentrations (Levine et al, 2011). To support the calibration of the sediment digenesis model a field effort was designed to measure P release rates under anoxic and oxic conditions. Additional water quality and surficial sediment data were also collected during sediment core retrievals. More detail on the 2010 data collection effort is provided in the next section and Appendix B on the 2010 data collection effort.

2.5.3 Data Approach

To support the calibration and parameterization of the Missisquoi Bay phosphorus model a combined process experimental and field monitoring program was conducted in 2010. First, intact sediment cores were collected from throughout the bay and incubated under both oxic and anoxic conditions to estimate the flux rate of dissolved phosphorus from the sediments to the water column. Second, water column grab samples and vertical profiles were collected at the same stations as the sediment cores on several occasions in 2010 to capture the spatial distribution of water quality. The water column samples were collected late in the summer and early fall to characterize water quality conditions. Historical sampling indicates shows that this period has the highest TP and chlorophyll concentrations. Field data collection efforts were coordinated with the Vermont DEC and the LCBP to avoid duplication of efforts and to maximize the spatial and temporal coverage of water quality sample collection.

3. MODEL DEVELOPMENT

This section discusses the major components of the model framework and how it was configured to specifically address the objectives of the project.

3.1 MODEL OVERVIEW

The fine-scale, linked hydrodynamic – water quality model framework developed for Missisquoi Bay utilizes the following model components:

- *Environmental Fluid Dynamics Code* (EFDC) for the hydrodynamic, and temperature sub-models; and
- A LimnoTech-modified version of the *Row-Column AESOP* (RCA) model code for the water quality / eutrophication sub-model.

Together the linked models form the basis of the Advanced Aquatic Ecosystem Model (A2EM). The linked models are designed to simulate the transport of nutrients from the tributaries, through Missisquoi Bay, and out to the northeast arm of Lake Champlain. This section describes the key features of the hydrodynamic and water quality model components.

3.1.1 Hydrodynamic Model

EFDC is a state-of-the-art finite difference model that can be used to simulate hydrodynamic, sediment transport, and water quality behavior in one, two, or three dimensions in riverine, lacustrine, and estuarine environments (TetraTech, 2007a). EFDC was developed by John Hamrick at the Virginia Institute of Marine Science in the 1980s and 1990s, and the model is currently maintained under support from the USEPA. The model has been applied to hundreds of water bodies, including Chesapeake Bay and the Housatonic River. Recently, LimnoTech has successfully applied EFDC to a number of sites in the Great Lakes, including Maumee Bay, Maumee River, Saginaw Bay, Saginaw River, and the Tittabawassee River. The EFDC model is both public domain and open source, meaning that the model can be used free of charge, and the original source code can be modified to tailor the model to the specific needs of a particular application. As a result, EFDC provides a powerful and highly flexible framework for simulating hydrodynamic behavior for the Missisquoi Bay system.

3.1.2 Water Quality Model

The RCA model is part of a family of generalized water quality models developed by HydroQual, Inc. and known as "Advanced Ecological Systems Modeling Program" (AESOP) (HydroQual, 2004). LimnoTech has modified the original RCA model to represent water quality components of specific interest in large water bodies, including sub-models that simulate bioenergetics for *Dreissenid* mussels and *Cladophora*. The modified RCA model framework (A2EM), is capable of simulating water quality dynamics on a fine-scale, multi-dimensional computational grid based on a linkage to an external hydrodynamic model application. At present, 35 water quality state variables are available for simulation within the framework, including organic and inorganic nutrients (carbon, nitrogen, and phosphorus, and silica), dissolved oxygen, and multiple pelagic algal classes (including blue-greens) and zooplankton classes, and the benthic alga *Cladophora*. In addition, the model is capable of simulating the impact of benthic filter feeders, such as *Dreissenid* (zebra and quagga) mussels on nutrient cycling and their impact on water clarity and primary productivity in the water column. Similar

to EFDC, RCA is an open source, public domain model that provides a flexible environment for simulating and evaluating system water quality responses. The original RCA code was designed to interface directly with the ECOMSED hydrodynamic model. However, the enhanced version developed by LimnoTech for application to Saginaw Bay includes a linkage to EFDC hydrodynamic, temperature, and sediment transport outputs.

For this project the primary nutrient of concern is phosphorus. Figure 3-1 below shows a simplified version of the phosphorus (P) cycle utilized by A2EM for this project. The simplified cycle includes available, total unavailable, and algal-bound phosphorus pools. Within the active sediment layer forms of available and unavailable phosphorus are tracked separately. Not shown on this figure is the outflow of phosphorus from the system.

While watershed loads are usually composed primarily of unavailable P (particulate and dissolved), understanding the internal processing that converts the unavailable P to available P (dissolved orthophosphate) is critical to quantifying both long- and short-term phosphorus cycling and the potential growth of nuisance algae. The linked model framework will be able to simulate P movement in and out of the bay, kinetic transformations, settling, resuspension and diffusion, and subsequent burial of phosphorus throughout every grid cell in the model domain. Environmental forcing functions will also be included to support dynamic simulation of temperature, dissolved oxygen, and other water quality variables.

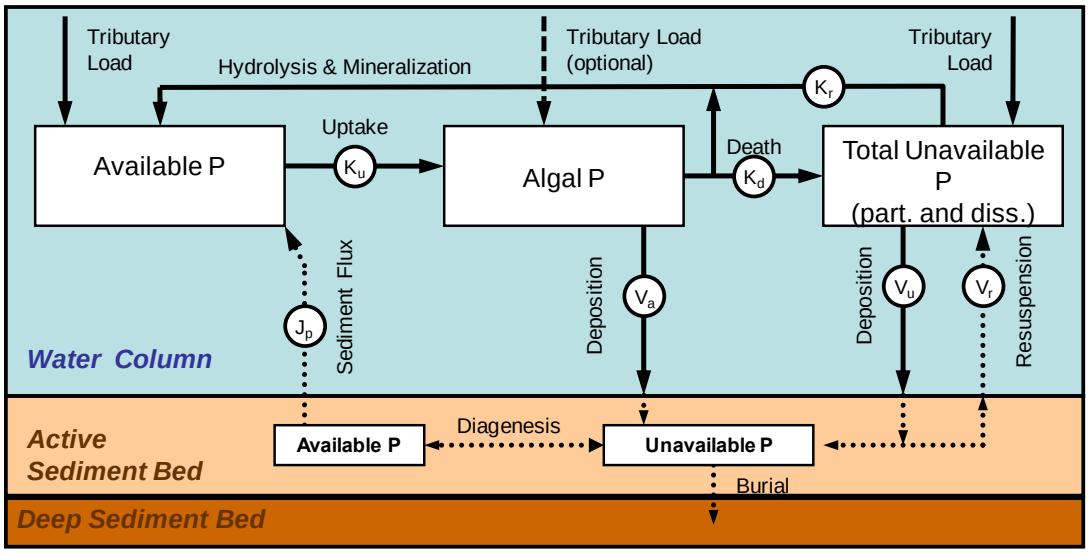

Figure 3-1. Schematic of the phosphorus cycle for the Missisquoi Bay water quality model.

While the other nutrient cycles (nitrogen, silica, and carbon) are still active in the model framework, they are not shown here. Reasonable concentrations of each of these other nutrients were input to the model to ensure that none of these other nutrients would be limiting algal uptake of dissolved orthophosphate. More information will be provided on carbon inputs as carbon decomposition is an important component in the simulation of dissolved oxygen. Additional detail on these nutrient cycles can be found in the RCA manual (HydroQual, 2004). A more thorough description of the sediment diagenesis model can be found in DiToro (2000).

3.2 SEGMENTATION AND BATHYMETRY

A cumulative histogram of the Missisquoi Bay depth profile based on surface area is shown below in Figure 3-2. The bay is relatively bowl shaped with close to 30% of the bay having a depth close to 12 ft. The shallowest portion of the bay is the southeast corner, which has an average depth of approximately 5 ft.

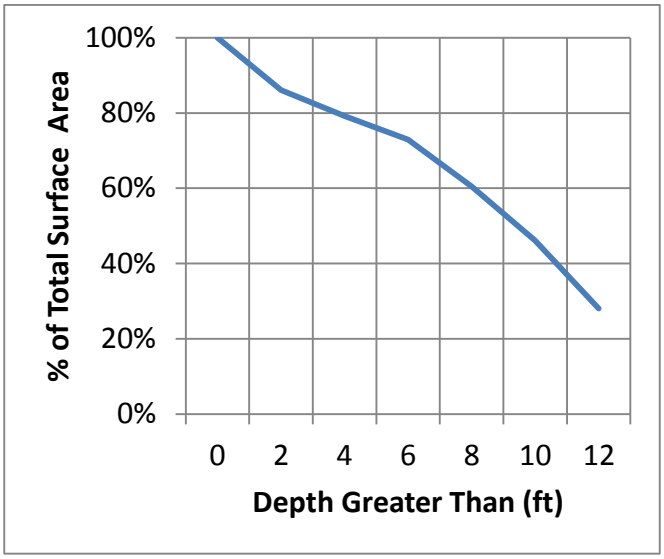

Figure 3-2. Cummulative depth histogram for Missisquoi Bay.

A model grid was designed to cover all of Missisquoi Bay with enough detail to simulate the impacts of the major tributaries on the nearshore portions of the Bay. In addition, the model grid was developed to accurately represent key bathymetric features in the system while minimizing the time required for running multi-year model simulations. The bathymetry of Missisquoi Bay overlain on the model grid is shown in Figure 3-3. An open model boundary is located at the southern edge of the model grid at the Highway 78 bridge causeway. The total number of grid cells used in the model grid is 1,486. Each grid cell is approximately 240 m on a side, with a surface area of approximately 58,000 m^2 (5.8 hectares). For most locations in the three-dimensional grid, a single layer represents approximately 1 foot of water depth.

For simulating hydrodynamics in three dimensions, EFDC provides the option of using either a "sigma" (or stretched) vertical grid or a "generalized vertical coordinate" (GVC) system (TetraTech, 2006). The sigma (or "stretched") vertical grid system requires that a consistent number of layers be used across all horizontal grid cell locations. This approach can be problematic when there is considerable variation in water depth across the model domain. For example, if many vertical layers are used to represent deeper water regions, there will more layers than necessary in shallow water areas, and long runtimes will be needed to complete model simulations. In addition, when representing a constant number of layers across adjacent cells with significantly different water depths, artificial mixing will occur across the vertical layers.

In contrast to the "sigma" grid, the GVC option allows for a variable number of vertical layers across the horizontal grid locations represented in the model domain. This approach allows for a greater numbers of layers to be used in deeper water regions (in the center of the bay) and fewer layers to be used in shallow water regions (near the shore). As a result, the appropriate level of vertical resolution can be used throughout the model domain, while maintaining more efficient

simulation runtimes and better accuracy relative to a sigma grid. For most locations in the three-dimensional grid, the typical vertical layer thickness was approximately one meter of water depth.

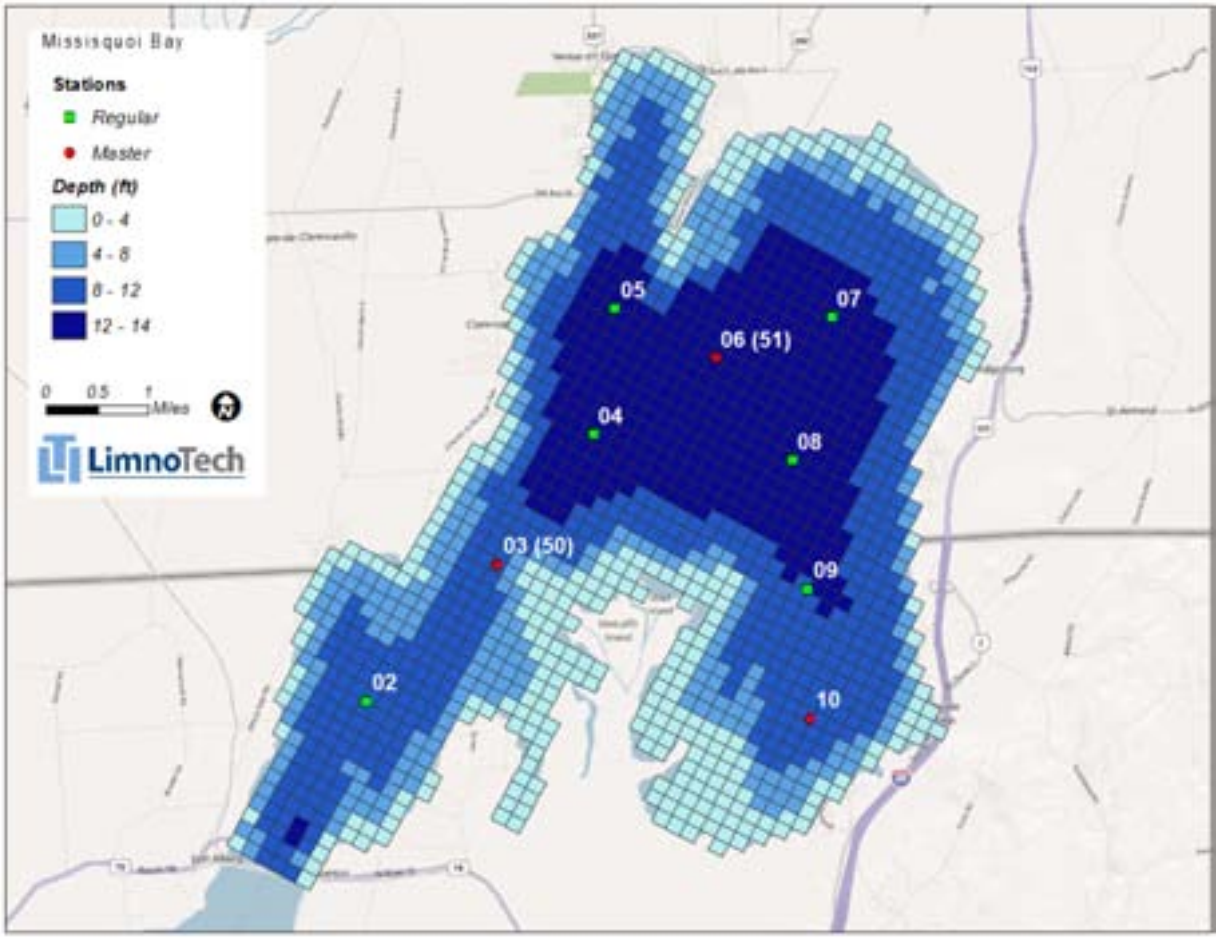

Figure 3-3. Model segmentation, bathymetry, and sampling stations.

4. DATA SOURCES AND MODEL INPUTS

This section gives an overview of data sources used to develop model inputs and data sources used to evaluate calibration and confirm model performance.

4.1 SUMMARY OF DATA SOURCES

The data sources utilized in this project originated from a range of sources including samples collected by the Miner Institute as part of this project, routine tributary and lake monitoring data from the VT DEC, daily water level, tributary flow, and load estimates from the USGS, daily tributary flow estimates from the Quebec Ministry of Environment, and atmospheric data from NOAA sponsored weather stations. Data were either downloaded from the internet where available or obtained directly from a contact at each agency.

The atmospheric and tributary datasets were used to generate model boundary conditions (discussed in the next Section 4.2 and 4.3 below), while the datasets collected in 2010 by the Miner Institute in the bay and from the long-term data collected by VT DEC in the bay were used in the calibration and confirmation of the model (Section 5 and 6).

4.1.1 2010 Field Data

As discussed in Section 3, additional water quality and sediment data were collected in 2010 to fill data gaps identified during the proposal stage of this project. The 2010 field program was designed to capture spatial trends in water quality (specifically TP) in the late summer and fall when TP concentrations are elevated. Sediment cores were also collected and incubated in the lab under oxic and anoxic conditions to determine the flux rate of phosphorus from the sediments. The ten stations that were sampled as part of this study are shown in Figure 3-3. A summary of the sampling dates is shown below in Table 4-1. Additional details and a full set of sampling results are shown in Appendix B.

Table 4-1. Date of Miner Institute sampling trips.

Cruise	Date	Conditions	Sample notes
1	6/3/10	**Pre-bloom**	Initial cruise under extremely windy conditions. Sampled stations 5-9 only
2	7/15/10	**Pre-bloom**	Clear, calm conditions. Collected water column and first set of sediment core samples at all 10 stations.
3	9/3/10	**Bloom**	Clear, calm conditions. Collected water column samples at all 10 stations.
4	9/9/10	**Bloom**	Overcast, cool, 5-10mph W wind. Collected water column samples and second set of sediment cores samples at all 10 stations.
5	10/7/10	**Post-bloom**	Very cold, windy conditions. Collected water column samples at all 10 stations.

4.1.2 VT DEC

The major tributaries in the Missisquoi Bay watershed and stations in Missisquoi Bay are routinely monitored as part of the Lake Champlain Long-Term Water Quality and Biological

Monitoring Program, which began in 1992. The stations near the river mouths are located as close to the flow monitoring stations as possible, and the two bat stations are located near the US/Canadian border and in the middle of the bay. Tributary stations are very close to the flow stations shown in Figure 2-2 and the monitoring stations sampled by the VT DEC are shown in Figure 3-3. Tributary samples are obtained from bridges using depth and velocity-integrating sampling devices. Approximately 20 samples are collected each year per tributary including as many samples as possible during high flow conditions. Additional base flow samples were added in 2006 to improve load estimates. The bay stations are sampled approximately biweekly from May to early November each year. A list of the major parameters sampled in the tributary and bay stations is shown below in Table 4-2. Figures 4-1 and 4-2 show the TP data and the dissolved P data, respectively, reported for VT DEC stations 50 and 51 Additional detail on the sampling program can be found in VT DEC and NYSDEC (2009).

Table 4-2. List of parameters sampled by the VT DEC.

Parameter	Tributary	Lake
Total Phosphorus	x	x
Dissolved Phosphorus	x	x
Chloride	x	x
Total Nitrogen	x	x
Temperature	x	x
Conductivity	x	x
pH	x	x
Total Suspended Solids	x	
Chlorophyll		x
Secchi		x
Algal & Zoo Counts		x

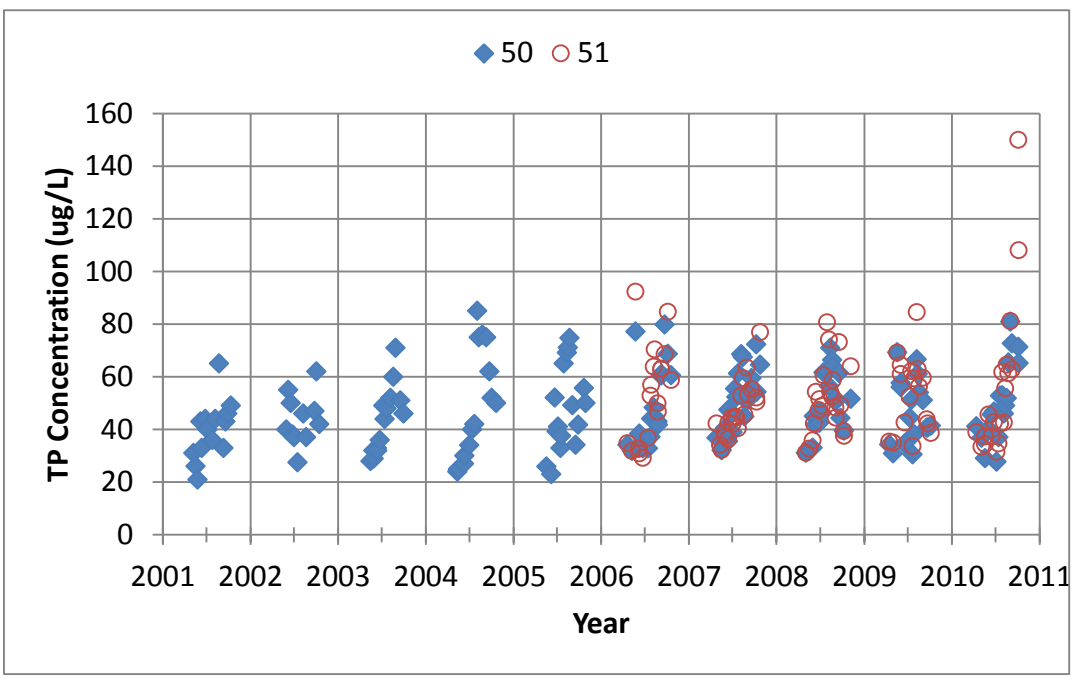

Figure 4-1. Total phosphorus concentration at VT DEC stations 50 and 51.

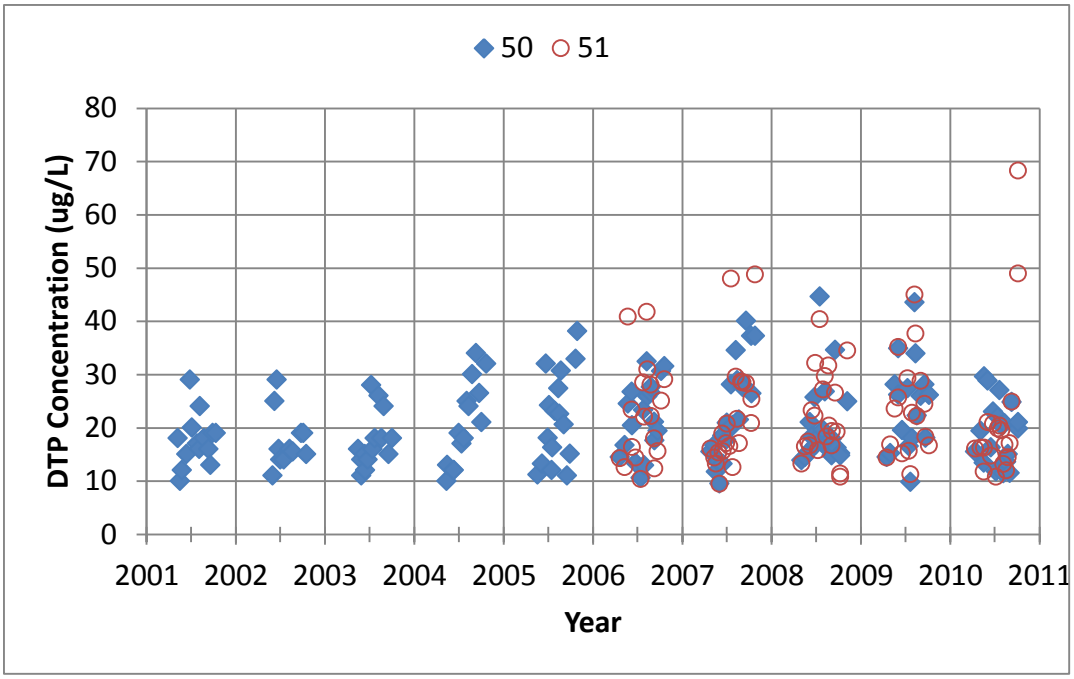

Figure 4-2. Dissolved total phosphorus concentration at VT DEC stations 50 and 51.

4.1.3 USGS and MDDEP

Daily average flow, water level, and tributary load estimates were provided by the USGS. Flow data were also provided by the Québec Ministère du Développement durable, de l'Environment et des Parcs (MDDEP). These datasets were used in the development of boundary conditions for the hydrodynamic model (flow and water level) and the water quality model (daily total suspended solids (TSS), TP, and dissolved TP (DTP) loads).

Flow

The three major tributaries that flow into Missisquoi Bay are the Missisquoi, Pike, and Rock Rivers. Figure 2-2 previously showed the major watersheds and location of flow gages. Table 4-3 below shows the gaging station number, gaged area, and total watershed area. The direct drainage areas mentioned previously in Table 2-2 were combined with the closest major tributary to simplify calculation of flow and water quality loading inputs. Flow was estimated at the mouth of each river by dividing the daily average flow by the gaged area percentage shown in the table below. This assumes that areas downstream of the gaging station contribute the same flow per unit area as areas upstream of the gaging station. Any errors in this assumption are minimal for the Missisquoi and Pike Rivers due to the high percent of gaged area. However, less than 50% of the Rock River is gaged, which would introduce a higher uncertainty in the calculation of the flow and nutrient loads from this tributary. Fortunately, the overall contribution of flow and nutrient loads to Missisquoi is minor, as the Rock River represents only 5% of the total watershed area.

Table 4-3. Major tributaries to Missisquoi Bay

Watershed	Flow Station	Gaged Area (km^2)	Total Area (km^2)	Gaged Area
Missisquoi	4294000	2,201	2,247	98%
Pike	30424	586	726	81%
Rock	30425	71	154	46%
	Total	2,858	3,127	91%

Water Level

Daily average water level data were obtained from the USGS station at Rouses Point, NY (04295000). The daily time series was used to force the open boundary water level at the Highway 78 bridge. The daily average time series is shown in Figure 4-3 below.

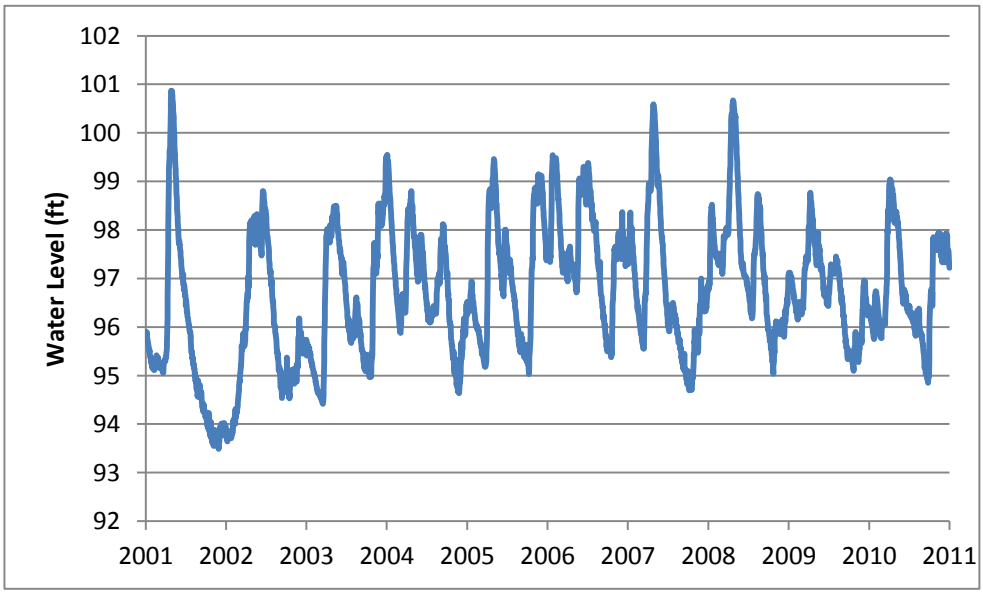

Figure 4-3. Daily average water level at USGS station 04295000.

Loads and Concentrations

The USGS has been involved with estimating loads of TP for the Missisquoi and Pike Rivers using a new technique designed to estimate loads in tributaries with limited monitoring data. The new technique, called "Weighted Regressions on Time, Discharge, and Season" (WRTDS), has been applied and tested previously on nine major tributaries to Chesapeake Bay from 1978 to 2008 (Hirsch et al, 2010). Early on in this project the USGS agreed to assist with developing load estimates for TP, DTP, and TSS for the Missisquoi and Pike Rivers. . The USGS obtained tributary monitoring data from VT DEC and flow data from the sources mentioned above and applied the WRTDS program to tributary data for the 1990 to 2010 time period. The output of the model was a daily estimate of the TP, DTP, and TSS loads. Since the load estimates were calculated at the gaging stations, the concentration was first backed out of the load calculation and then the scaled up flows for each watershed were applied to estimate the load at the mouth of the river. The USGS did not estimate loads for the Rock River due to its small size and the lack of a long term monitoring dataset. The details of how Rock River concentrations were estimated are included in the next section.

Figure 4-4 to 4-6 below shows the average concentration output of the load analysis for the Missisquoi and Pike Rivers for TP, DTP, and TSS. The estimated concentrations for the Rock River are also shown for comparison in these figures. The ten- year average tributary concentrations for TP, DTP, and TSS are shown below in Table 4-4. The June to September average concentrations are shown in parenthesis.

Table 4-4. Ten year average tributary concentrations. June to Sept average is shown in parenthesis.

Variable	Missisquoi	Pike	Rock
TP (ug/L)	50 (35)	60 (38)	127 (112)
DTP (ug/L)	20(15)	31 (24)	72 (82)
TSS (mg/L)	15 (10)	15 (5)	5 (2)

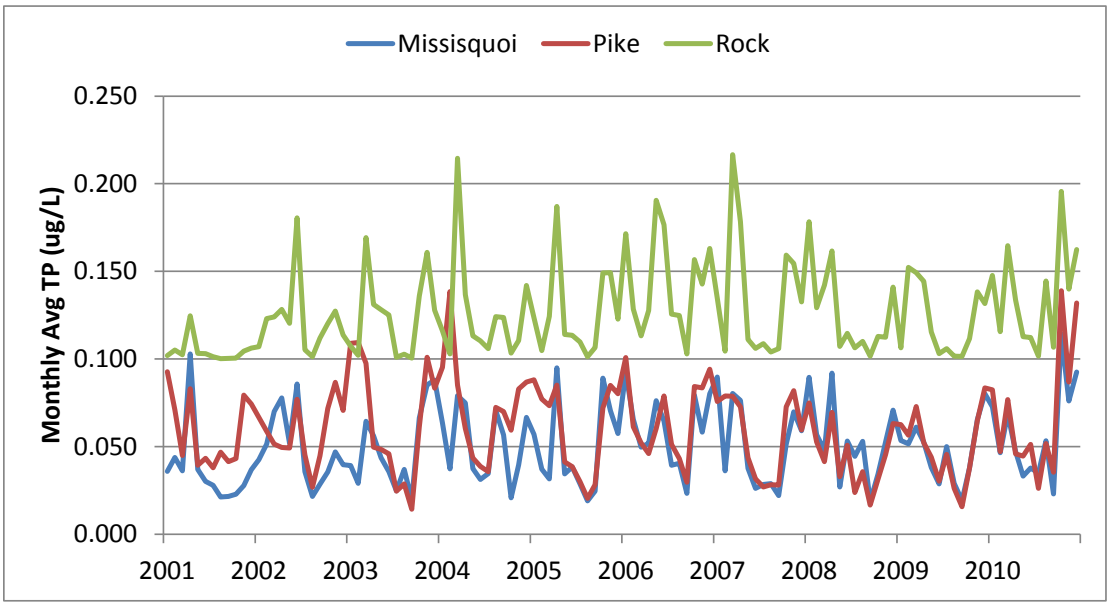

Figure 4-4. Monthly average tributary TP concentration.

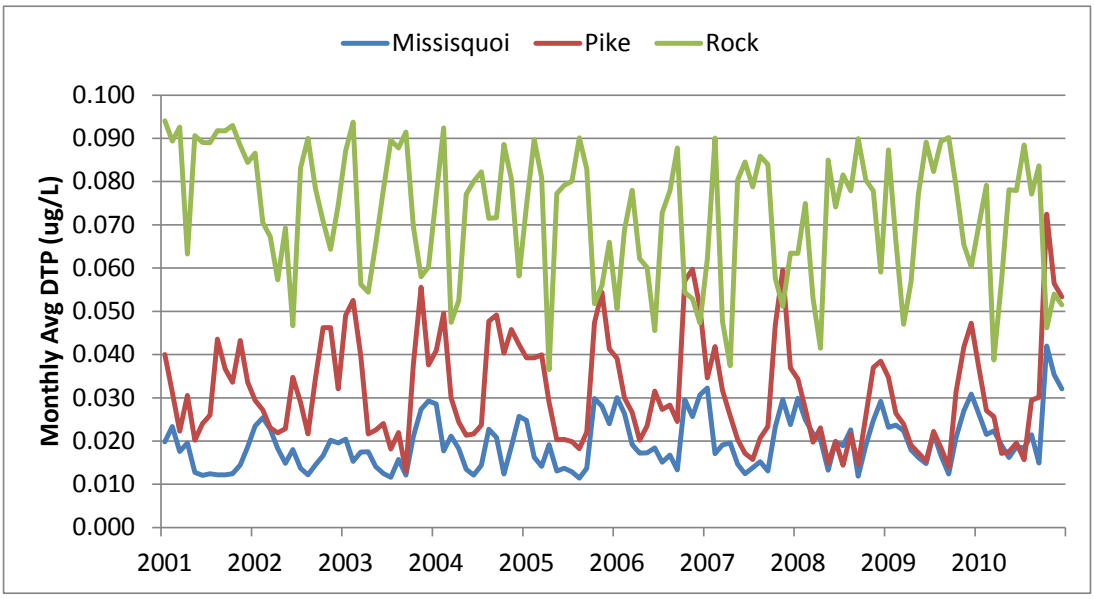

Figure 4-5. Monthly average tributary DTP concentration.

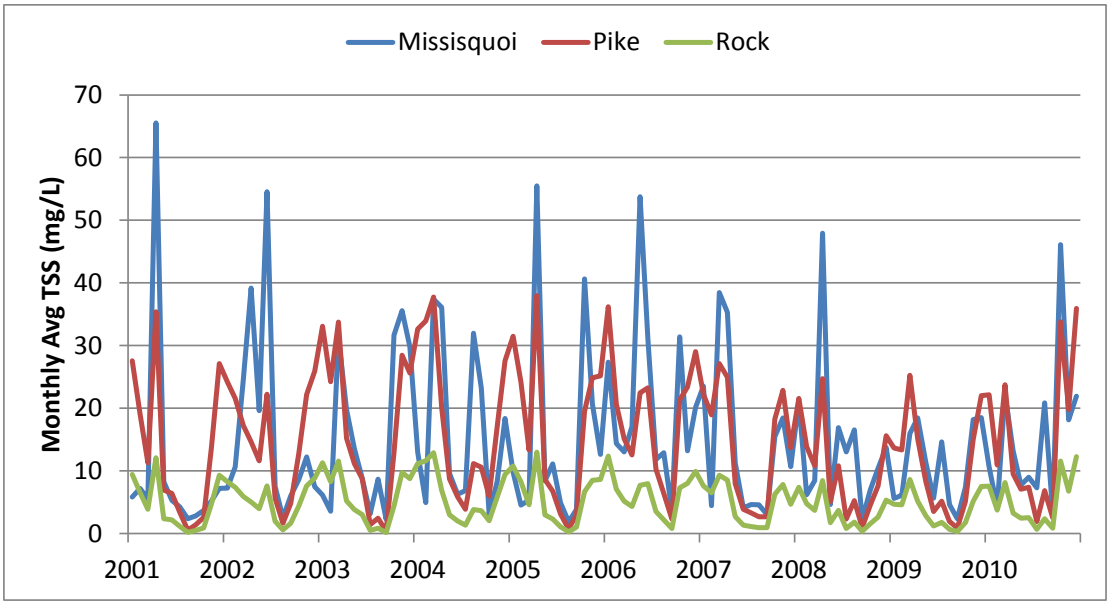

Figure 4-6. Monthly average tributary TSS concentration.

4.1.4 NOAA

Historical, quality-controlled atmospheric data from nearby airports were obtained through the NOAA National Climatic Data Center website. Meteorological data from surrounding airports were used as inputs for the hydrodynamic and temperature model. Figure 2-1 shows the location of nearby weather stations. The Burlington Airport was used as the primary weather station for barometric pressure, air temperature, relative humidity, wind speed and direction, and cloud cover as it had the longest period of record for the most parameters. Air temperature and wind speed data were used in select years from the Frelighsburg, QC and Swanton, VT airports. A typical year solar radiation time series was used from the Adirondack Airport in Albany, NY obtained from the National Solar Radiation Database (reference). Solar radiation data could be estimated from cloud cover data; however, a reliable source of cloud cover data was not found that provided the observations in the necessary units of tenths.

4.2 HYDRODYANMIC MODEL INPUTS

The hydrodynamic model requires atmospheric forcings, tributary flows, open boundary water levels, and temperature time series for the tributaries and open boundary. Each of these inputs is discussed below.

Atmospheric Inputs

As mentioned in the previous section atmospheric data were obtained from NOAA weather stations operated in cooperation with nearby airports. Since nearby stations did not have a complete record of atmospheric conditions for the simulation period a master atmospheric forcing file was created by using the best available data source for a given year. The master file was then reviewed for inconsistencies and applied evenly across the whole model domain. The atmospheric inputs include air temperature, relative humidity (calculated from dew point and air temperature), wind speed and direction, barometric pressure, cloud cover, and solar radiation. An hourly time series was generated by combining data from various stations. Table 4-5 shows the stations that were used by meteorological parameter for the simulation period.

Table 4-5. Summary of atmospheric stations and data period.

Parameter	Burlington	Franklin County	Adirondack
Air Temperature	2001-2008	2008-2010	
Relative Humidity	2001-2008	2008-2010	
Barometric Pressure	2001-2010		
Wind Speed and Direction	2001-2008	2008-2010	
Cloud Cover	2001-2010		
Solar Radiation			2001-2010

Tributary Flow

As discussed in the data section, daily average flow data from the USGS and MDDEP were used to define the tributary inflow time series for the three major tributaries. The Missisquoi River has the largest watershed of the three tributaries and represents the majority of the inflow into the bay. Figure 4-7 shows the average annual flow for each tributary. Between 2001 and 2010 the Missisquoi River averaged 79% of the average inflow to the bay with the Pike and Rock contributing 18% and 3%, respectively. On a year-to-year basis the annual flow remains fairly stable, with higher than average flows in 2006 and lower than average flows in 2001. The average annual inflow is approximately 2,500 cfs for the 2001 to 2010 period. During the June to September period, the average flow is approximately 1,500 cfs. Assuming a lake volume of 0.22 km^3 this would translate to an average hydraulic retention time of 36 days for the whole year and 60 days for the June to September period.

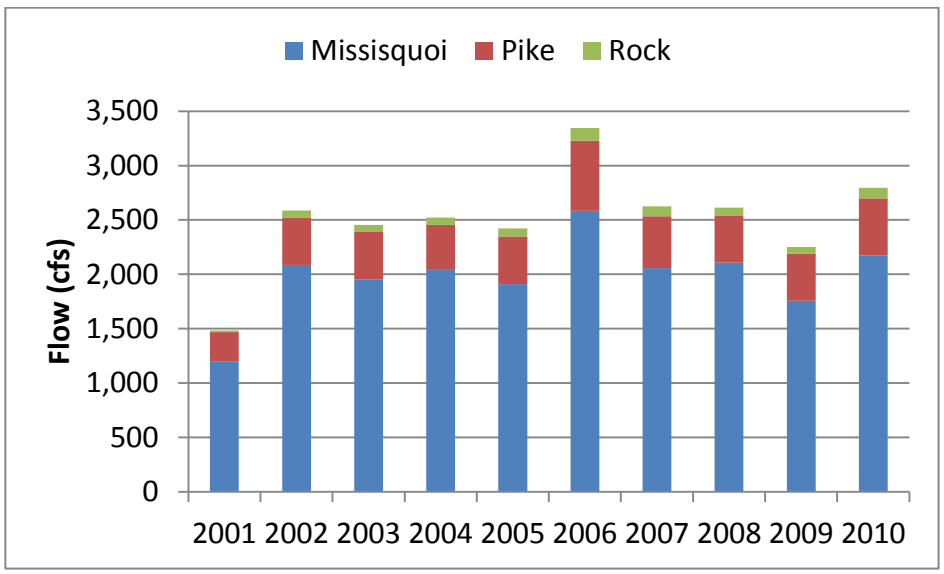

Figure 4-7. Average annual flow of Missisquoi, Pike, and Rock Rivers.

Water Temperature

Daily water temperature data were not available for the tributaries or near the open boundary. To generate a daily time series, a monthly average time series was estimated from VT DEC routine monitoring on the Missisquoi River. Figure 4-8 below shows the monthly average temperature time series that was applied to each tributary. This time series was also applied to the open boundary of Missisquoi Bay. At the open boundary this temperature is only applied if water is flowing into the bay from the northeast arm. This condition is relatively short lived and

does not have an impact on the water temperatures predicted at station 50 and 51 (as demonstrated in the calibration section).

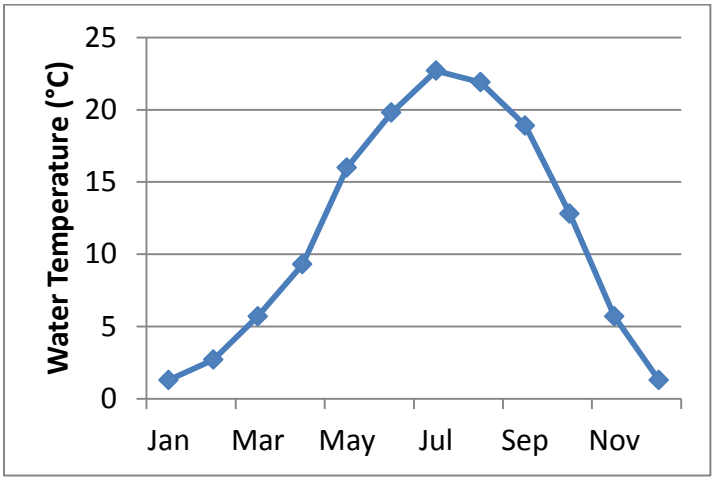

Figure 4-8. Monthly average tributary temperature time series.

4.3 WATER QUALITY MODEL

The water quality model discussed in the model development section requires a time series for each tributary and open boundary for every state variable being simulated. This section will only review in detail the development of boundary conditions for total phosphorus (TP), dissolved total phosphorus (DTP), and total suspended solids (TSS).

The loads from the USGS were calculated using a time weighted flow regression approach, which gives a higher weight to data points that are closer in time to the simulation year. This approach is ideal for rivers with relatively small annual datasets because it pools data together across multiple years. The flow and concentration data used as input to the load model come from the USGS flow gage stations and the VT DEC tributary monitoring stations on each river. To adjust for a larger watershed area than what was used in the USGS calculations the daily load estimates were converted to daily concentrations. These concentrations were then applied to the scaled up daily average flows as described in the previous section.

4.3.1 Point Source Loads

Point sources of phosphorus within the Missisquoi Bay watershed are mostly located upstream of the sampling stations. However, their effluents typically contain concentrations of TP that are much higher than ambient waters. While the USGS load estimates implicitly incorporate point source loadings that enter upstream of the sampling station they don't include sources downstream of the sampling station. An analysis of the point source load contribution was made by the Missisquoi Bay Phosphorus Reduction Task Force (2008). The report estimated an average of 4 MT/yr was discharged throughout the watershed between 2002 and 2005. This equals approximately 2% of the annual average tributary load from 2001 to 2010. A constant load of 4 MT/yr (11 kg/d) was added to the model as a point source of dissolved inorganic phosphorus (DPO4).

4.3.2 Nutrient and Solids Boundary Conditions

Tributary loads of total phosphorus, dissolved phosphorus, and total suspended solids were obtained from the USGS (personal communication, Laura Medalie, USGS) for the Missisquoi

and Pike Rivers. As mentioned previously, the daily load estimates were converted to daily concentrations and then applied to the scaled up tributary flows. Rock River TP, DTP, and TSS concentrations were estimated from concentrations/flow regressions using monitoring data from 2006 to 2010 and daily average flow data. Table 4-6 below lists all of the state variables available in the RCA model framework. The model has the capability to accept a time series input for each state variable for every boundary location.

To meet the objectives of this project, only a subset of the state variables used a daily time series (phosphorus species and TSS). When only limited data were available a monthly time series was used (phytoplankton abundance, dissolved oxygen). The other state variables were either not used (concentration = 0) or were set to a constant value. The state variables that were set to constants values (all nitrogen species, silica, and dissolved organic carbon) used either average monitoring data for that parameter or literature values.

4.3.2.a Phosphorus

Total and dissolved phosphorus concentrations were provided by the USGS as mentioned previously. To convert TP and DTP measurements into the state variables used by the model some assumptions were made. A summary of the process used to convert the concentrations into state variable concentrations are shown below. Model state variables are enclosed in brackets.

Particulate Organic Phosphorus = POP = TP – DTP – ∑PHYT/40 ,

*Refractory POP = [RPOP] = 0.85 * POP,*

*Labile POP = [LPOP] = 0.15 *POP*

Dissolved Organic Phosphorus = DOP = DTP – DPO4,

*Refractory DOP = [RDOP] = 0.85 *DOP,*

*Labile DOP = [LDOP] = 0.15*DOP*

Total Orthophosphate = [PO4T] = ∑PHYT/40 +DPO4

*Dissolved Orthophosphate = DPO4 = %DPO4 * DTP*

For all tributaries, refractory and labile fractions of particulate and dissolved organic phosphorus comprised 85% and 15% of the total for each species, respectively. For the Missisquoi, Pike, and Rock Rivers, the percent of DTP that is DPO4 (%DPO4) equals 30%, 30%, and 25%, respectively. These percentages were estimated from the SRP (assumed equivalent to DPO4) data collected by the Miner Institute in 2010 at the tributary stations. The total phytoplankton abundance (∑PHYT) is discussed in the next section. While the monthly average TP values are shown in Figures 4-4, daily average concentrations were input into the model. Components of TP were divided as described above into organic and inorganic components.

Table 4-6. MBPHOS Water Quality State Variables

No	ID	State Variable Description	Notes
1	CHL	Chloride	Not Used
2	***PHYT1***	***Phytoplankton - Blue-Green Algae***	***Monthly estimate***
3	***PHYT2***	***Phytoplankton - Winter Diatoms***	***Monthly estimate***
4	***PHYT3***	***Phytoplankton - Summer Diatoms & Greens***	***Monthly estimate***
5	PHYT4	Others	Not Used
6	PHYT5	N2-fixing Blue-Greens	Not Used
7	***RPOP***	***Particulate Organic Phosphorus - refractory***	***% of total particulate P (USGS)***
8	***LPOP***	***Particulate Organic Phosphorus - labile***	***% of total particulate P (USGS)***
9	***RDOP***	***Dissolved Organic Phosphorus - refractory***	***% of total dissolved P (USGS)***
10	***LDOP***	***Dissolved Organic Phosphorus - labile***	***% of total dissolved P (USGS)***
11	***PO4T***	***Total Inorganic + Algal Phosphorus***	***Algal + DPO4 (% of TDP) (USGS)***
12	RPON	Particulate Organic Nitrogen - refractory	Constant
13	LPON	Particulate Organic Nitrogen - labile	Constant
14	RDON	Dissolved Organic Nitrogen - refractory	Constant
15	LDON	Dissolved Organic Nitrogen - labile	Constant
16	NH4T	Total Ammonia + Algal Nitrogen	Constant
17	NO23	Nitrite + Nitrate	Constant
18	BSI	Biogenic Silica	Constant
19	SIT	Total Available Silica	Constant
20	***RPOC***	***Particulate Organic Carbon - refractory***	***% of TSS***
21	***LPOC***	***Particulate Organic Carbon - labile***	***% of TSS***
22	RDOC	Dissolved Organic Carbon - refractory	Constant
23	LDOC	Dissolved Organic Carbon - labile	Constant
24	EXDOC	Dissolved Organic Carbon - algal exudate	Not Used
25	REPOC	Particulate Organic Carbon - reactive	Not Used
26	REDOC	Dissolved Organic Carbon - reactive	Not Used
27	O2EQ	Aqueous SOD	Not Used
28	***DO***	***Dissolved Oxygen***	***Monthly estimate***
29	***SS1***	***Suspended Solids, fine***	***USGS***
30	SS2	Suspended Solids, coarse	Not Used
31	ZOO1	Zooplankton - cladocerans	Not Used
32	ZOO2	Zooplankton - copepods	Not Used
33	ZOO3	Zooplankton - microzooplankton	Not Used
34	BALG	Benthic algae detritus	Not Used
35	DYE	Conservative Tracer	Not Used

4.3.2.b Phytoplankton

The three phytoplankton functional groups simulated by the MBPHOS model include blue-green algae, winter assemblage, and summer assemblage. The three functional groups do not represent individual species of phytoplankton, but rather a community of phytoplankton that have similar physical and biological properties that prosper under unique temperature and nutrient conditions. The boundary conditions for

As discussed earlier, Missisquoi Bay can have a hydraulic retention time ranging from several days during high flow events to several months during low flow summer periods. During high flow periods phytoplankton concentrations in the tributaries can have a large impact on chlorophyll concentrations measured throughout the bay. While chlorophyll data were not available for the tributary stations a reasonable estimate of the monthly chlorophyll concentrations in each major algal class are represented below in Figure 4-9.

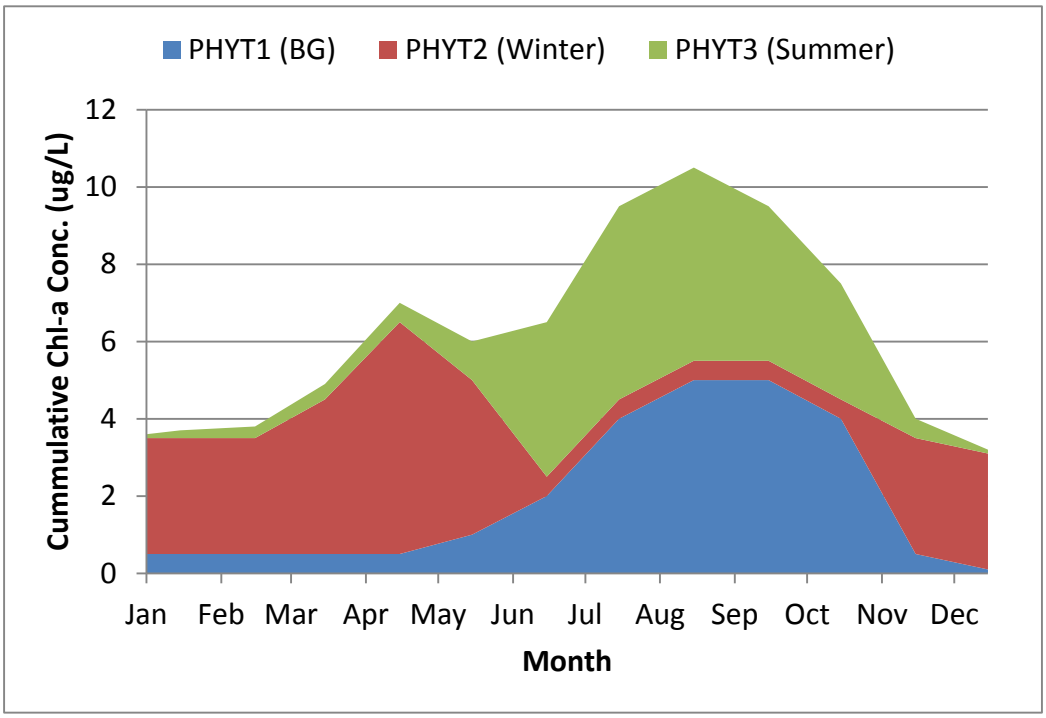

Figure 4-9. Estimated phytoplankton abundance by functional group in tributaries.

4.3.2.c Suspended Solids

Total suspended solids concentrations were estimated from the USGS data as mentioned previously. The model does not simulate TSS separately, but rather simulates the non-algal organic (particulate organic carbon), algal (PHYT), and inorganic suspended solids components of TSS. The equation below shows how each of these components is added together to simulate TSS. This assumes that 40% of the total phytoplankton and POC mass is organic.

$$TSS = \sum[PHYT] / 0.4 + ([RPOC]+[LPOC])/0.4+[SS1]$$

5. CALIBRATION AND CONFIRMATION

5.1 OVERVIEW

There were two primary datasets used in the model calibration and confirmation process. The first dataset was collected by VT DEC on a weekly to biweekly basis between May and September at two primary stations. This data collection program has been ongoing at Station 50 since 1992 and Station 51 since 2006. The second dataset was collected as part of this project by the Miner Institute at ten stations during the late summer and fall of 2010. In addition, sediment cores were collected in 2010 to estimate the diffusive flux of phosphorus from the sediments to the water column. Both sets of stations are shown in Figure 3-3.

The model calibration approach was to focus first on the hydrodynamic model and then on the water quality model. Model calibration was done primarily using a visual comparison of monthly averaged model and data results. Some comparisons to daily results are shown below for 2010; however, the intent is not to use the model results for this short of a time scale. Because additional data were collected in 2010 as part of this study, model calibration focused on this year first. Once a reasonable model to data fit was achieved then model calibration focused on the 2006 to 2010 time period using data from VT DEC at stations 50 and 51. During this five year period there was sufficient variability in tributary load and flow to warrant evaluating only this period for calibration. Once a reasonable model to data fit was achieved, then the model was run for the 2001 to 2005 period and compared with data from VT DEC station 50. The 2001 to 2005 time period is treated as the model confirmation period since model coefficients were not altered to achieve a better fit during this time period.

The sections below present the hydrodynamic model calibration and confirmation and then the water quality model calibration and confirmation.

5.2 HYDRODYNAMIC CALIBRATION

The hydraulic model developed for this project was designed to be relatively simple, yet refined enough to simulate the transport of nutrients from tributary mouths, through Missisquoi Bay, and out into the northeast arm of Lake Champlain. The primary purpose of the hydrodynamic model is to simulate the three dimensional movement of water (velocity and direction) in and out of each model grid cell and vertical layer within the model domain given forcings of wind, tributary flow, open boundary water level, and density driven water movement. A full heat balance was also calculated to dynamically simulate temperature throughout the model domain. Calibration of the hydrodynamic model consisted of comparing water level and temperature monitoring data to predicted results.

Water Level

Daily average water level data were obtained through the Water Survey of Canada in Philipsburg, QC in the northeast corner of Missisquoi Bay. Figure 5-1 below shows the daily average model predicted water level and the daily average measured water level. It is difficule to distinguish the two because they track each other very closely.

The inter annual fluctuation in water level ranges from 4ft to almost 8 ft, which can significantly alter the total volume of Missisquoi Bay. Lower water levels translate into a lower volume of water to dilute internal releases of phosphorus during the low flow summer months. However, higher flow events on the tributaries can flush lake water out of the system faster. The opposite conditions hold true for higher than normal water levels.

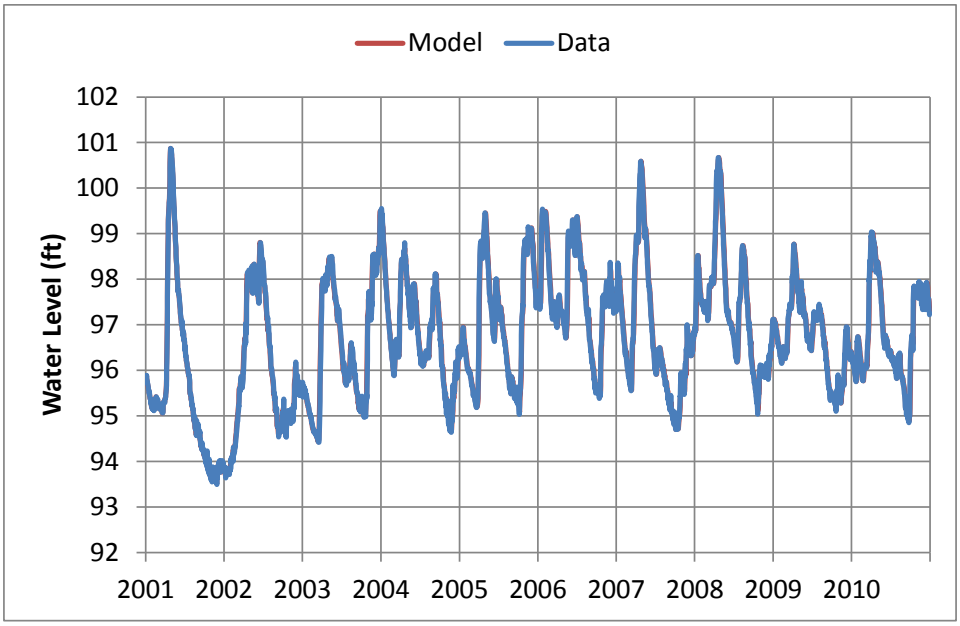

Figure 5-1. Modeled and measured water level (both fall on the same line).

Water Temperature

Most of the development time for the hydrodynamic model was spent refining the atmospheric forcings (air temperature and wind speed), because continuous observations were only available in some years from stations located 45 miles away. Figure 5-2 and 5-3 below show the average monthly water temperature at the two VT DEC monitoring stations at the surface respectively from 2006 to 2010. The red dots represent the monthly average of measured data. The error bars on the data points indicate the standard deviation if more than two measurements were taken that month. The solid blue line represents the monthly average model predicted temperature from the model cell associated with the station location. The dashed lines represent the highest and lowest five-day average as calculated by the model.

Bottom temperature results are shown in Figures 5-4 and 5-5. In Figure 5-4, predicted surface water temperature compare favorably to measured temperatures. The data points are located within one or two degrees Celsius of the predicted values for the May through September period. In Figure 5-5, the predicted bottom water temperatures tend to be cooler than measured values in May and June by several degrees Celsius. However, the model does a better job matching bottom temperatures in the July to September period.

The primary driver of vertical mixing in the water column is wind-induced mixing. Since wind measurements were taken from land based stations located up to 45+ miles away this might the explain the under prediction of bottom water temperatures in 2006, 2007, and part of 2008. In the spring, there is likely to be a larger difference between the temperature of the air and water. The temperature difference is likely to drive local winds, which may not be present at land based measurement sites.

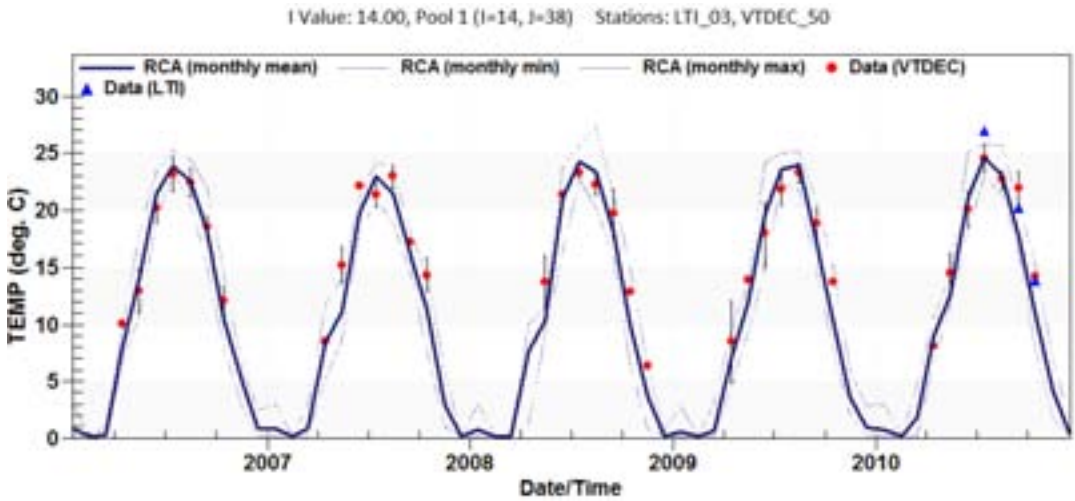

Figure 5-2. Average monthly surface temperature at VT DEC Station 50.

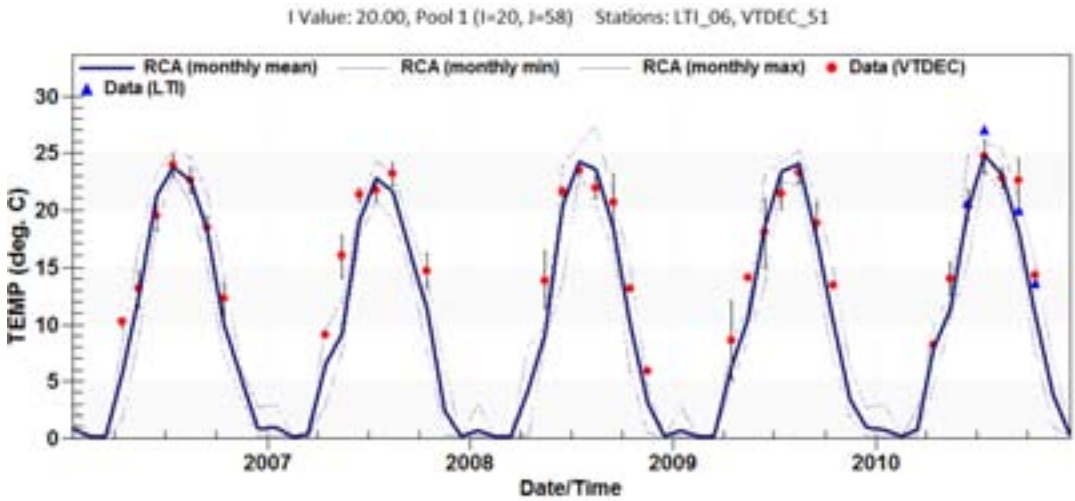

Figure 5-3. Average monthly surface temperature at VT DEC Station 51.

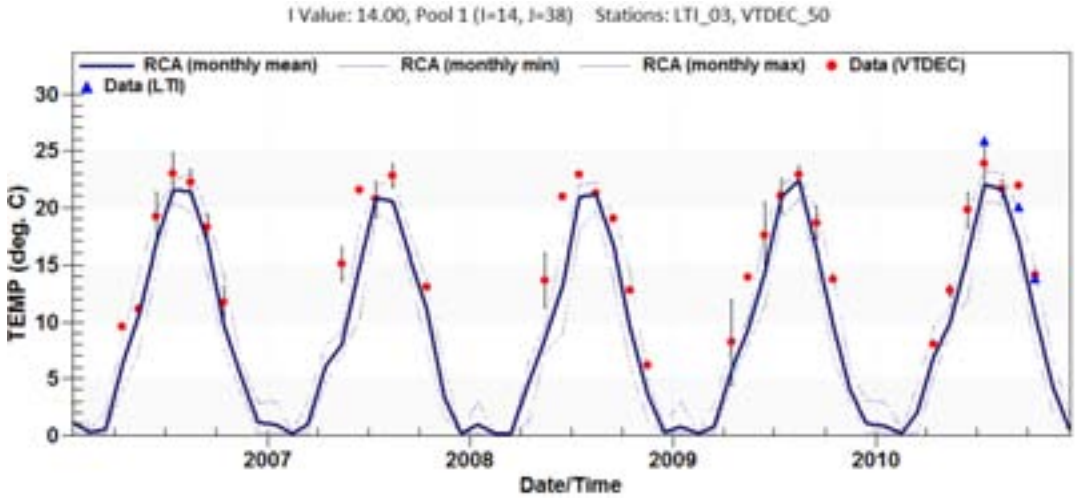

Figure 5-4. Average monthly bottom temperature at VT DEC Station 50.

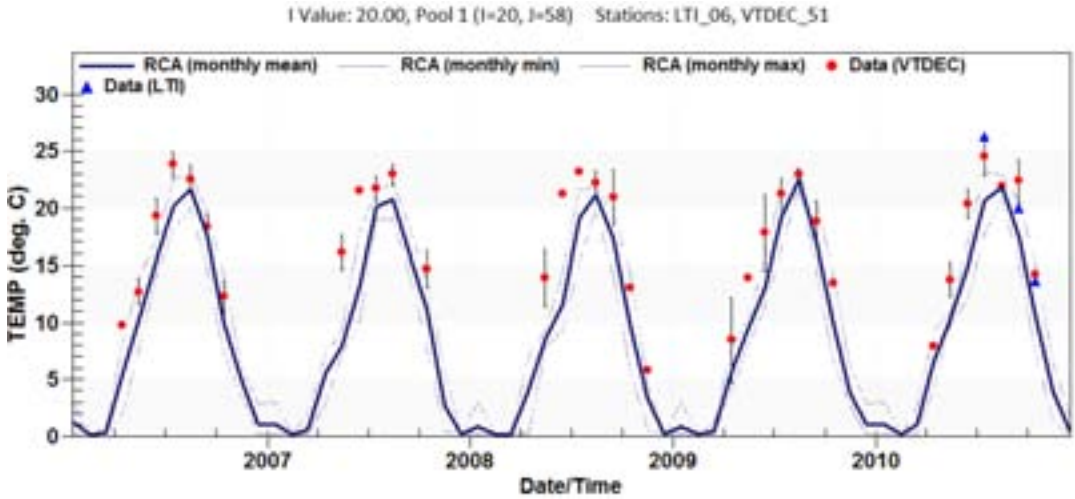

Figure 5-5. Average monthly bottom temperature at VT DEC Station 51.

5.3 HYDRODYNAMIC CONFIRMATION

Figure 5-6 and 5-7 below shows predicted and measured water temperature at the surface and bottom of the water column from 2001 to 2005 at VT DEC station 50. Again the model is performing well at the surface, where the monthly averaged data fall almost squarely on the model prediction line and the standard error bars fall within the minimum and maximum five-day average model results for the month. Near the bottom of the water column, the model appears to be performing better in the 2001 to 2005 time period relative to the 2006 to 2010 time period.

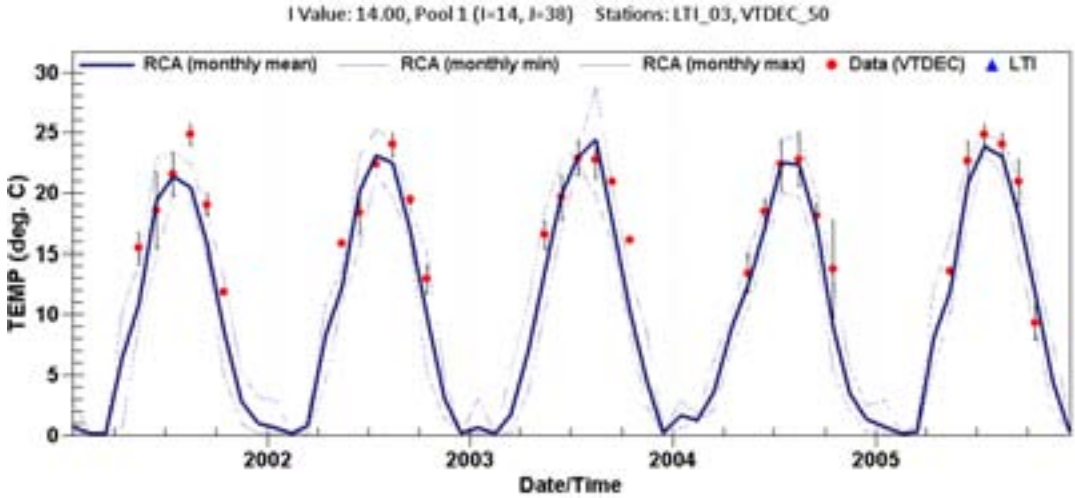

Figure 5-6. Average monthly surface temperature at VT DEC Station 50.

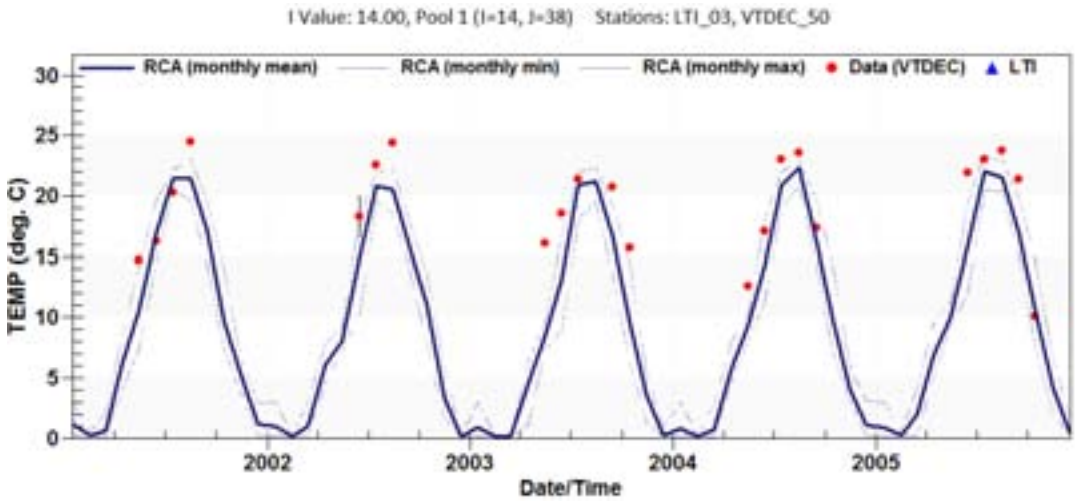

Figure 5-7. Average monthly bottom temperature at VT DEC Station 50.

5.4 WATER QUALITY

The water quality calibration focused primarily on model-observation comparisons of total phosphorus data over several spatial and temporal scales. In this section model to data comparisons are made for:

- 2010, which includes high temporal and spatial comparisons;
- 2006 to 2010, which represents the full calibration period; and
- 2001 to 2005, which represents the confirmation time period.

5.4.1 Model Coefficients

The water quality and sediment diagenesis model contains a large number of coefficients to parameterize all of the kinetic, physical, and biological algorithms for every state variable. Table 5-1 and 5-2 below show a subset of model coefficients for the water quality and sediment diagenesis model, respectively. These are the key coefficients that were scrutinized during the model calibration process. All of the final values fall within the range of values specified in the RCA guidance manual (HydroQual, 2004).

Table 5-1. Key water quality model coefficients.

ConstID	Value	PHYT1	PHYT2	PHYT3	Units	ConstDescr
TOPT		28	15	22	deg C	Optimal growth temperature
K1C		1.6	1.4	1.4	/day	Max. phytoplankton growth rate at TOPT
CRBP11		40	40	40	mg-C/mg-P	Carbon to phosphorus ratio
CCHL1		50	75	50	mg-C/mg-Chl-a	Carbon to chlorophyll-a ratio
VSBAS1		-0.5	0.05	0.05	m/day	Base algal settling rate
K57C	0.01				/day	Hydrolysis rate of RPOP to RDOP
K68C	0.07				/day	Hydrolysis rate of LPOP to LDOP
K79C	0.005				/day	Mineralization rate of RDOP to PO4
K89C	0.1				/day	Mineralization rate of LDOP to PO4
KLMIN	0.1				m/day	Minimum reareation coefficient
VSPOM	0.1				m/day	Particulate organic matter settling rate
KADPO4	197000				L/mg-ss	Partition coefficient for Psorption to SS1
WSS1	0.3				m/day	Water column settling rate for SS1

Table 5-2. Key sediment diagenesis water quality model coefficients.

ConstID	Value	G1	G2	G3	Units	ConstDescr
FRPPH1		0.6	0.2	0.2		% P going to Gx for PHYT and POP
KPDIAG		0.1	0.01	1E-06	/day	Diagenesis rates for POP G1, G2, G3 fractions
DPTHTA		1.1	1.15	1.17		Temperature coefficients
M1	0.8				kg/L	Bulk density of sediments (aerobic)
M2	0.8				kg/L	Bulk density of sediments (anaerobic)
Dd0	1E-04				m2/day	Minimum porewater diffusion coefficient
THTADd0	1.17					Temperature coefficient for Dd0
PIE1PO4	45					Multiplier for aeroebic PO4 partition coefficient
PIE2PO4	125				L/kg	Anaerobic layer PO4 partition coefficient
O2CRIT	5				mg-O2/L	DO threshold for PO4 partition increase

5.4.2 2010 Calibration

As part of this study water quality data were collected at many stations across the bay in 2010 during four cruises. This dataset was used to assess the spatial and temporal variability of phosphorus concentrations.

Figure 5-8 and 5-9 below shows the five day average total phosphorus concentration as predicted by the model compared to discrete surface grab samples at stations 50 and 51, respectively. The model predicts the TP concentrations well from April to July, when the average concentration is approximately 50 ug/L. The model is also capturing the slow increase in total phosphorus observed in the data for July, August, and September.

Figure 5-10 and 5-11 shows the model comparison with total dissolved phosphorus and chlorophyll concentration data for 2010 at Station 51, respectively. The dissolved phosphorus data are highly variable in 2010 and shows a slight declining trend throughout the summer. Since TP was increasing during this time period (as shown above) it is likely that algal uptake of dissolve P is accounting for the decrease in dissolved P. This is confirmed by the predicted and measured chlorophyll concentration during 2010 at station 51 (Figure 5-11). While chlorophyll *a* (e.g. algal abundance) was not a primary calibration metric for this project, it was simulated to allow for a reasonable estimate of the algal bound TP. The fact that the model under-predicted chlorophyll *a* concentration in August and September explains its over-prediction of dissolved phosphorus during this same time period. However, the total phosphorus model-data comparison is not affected by this shift in dissolved and particulate phosphorus.

Figure 5-13 and 5-14 show a spatial comparison between the predicted (5 day average) and measured TP concentration on July 17 and October 10, 2010, respectively. The color of the circles match the same legend used to color the model results shown on the model grid. On July 17, the model is slightly over predicting the concentration throughout the bay while under predicting the concentration in the southeast corner. On October 10 the opposite is true. This suggests that the current model is limited in terms of accurately predicting the sub-weekly TP concentration. Because there is a high flow event in late September, the likely cause for the model over prediction in October is incorrect tributary loads or an inability to capture the higher settling rates of material delivered during the high flow event. An improved understanding of nutrient and sediment conditions following large storm events would help to answer this question. A summary of the summer average TP concentration is shown in the Section 5.6.

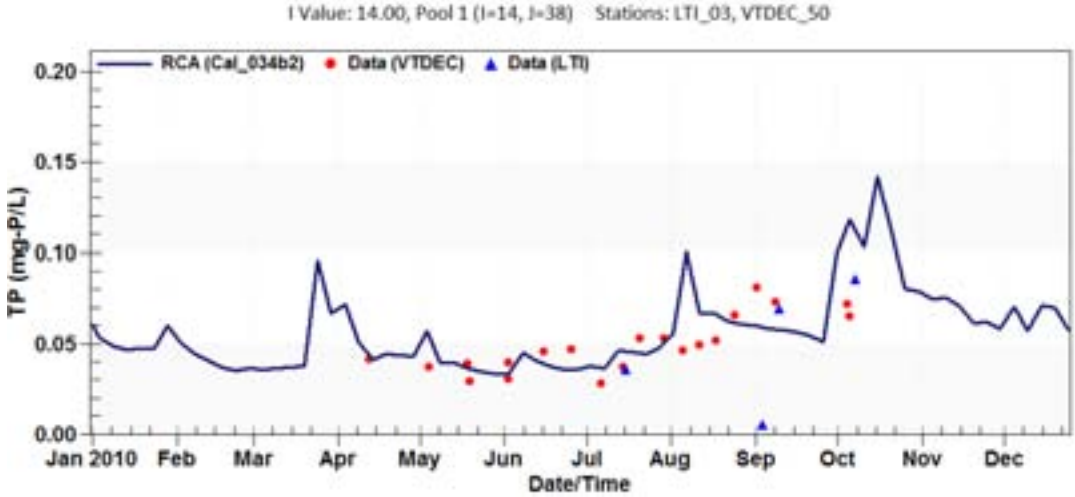

Figure 5-8. Five day average predicted and measured TP at VT DEC Station 50 in 2010.

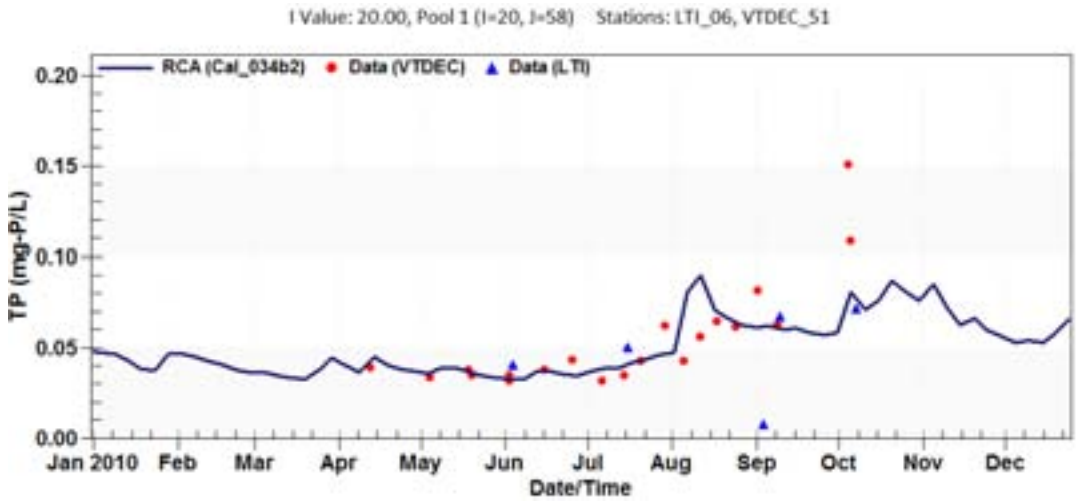

Figure 5-9. Five day average predicted and measured TP at VT DEC Station 51 in 2010.

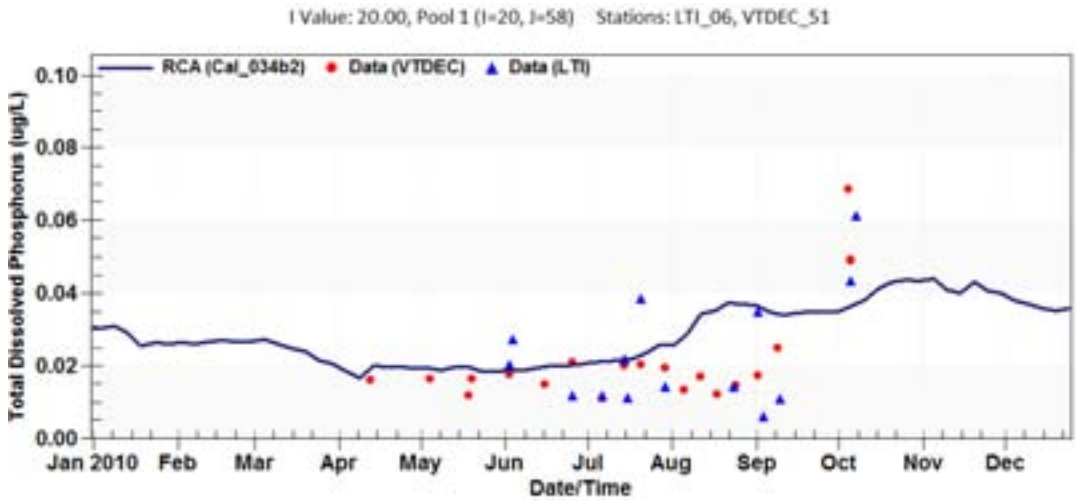

Figure 5-10. Five day average predicted and measured DTP at VT DEC Station 51 in 2010.

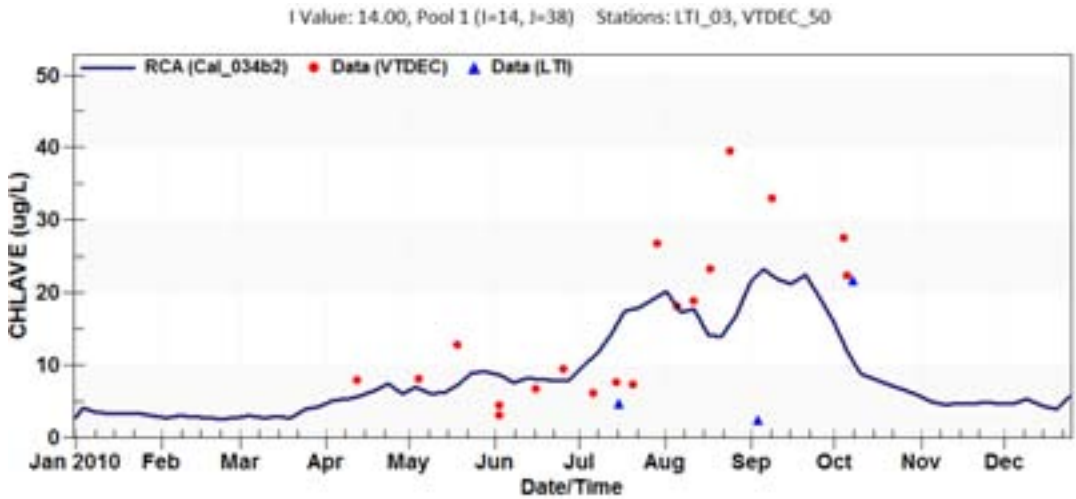

Figure 5-11. Five day average predicted and measured CHL at VT DEC Station 51 in 2010.

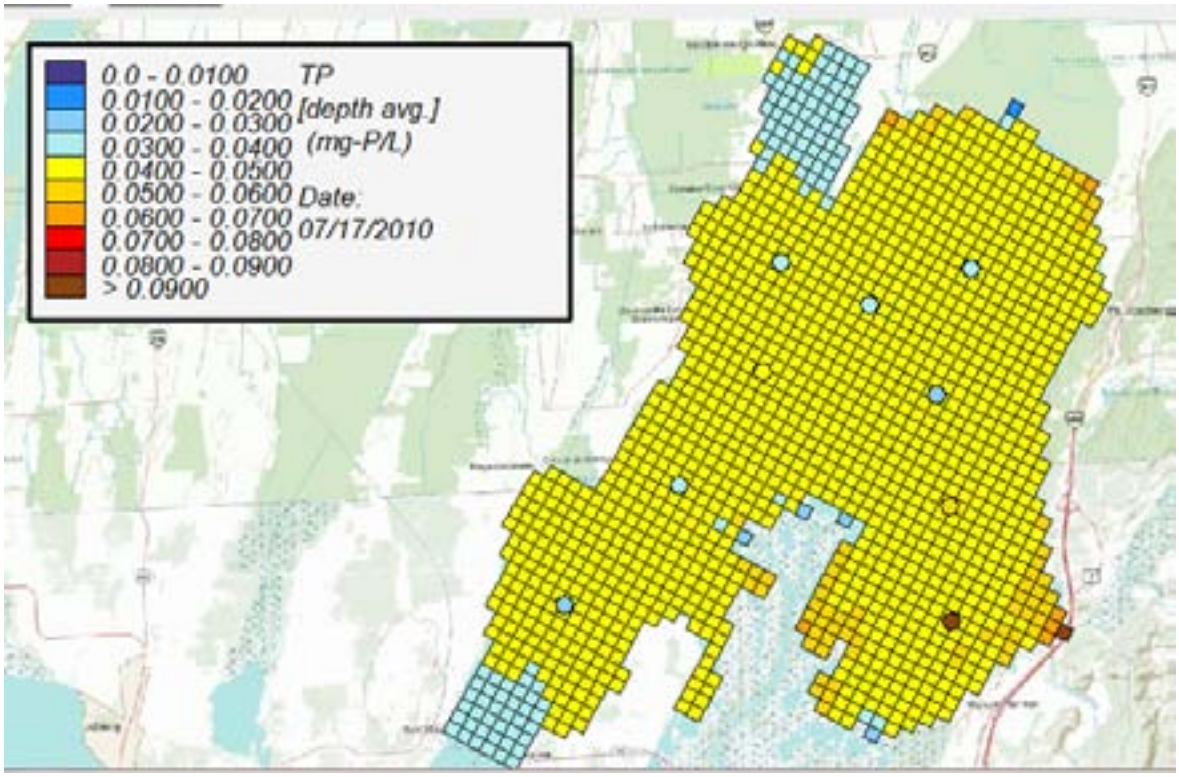

Figure 5-12. Map-based comparison of model (squares cells) and data (circles) for TP on July 17, 2010

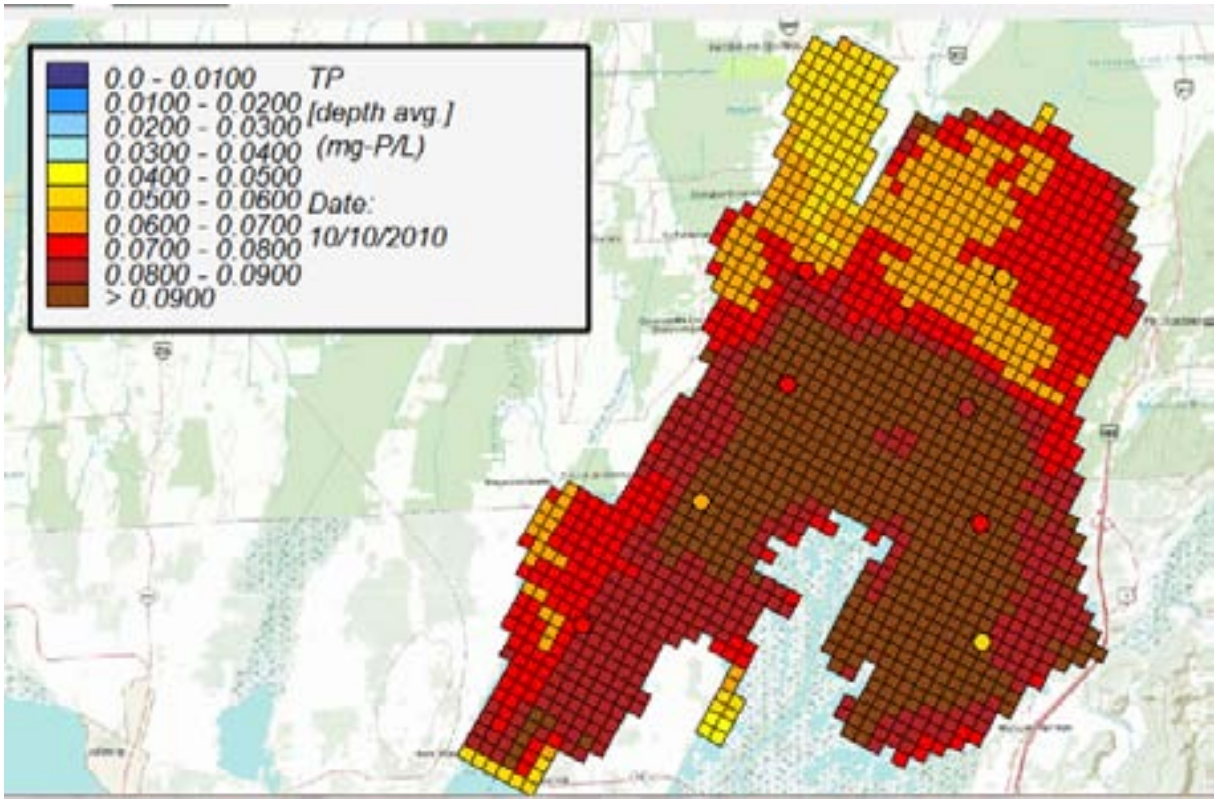

Figure 5-13. Map-based comparison of model (square cells) and data (circles) for TP on October 10, 2010

5.4.3 2006 to 2010 Long Term Calibration

The main focus of the water quality model calibration was obtaining a good agreement between the predicted and measured TP concentration from 2006 to 2010. Figure 5-15 and 5-16 shows the monthly average comparisons at VT DEC stations 50 and 51, respectively. The red dots represent the monthly average of measured data. The error bars on the data points indicate the standard deviation if more than one measurement was taken that month. The solid blue line represents the monthly average model predicted temperature from the same model cell that the data station is located. The dashed lines represent the highest and lowest five-day average as calculated by the model. While some years are better than others, overall the model is matching the data very well. Monthly average TP concentrations range from 40 ug/L to 90 ug/L. Additional calibration graphics for chlorophyll and dissolved oxygen are shown in Appendix A. The model was able to accurately capture the late 2010 summer and fall P concentrations very well. In general the model was predicting higher variability in P concentrations at station 50, which was not always reflected in the monitoring data Again, the proximity of station 50 to the mouth of the Missisquoi River suggests that the model might be limited in its ability to capture the solids and nutrients dynamics following high flow events. The dissolved phosphorus comparisons are shown in Figure 5-17 and 5-18 for VT DEC Stations 50 and 51, respectively. The predicted DTP concentration is typically within 10 ug/L of the average monthly measured concentration, but deviates substantially from the data in 2010. This is likely due to an under prediction of the portion taken up by algae during this time period.

5.5 MODEL CONFIRMATION

Figures 5-19 and 5-20 compare the monthly average predicted and measured TP and DTP concentrations, respectively from 2001 to 2005 at VT DEC Station 50. Again the model is matching the data well in most years, which is similar to that of the calibration period. A summary of the summer average TP concentration is shown in the next section.

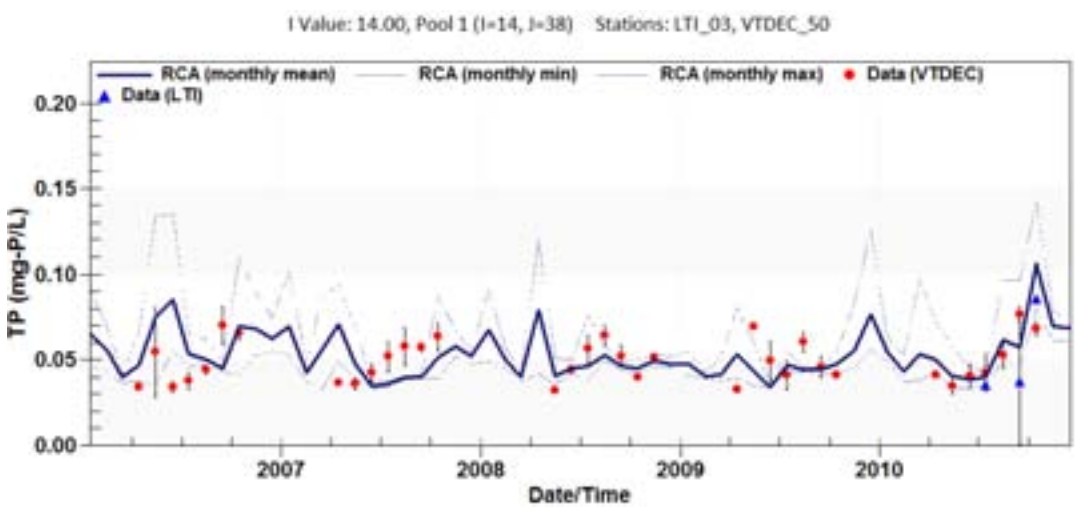

Figure 5-14. Monthly average TP at VT DEC Station 50 from 2006 to 2010.

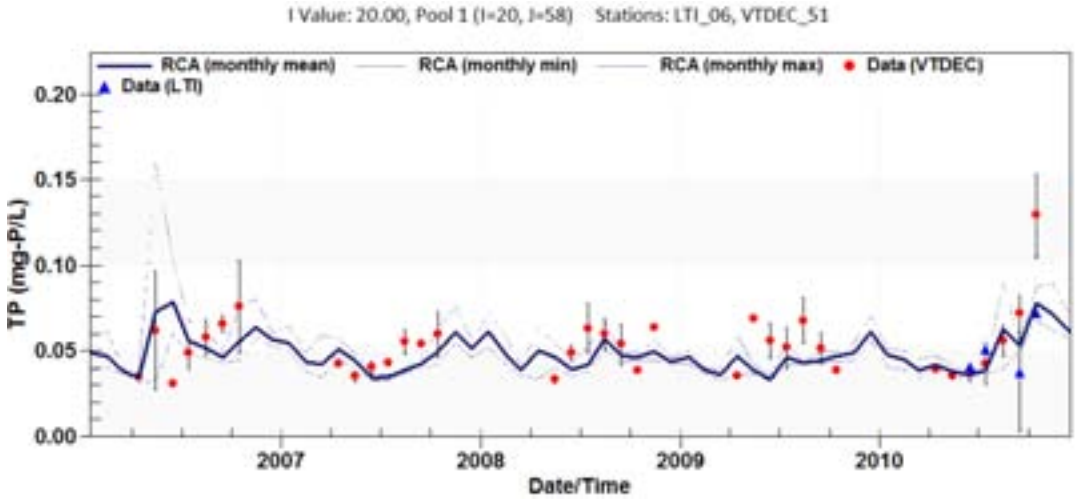

Figure 5-15. Monthly average TP at VT DEC Station 51 from 2006 to 2010.

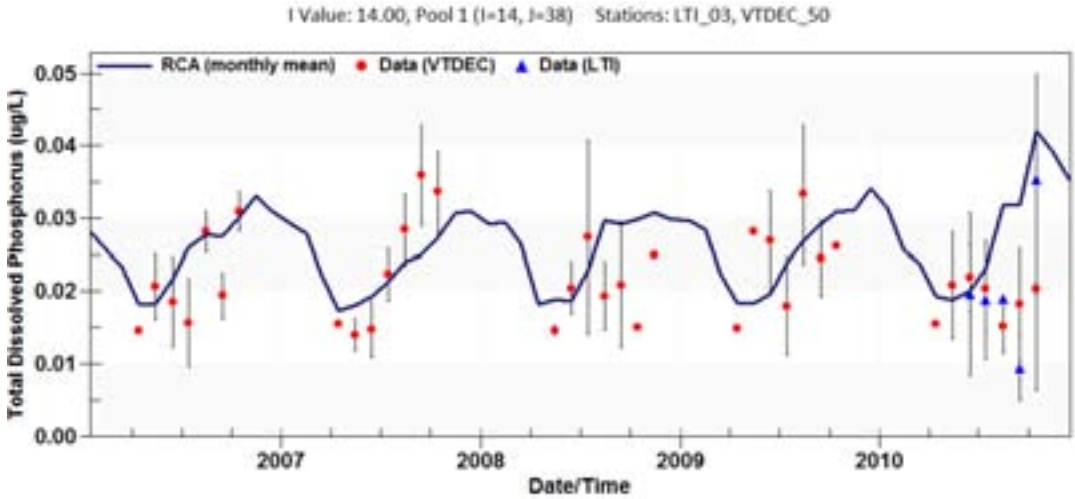

Figure 5-16. Monthly average DTP at VT DEC Station 50 from 2006 to 2010.

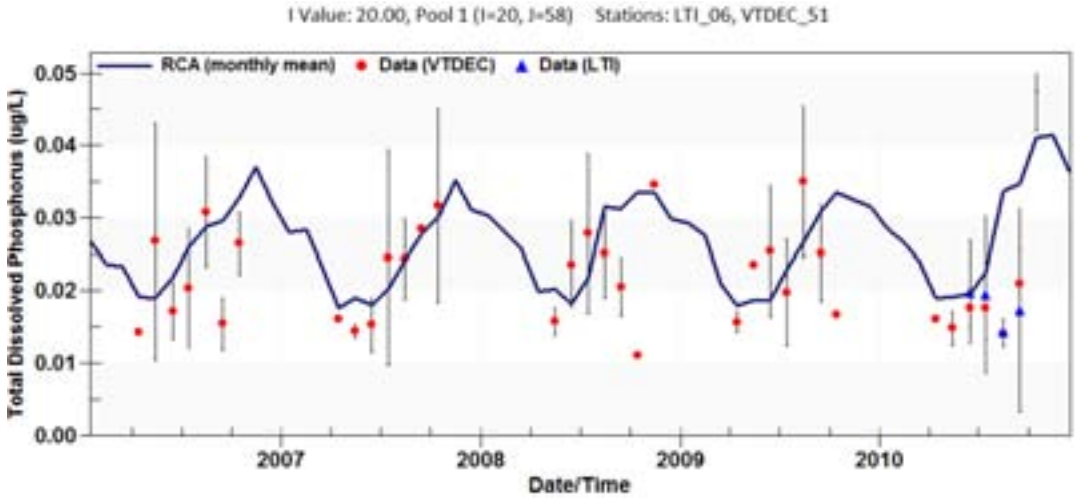

Figure 5-17. Monthly average DTP at VT DEC Station 51 from 2006 to 2010.

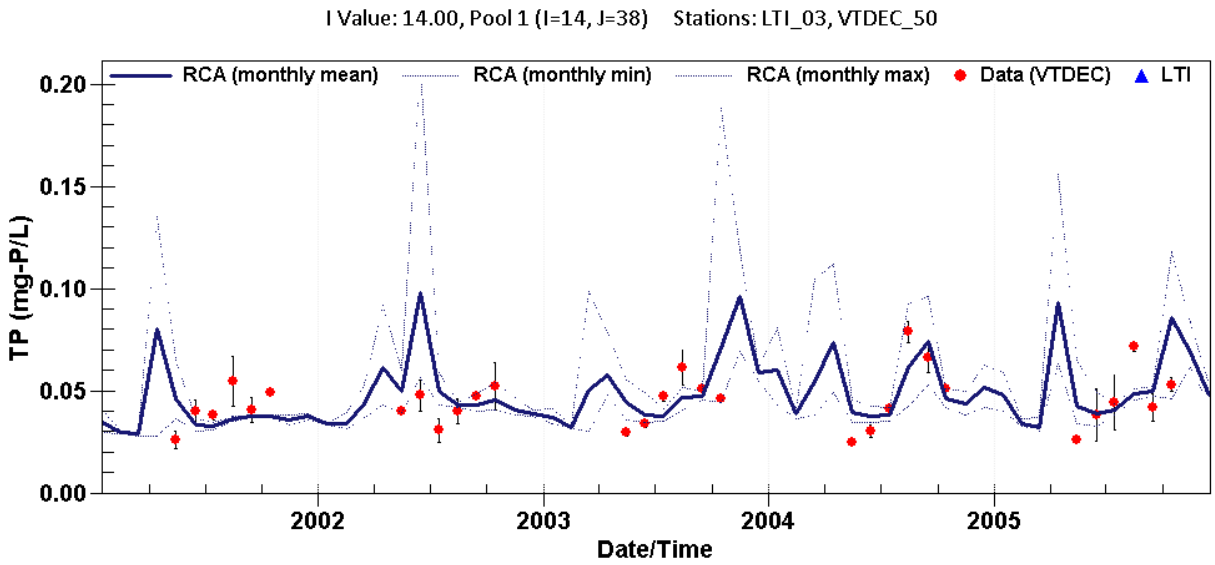

Figure 5-18. Monthly average TP at VT DEC Station 50 from 2001 to 2005.

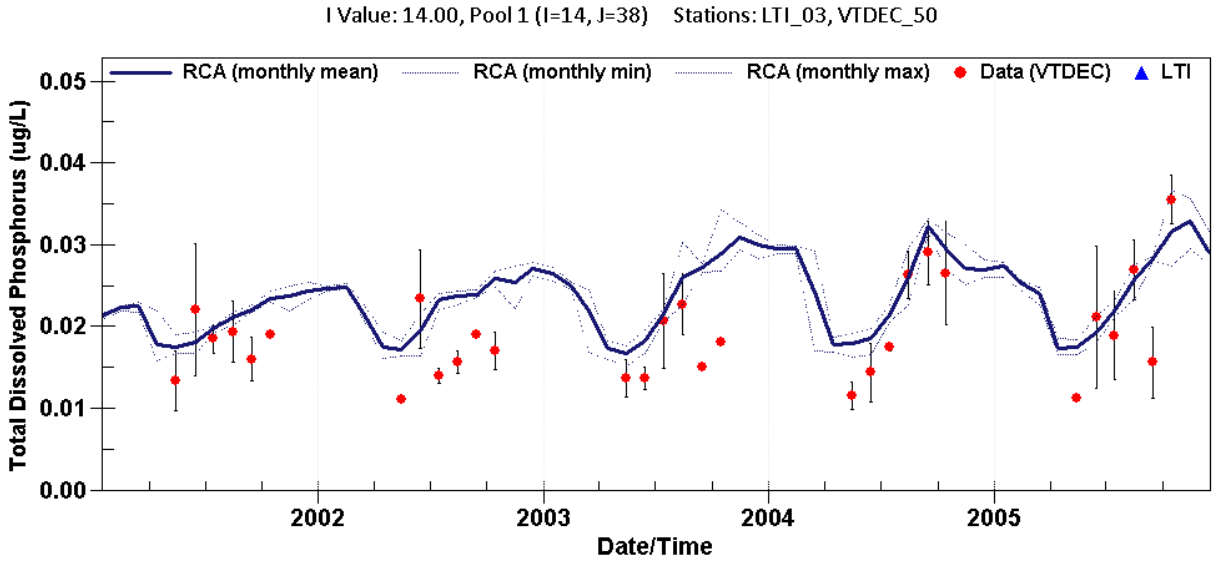

Figure 5-19. Monthly average DTP at VT DEC Station 50 from 2001 to 2005.

5.6 SUMMER AVERAGE TP COMPARISON

The previous sections showed how the model performs on a daily scale in 2010, and on a monthly scale from 2001 to 2010. However, the original model calibration target was a long term mass balance model that can be used to assess the relative contributions of phosphorus from major source categories. Figure 5-20 below shows the annual summer average (June to September) surface bay-wide model estimated TP concentration versus the measured surface concentration over the same time period at VT DEC stations 50 and 51. The standard deviation of the 5-day average bay-wide model results and standard deviation for all of the data points for a given station from June to September is shown by the error bars. This plot shows that the average model predicted concentration for a given year is very close to the measured value and well within the standard deviation of the measured data. Table 5-3 presents a statistical summary of the calibration metrics for every year. The ten-year model and data averages are almost identical, with only a 2% difference. The year to year variation in the median relative error is very reasonable at 7%, and even the average relative error is 12%. These statistics demonstrate that the model is well calibrated to the season average TP concentration.

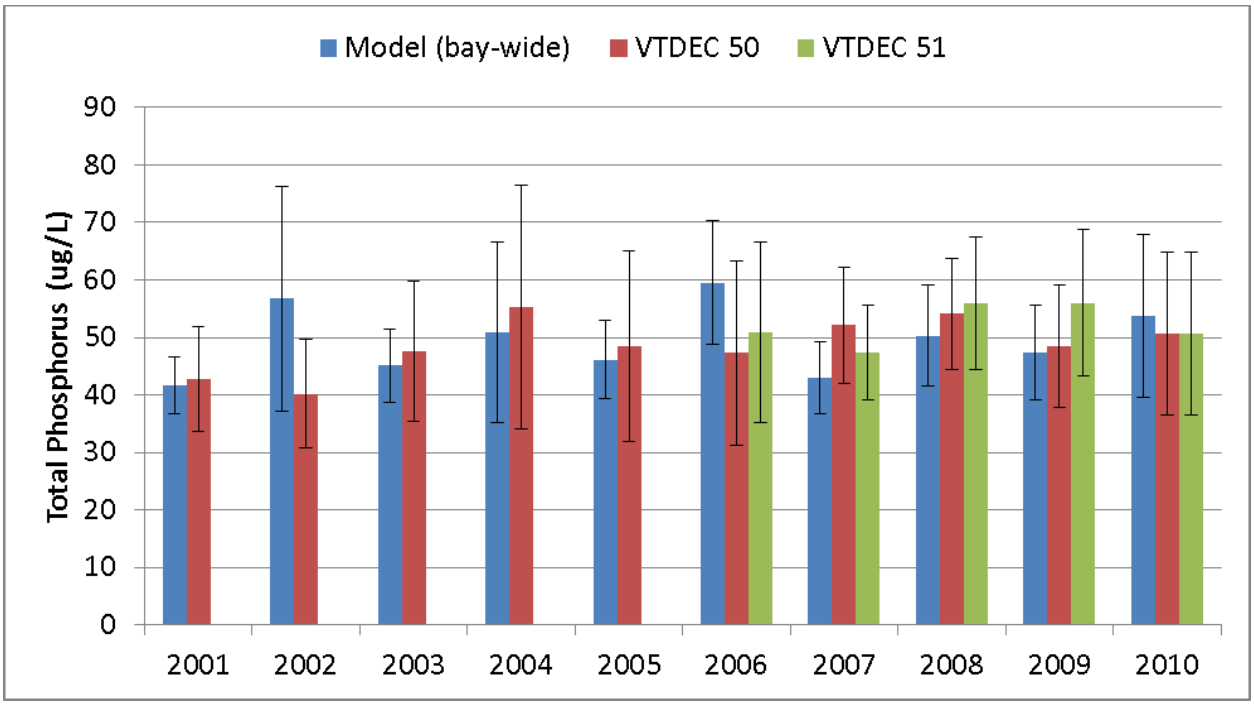

Figure 5-20. Bay-wide model predicted versus the measured summer average TP concentration (+/- stdev).

Table 5-3. Annual summer average TP (ug/L) model predicted versus data.

Year	Model	VTDEC 50	% Diff.
2001	41.7	42.7	-2
2002	56.7	40.2	41
2003	45.1	47.6	-5
2004	50.9	55.3	-8
2005	46.1	48.5	-5
2006	59.5	47.3	26
2007	43	52.1	-17
2008	50.3	54.1	-7
2009	47.4	48.4	-2
2010	53.7	50.6	6
Average	**49.5**	**48.7**	**2**
Average absolute % Error			12
Median absolute % Error			7

6. APPLICATION

This section describes the types of products that can be derived from output of the calibrated phosphorus model of Missisquoi Bay. The diagnostic simulations aggregate the inputs and outputs of the model into a mass balance understanding of phosphorus within the system, while the load reductions scenarios predict the expected bay-wide average P concentration under a range of tributary P reduction conditions.

6.1 DIAGNOSTIC

Diagnostic applications refer to analysis or sensitivities that can be conducted from the calibration model to identify or characterize the model.

6.1.1 Mass Balance

The primary objective of this project is to generate a mass balance understanding of phosphorus in Missisquoi Bay. A simple mass balance diagram is shown below for 2010 (Figure 6-1) and an average mass balance diagram for the 2001 to 2010 simulation period is shown in Figure 6-2. The tributary term includes all three major tributaries plus the point source of TP added at the mouth of each tributary. The outflow term represents the net flow of phosphorus out of the open boundary of the model. The deposition term to the sediments represents the gross deposition of phosphorus to the sediment bed. The flux of phosphorus from the sediments to the water column includes both resuspension and diffusion driven fluxes. The delta in the water column represents the change in the water column mass of phosphorus over the simulation period. The same is true for the delta term in the sediment box. The burial of phosphorus out of the active sediment layer (10 cm) is also shown on the graphic.

For 2010 (Figure 6-1), the annual mass balance is shown on the left and the June to September mass balance is shown on the right. All units are metric tons per time period of the mass balance. In 2010, phosphorus deposition is similar in magnitude to outflow. However, additional phosphorus is added to the water column from the sediments. The net effect is almost no change in the mass of total phosphorus in the water column over the year. Flux of TP to the water column accounts for 21% of the total P inputs to the water column. During the June to September period sediment flux accounts for 39% of the total P inputs. Over the ten year period sediment flux averages 20% and 43% of the total P inputs during the whole year and summer period, respectively.

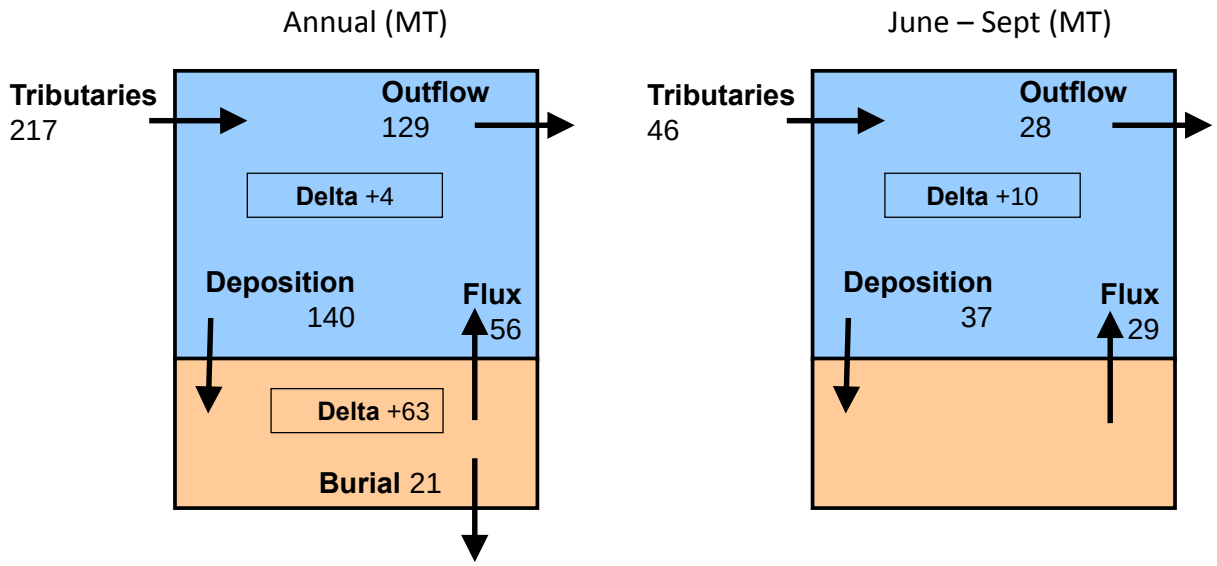

Figure 6-1. Total phosphorus (metric tons) mass balance for 2010.

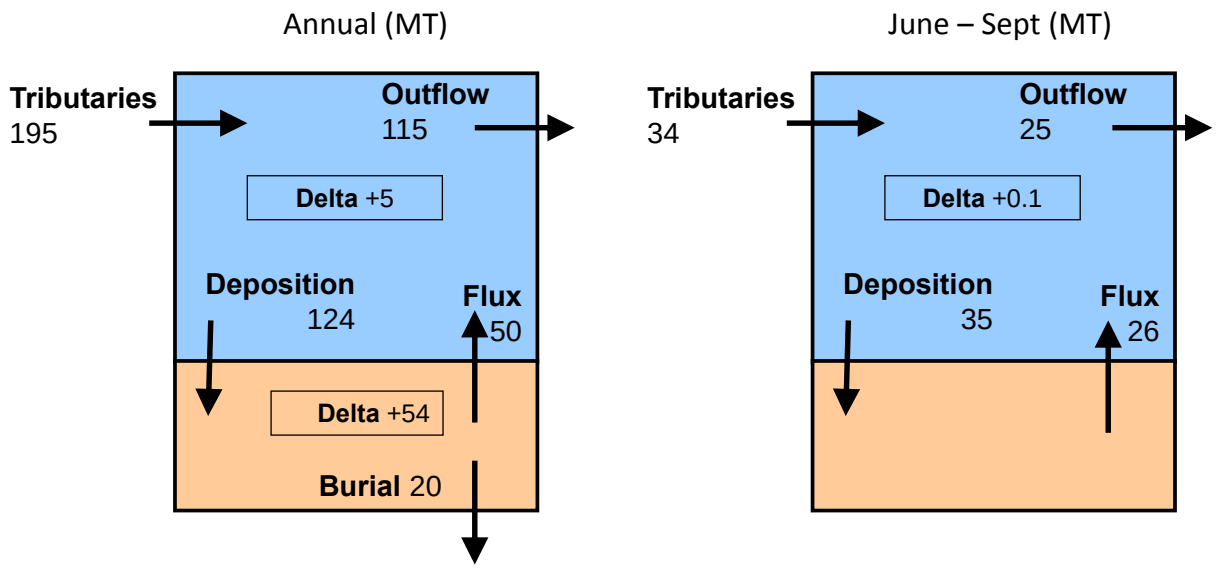

Figure 6-2. Average total phosphorus (metric tons) mass balance for 2001 to 2010.

Tables 6-1 and 6-2 below show the annual and summer (June to September) mass balance components from 2001 to 2010 for the whole lake. On average TP in Missisquoi Bay is very close to being at steady-state with the current external phosphorus loading.

Table 6-1. Annual mass balance components (metric tons) from 2001 to 2010.

Source	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	Avg
Tributary	115	197	191	195	211	308	206	177	130	217	195
Deposition	82	120	117	130	127	173	130	123	95	140	124
Outflow	71	111	103	126	122	177	122	110	81	129	115
Sediment Flux	35	44	50	49	53	52	52	53	55	56	50
Sediment Burial	16	20	18	21	21	35	19	17	10	21	20
Delta Sed.	31	56	49	60	54	86	59	52	30	63	54
Delta W.C.	-3	10	22	-12	14	10	5	-3	8	4	5

Table 6-2. Summer mass balance components (metric tons) from 2001 to 2010.

Source	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	Avg
Tributary	6	70	15	62	15	59	10	40	20	46	34
Deposition	19	48	27	45	27	57	23	36	28	37	35
Outflow	7	45	12	37	14	47	14	31	18	28	25
Sediment Flux	18	22	26	25	28	27	27	29	29	29	26
Delta W.C.	-2	-1	1	5	2	-19	0	2	3	10	0

6.1.2 Sediment flux

One of the primary objectives of this project was to evaluate the impact of internal sediment flux on TP concentrations on the phosphorus budget of Missisquoi Bay. Figure 6-3 below shows the impact of internal sediment release on the water column at VT DEC station 51 in 2010. The blue line (base) represents the calibrated model and the green line (SedOff) simulates the same period, but with the sediment diagenesis model turned off. This effectively eliminates feedback between the sediment and the water column for both diffusive fluxes of phosphorus and resuspension driven fluxes of phosphorus to the water column. This particular model run was only conducted to "bound" the impact of the sediment on the water column. It was not meant to simulate a specific management action (such as an alum treatment). The bay-wide average water column TP concentration from June to September decreases from 54 ug/L to 31 ug/L (a 43% decrease) when fluxes of TP from the sediment are eliminated. The spike in TP in early August 2010 is the result of a high flow event that discharges a considerable load of TP into the bay. Higher flows again in October and November elevate TP concentrations.

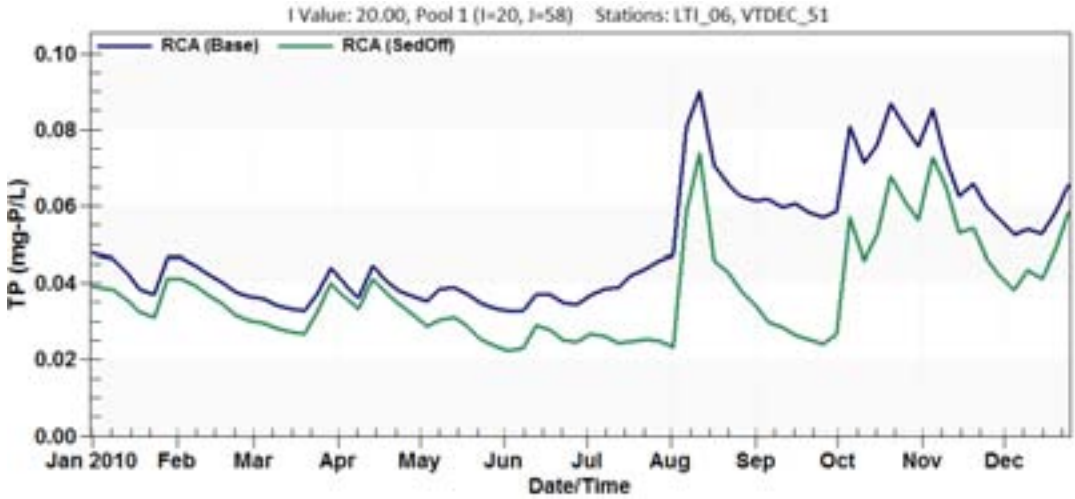

Figure 6-3. TP concentration at VT DEC station 51 with and without sediment flux.

On a longer term scale the monthly average dissolved phosphorus flux to the water column is shown in Figure 6-4 below for VT DEC station 51. The flux rate averages 0.5 mg-P/m^2/d in the cold winter months and increases to approximately 2.5 mg-P/m^2/d in August. The increase in the rate is due to an increase in sediment temperature as well as a decrease in bottom water DO. The pore-water diffusion rate has a temperature correction term on it (see Table 5-2) that increases the rate with increasing temperature. In addition, the PO4 partition coefficient increases as dissolved oxygen in the bottom layer decreases. This is the mechanism that releases dissolved P from the sediments under anoxic (or near anoxic) conditions. In 2008, the bottom DO was well below 5 mg/L for almost the entire month and subsequently the DPO4 release rate is significantly higher. Sediment flux experimental data from the Miner Institute is shown in Table 6-3. At station 6 (VT DEC station 51), which is in the center and deepest portion of Missisquoi Bay, the highest oxic and anoxic flux rates were measured at 0.42 and 5.20 mg-P/m^2/d, respectively. These rates are very similar to the rates shown in Figure 6-4.

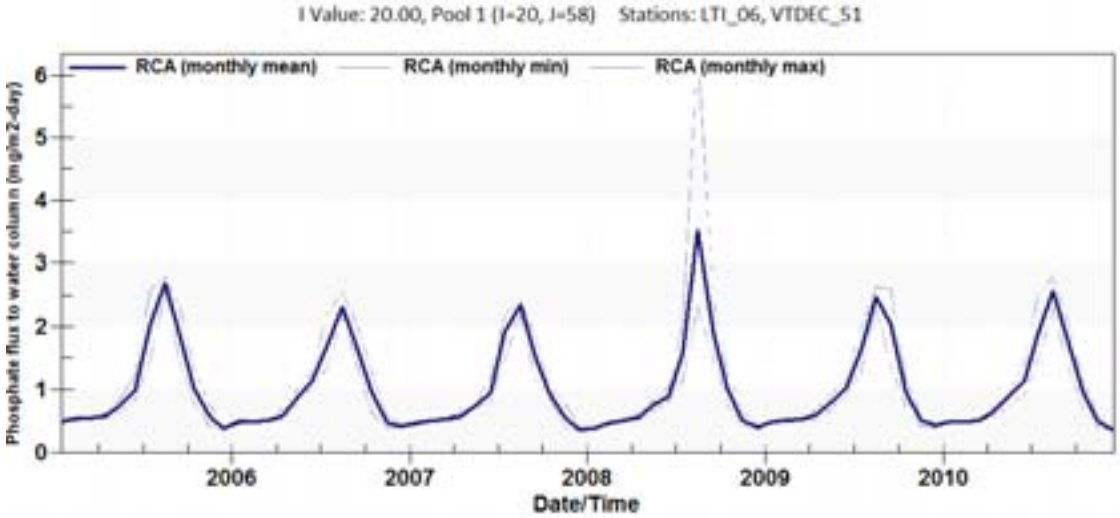

Figure 6-4. Model predicted P release rate (*mg P/m^2/d)* at VT DEC station 51.

Table 6-3. Summary of P release data for Missisquoi Bay.

Station	SRP release rate (mg P/m^2/d)	
	Anoxic	Oxic
1	*6*	*0.07*
3 (50)	*3.8*	*0.02*
6 (51)	*5.2*	*0.42*
10	*4.4*	*0.38*
Mean	*4.9*	*0.2*
Std. dev.	*1.0*	*0.2*

6.2 LOAD REDUCTION SCENARIOS

The calibrated model was run in a forecasting scenario mode to estimate the summer average TP concentration under a range of tributary TP load reductions. For each run, total phosphorus concentrations were reduced for all of the tributaries in equal proportions for every day of the year. Inorganic solids concentrations were not reduced for any of the scenarios. Atmospheric conditions, tributary flows, and concentrations from 2001 to 2010 were repeated three consecutive times to produce a continuous 30 year simulation. Tributary load reductions of 25%, 50%, and 75% were run for the 30 year period. A base simulation was also run for 30 years to simulate a 0% load reduction. Sediment concentrations of phosphorus were carried over between consecutive 10-year runs to produce a valid representation of sediment phosphorus trends for each load reduction scenario. While the across the board TP concentration reductions with no reductions in inorganic suspended solids simplify may not match the expected change that might occur with actual nutrient reduction practices, further development of future nutrient and solids scenarios is out of the scope of this project. The load reductions here are only meant to generate a load response curve between total annual TP load and whole-lake annual average TP concentrations over a very long simulation period (30 years). It should be noted that the load reductions scenarios posed here are not designed to represent actual conditions. They merely show what would have happened if the previous 10 years were run with across the board tributary load reductions. Future conditions will have different hydrology, P loads, and atmospheric conditions. A watershed model would be needed to accurately further refine the hydrology and nutrient and solids concentrations.

A plot of the June to September average water column TP concentration is shown below in Figure 6-5 for each of the load reduction scenarios. These scenario forecasts are also compared to attainment of the 25 ug/L State of Vermont standard for the water column. Faint dotted lines show a linear regression trend for each load reduction scenario. For the base case, the average TP concentration is increasing slightly with time. This is due to an increase in sediment TP concentrations over this time period, suggesting that the sediments have not quite reached equilibrium yet with the incoming/base TP loads. This forecast trend can also be influenced by the uncertainty of the net sedimentation rate used in the model. Additional sedimentation rate studies with radioisotope dated sediment cores could reduce this uncertainty. The graph also shows an attenuation of the year to year variability in TP concentrations as tributary loads are reduced. This trend suggests that tributary loads have a large influence on TP concentrations; however, as these loads are reduced the influence of sediment feedback plays a more important role. Also notice how the water column concentration for the 25% load reduction scenario is slowly increasing over time. The initial reduction is due to the tributary load reduction, but the

small increase is due to an increase in the sediment P concentration. Figure 6-6 shows the change in sediment TP concentrations over time for the base and 75% reduction load simulations. The P concentration for the base case is increasing, suggesting that the sediments are not at steady state with the long term P inputs. This assumes that the initial condition of P was set appropriately at the start of the simulation.

The graphic shows that in order to meet the 25 ug/L standard in the near future it is necessary to reduce tributary inputs by at least 75%. While this seems extreme, it shows that there is another loading mechanism that is contributing a significant amount of TP to the water column. This source of TP is the internal release of phosphorus from the sediments. As shown previously in Figure 6-2, the internal load of phosphorus to the water column represents 39% of the TP load during the June to September period. And the influence of that feedback does not seem to be diminishing significantly over the 30 year simulation period. This is consistent with the relatively slow net sedimentation rate in this system. It should also be noted that sediment feedback fluxes for other eutrophic systems such as Lake Erie will also take a very long time to diminish significantly.

Figure 6-7 shows a time averaged representation of the load reduction scenarios along with results from a set of runs where sediment flux to the water column is turned off. For each scenario the June to September bay-wide average TP concentration is averaged for the first ten years of the scenario run. Also shown on the plot is the 2001 to 2010 June to September average TP concentration (47 ug/L) as measured at VT DEC station 50. This value is very close to the model predicted ten year average concentration of 49 ug/L. This suggests a good agreement between model and data for the base run. These concentrations are significantly higher than the June to September average TP concentration of the Missisquoi River of 35 ug/L as shown in Table 4-4, again suggesting there is a significant additional internal contribution of phosphorus from the sediment.

If flux from the sediment is eliminated from the base case, then there is a significant decrease in the water column TP concentration down to 30 ug/L. This represents a 40% decrease in the June to September average water column concentration. At a load reduction of 75% the bay wide TP concentration without sediment feedback decreases to 9 ug/L, which represents a 66% decline from the same run with sediment flux included.

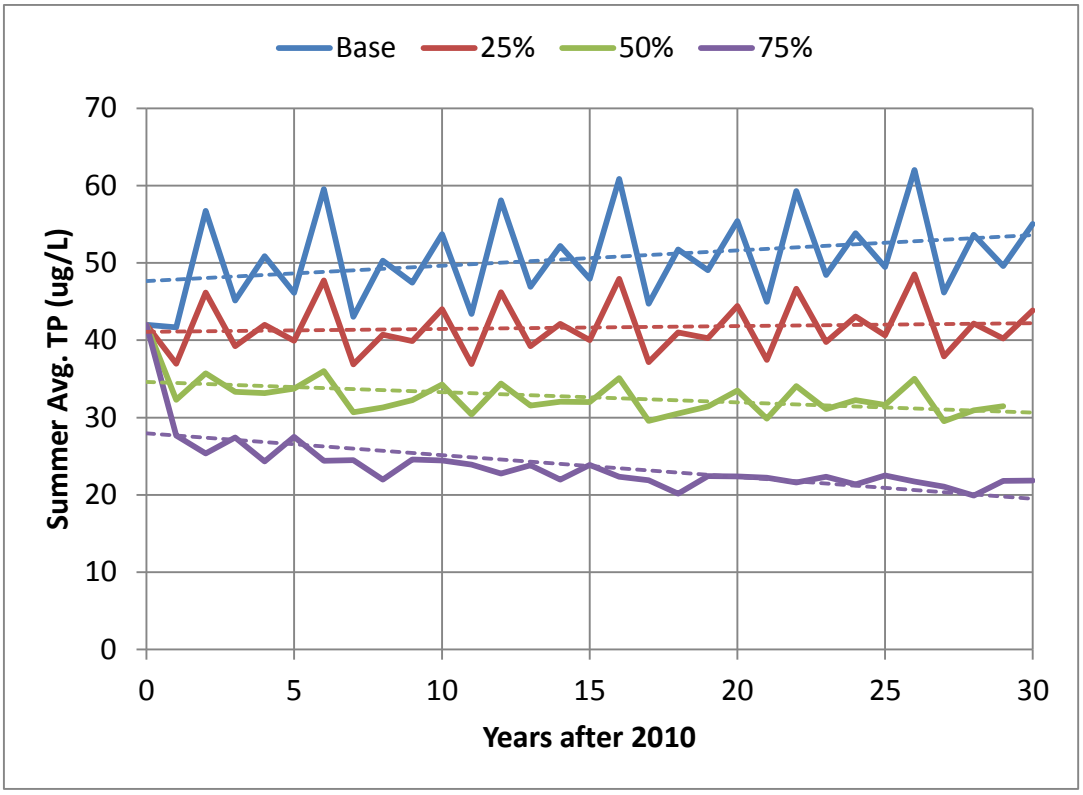

Figure 6-5. Bay-wide June-Sept TP concentration for 30 years after 2010.

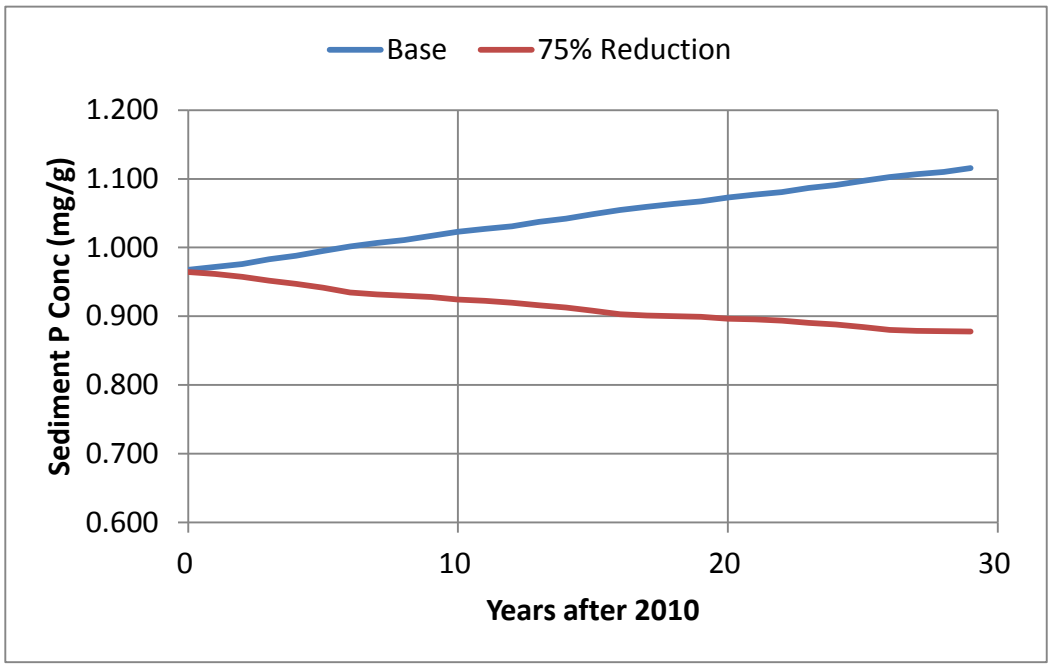

Figure 6-6. Change in sediment P concentration over time for base and 75% load reduction

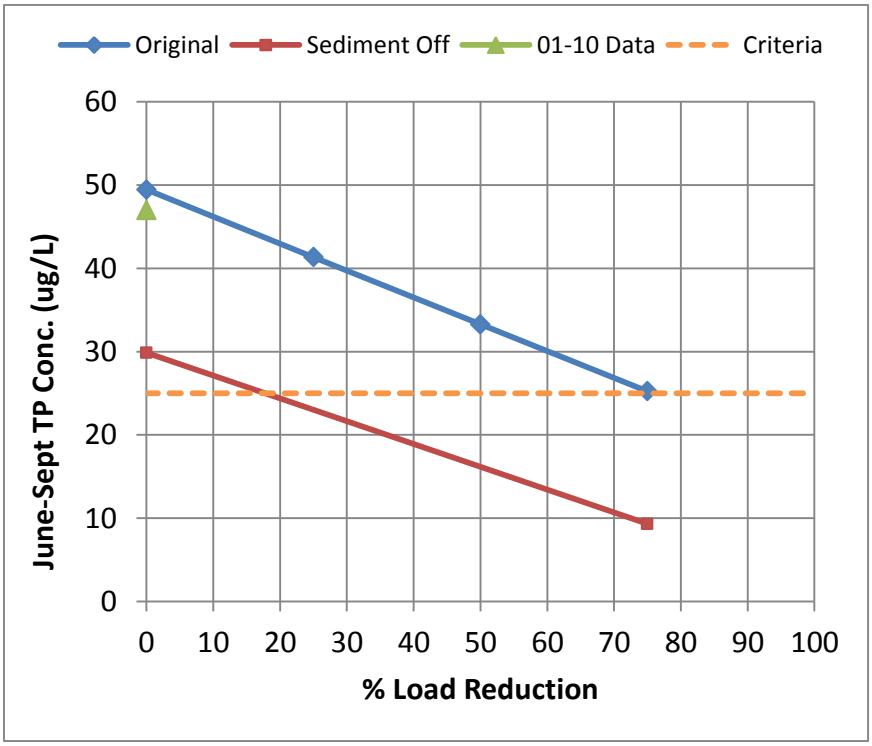

Figure 6-7. Average summer TP concentration for first 10 years of load reduction scenario run with and without sediment feedback.

7. CONCLUSION AND RECOMMENDATIONS

7.1 DISCUSSION OF SEDIMENT P FLUX

A closer look into the mass balance information obtained from the water quality model shows that the diffusive flux of phosphorus from the sediments averages approximately 31 MT/yr across the whole bay from 2001 to 2010. Resuspension of bottom sediments in the shallower parts of the bay contributes an additional 19 MT/yr. Resuspension rates are highest in the spring and late summer and fall when wind speeds are higher. The combined impact is the delivery of an additional 50 MT/yr of phosphorus to the water column per year. The timing of each of these sediment flux components is different as the diffusive fluxes are highest in the summer and the resuspension fluxes are higher in the fall. The average June to September diffusive flux is approximately 18 MT, while the resuspension flux is 8 MT for a total of 26 MT. While every attempt was made to accurately parameterize both the diffusive and resuspension fluxes only the total flux of phosphorus to the water column is known with certainty as it was adjusted during calibration in order to match the water column TP concentrations. Very little ambient solids data were available to develop and calibrate the resuspension portions of the model. However, the diffusive sediment flux rates appear to be reasonable based on release rates estimated as part of this project.

The historical TP monitoring data collected by the VT DEC consistently show an increasing trend in TP concentrations between April/May and August. The only reasonable source of additional TP during this low tributary flow time period would be from the sediments. We can make a back of the envelope calculation of the additional P mass required to match the increase in P concentrations during this time period. This assumes that the lake is completely mixed and water quality measured at station 51 is representative of the average concentration. The average minimum April/May TP concentration from 2001 to 2010 at Station 50 is 27 ug/L. The average maximum August concentration is 66 ug/L, which represents an increase of 39 ug/L. Assuming a lake volume of 0.30 km^3 (lake level at 10 year average of 96.7 ft) this represents a net phosphorus mass of 12 MT contained in the water column. While this data-based estimate is lower than the model estimated diffusive flux (18 MT), this calculation doesn't take into account the mass of phosphorus needed to overcome the net deposition loss of TP to the sediments during this time period. If we use the model's estimate of the average net TP deposition from 2001 to 2010 from June to September the average is 9 MT. This would mean that diffusion alone would have to add 21 MT of P over this time period to match the P concentrations at station 50, which is much closer to the model estimate of 18 MT.

This simple back of the envelope calculation validates the sediment flux component and puts the average summer diffusive flux of TP from the sediments at 18 MT and the annual average flux at 31 MT. Because the diffusive flux is more driven by sediment TP concentrations, which take decades to change, it is likely that Missisquoi Bay will continue to receive a large diffusive flux of P to the water column even if loads are reduced. The long term response of sediment P concentrations to changes in incoming loads was illustrated with the load reduction scenarios.

7.2 CONCLUSION

This report describes LimnoTech's development, calibration, and application of a linked hydrodynamic-water quality model of Missisquoi Bay, Lake Champlain. The model was developed as a tool to construct a mass balance understanding of internal and external loads of phosphorus to the water column and to gain a quantitative understanding of the magnitude and

timing of total phosphorus response to changes in the external loading rate. Monitoring data was utilized from several organizations, including data collected as part of this study, to develop model inputs and provide for a robust calibration dataset to evaluate model performance. The calibrated model was then utilized in a series of application scenarios to generate a relationship between internal and external TP loads and summer average bay-wide TP concentration response scenarios.

As discussed in the approach section, the water quality model utilized for this project, a LimnoTech modified version of the publicly available RCA model framework, is a state-of-the-art advanced eutrophication model that has capabilities well beyond the scope of this project. While the underlying model is fairly complex, the primary focus of the calibration process was total phosphorus. Every effort was made to input accurate loads of total phosphorus and loads for other parameters needed by the model utilized existing data or literature values.

The advantage of configuring RCA for this project is that it can easily be refined and updated with revised loads and recalibrated to meet other needs of the LCBP in the future, such as the impact of an invasion of Dreissenid mussels on the development of *Microcystis* blooms in the bay. A simplified phosphorus model would only have value for this project to answer a limited range of questions. The robust model applied here could be further developed to link phosphorus loads and concentrations to phytoplankton response. While phytoplankton was dynamically simulated in the present application adjustments were not made to coefficients to match chlorophyll data. A casual review of the chlorophyll data reveals that there are shorter term phenomena that contribute to large spikes in surficial chlorophyll concentrations. The dynamic simulation of algal blooms requires additional model calibration and a refined understanding of sediment release mechanisms and light extinction relationships.

The results of the model application provided useful insights into the phosphorus cycle in Missisquoi Bay. The mass balance results showed that the flux of phosphorus from the sediments to the water column is an important part of the phosphorus budget, especially during the low flow summer months, when additions of phosphorus to the water column can contribute to nuisance algal blooms. Future work can expand the phosphorus model to dynamically simulate algal abundance, more specifically the abundance of nuisance blue-green algae.

7.3 RECOMMENDATIONS

The recommendations below address data gaps that were identified throughout the course of this project that would further refine the phosphorus mass balance and the development of a full eutrophication model of Missisquoi Bay.

7.3.1 Data Gaps

The recommendations below address specific data gaps that were encountered during the model development, calibration, and application process. Each one is designed to improve our understanding of the system to improve future modeling efforts and decrease uncertainty about model inputs and major phosphorus transport pathways.

Recommendation #1 – Collect additional parameters during routine sampling of the tributaries and bay.

The tributary sampling program includes the collection of TSS samples, while the bay sampling program does not include TSS samples. Collect TSS samples at the bay stations to permit calibration of solids modeling of Missisquoi Bay, including the effects of wind-driven

resuspension. After the dried TSS filters are weighed, they should be burned in a muffle furnace at 550 °C until a constant filter weight is obtained. This will permit the calculation of the non-volatile and volatile fractions of total suspended solids. The bay monitoring program includes chlorophyll, while the tributary program does not include chlorophyll. During high flow tributary events the chlorophyll concentration of Missisquoi Bay can be heavily influenced by the chlorophyll concentration in the rivers. Collect chlorophyll samples in the tributaries (at least the Missisquoi River) so that algal biomass loads can be characterized.

Recommendation #2 – Coordinate atmospheric data collection at the Franklin County Airport.

The Franklin County airport began reporting quality controlled hourly atmospheric data in 2008 to NOAA. Work with them to maintain their year-round MET station. Add a solar radiation sensor to the MET package to improve the simulation of water temperature and algal growth.

Recommendation #3 – Install a real-time environmental monitoring buoy at VT DEC station 51.

The current sampling program captures a snapshot of environmental conditions on a weekly to bi-weekly basis. Install a real-time environmental monitoring buoy to provide a higher temporal resolution of water quality conditions. Equip the monitoring buoy with sensors to measure wind speed and direction, air temperature and relative humidity, and solar radiation (unless its measured at the airport). Install a multi parameter probe near the surface and/or bottom to monitor for water temperature, turbidity, conductivity, chlorophyll, and dissolved oxygen.

Recommendation #4 – Monitor nutrient and solids concentrations in the bay for several days after a large loading event.

While the current sampling program gives a good picture of nutrient concentrations across the summer season within the bay, it is uncertain how high tributary loads of phosphorus and solids are attenuated in the bay after a high flow event. A targeted high load sampling would mobilize during a high flow event and continue to monitoring for several days until nutrients concentrations returned to background levels.

Recommendation #5 – Collect and analyze additional high resolution sediment cores.

A crucial uncertainty in this modeling analysis was the rate of sediment and associated phosphorus burial rate in bottom sediments of the bay. Collection of a spatially distributed series of sediment cores followed by slicing the cores into 1 cm intervals and analysis of those slices for typical geochron radioisotopes (^{137}Cs and ^{210}Pb), sediment bulk density, and phosphorus concentration would provide information necessary for refinement of the sediment response time to phosphorus load reduction. This work would complement the work done by Levine et al (2011) where a single sediment core was collected from Missisquoi Bay.

7.3.2 Model Gaps

This section identifies several recommendations that would complement the work completed as part of this project. If all of the recommendations are carried out the MBPHOS model could be expanded used to provide a direct link between watershed actions and the recurrence frequency of blue-green algae blooms.

Recommendation #1 – Link Missisquoi watershed model to the bay model.

To better inform the load reduction scenarios we recommend that output from watershed models of flow, solids, and nutrients be used to generate more realistic load reduction scenarios that are based on specific watershed actions rather than across the board concentrations reductions. This would allow resource managers to connect watershed actions with water quality response variables to quantity the impact on water quality in Missisquoi Bay.

Recommendation #2 – Utilize remote sensing data as an additional model calibration tool.

Acquisition of water quality data from satellite images is a relatively low cost method to gather additional calibration datasets to verify model performance. A recent research project at the University of Vermont mapped cyanobacterial blooms in Missisquoi Bay (Wheeler et. al., 2011). Other parameters such as suspended solids concentration and dissolved organic matter can also be measured by satellites.

Recommendation #3 – Continue development and calibration of the water quality model to a larger set of water quality parameters.

The model presented above focused specifically on total phosphorus and represents a starting point to link phosphorus concentrations with algal abundance. While the present model framework includes all of the state variables required for a full algal model, coefficients were not adjusted to specifically match chlorophyll data and only a subset of state variables had temporally varying boundary conditions (time series). Also not calibrated during this project was the suspended solids and light extinction components of the model. Future development of the model should focus on calibrating to dissolved phosphorus, suspended solids, dissolved oxygen, algal abundance (chlorophyll), and algal speciation (algal counts) monitoring data. When this recommendation is combined a link to the watershed model (as highlighted in #1 above) to update reduction scenario loads this will allow managers to link specific watershed actions to reductions in blue-green algae concentrations.

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9. APPENDIX A – ADDITIONAL GRAPHICS

The graphics below show additional calibration and confirmation graphics for chlorophyll and dissolved oxygen (DO).

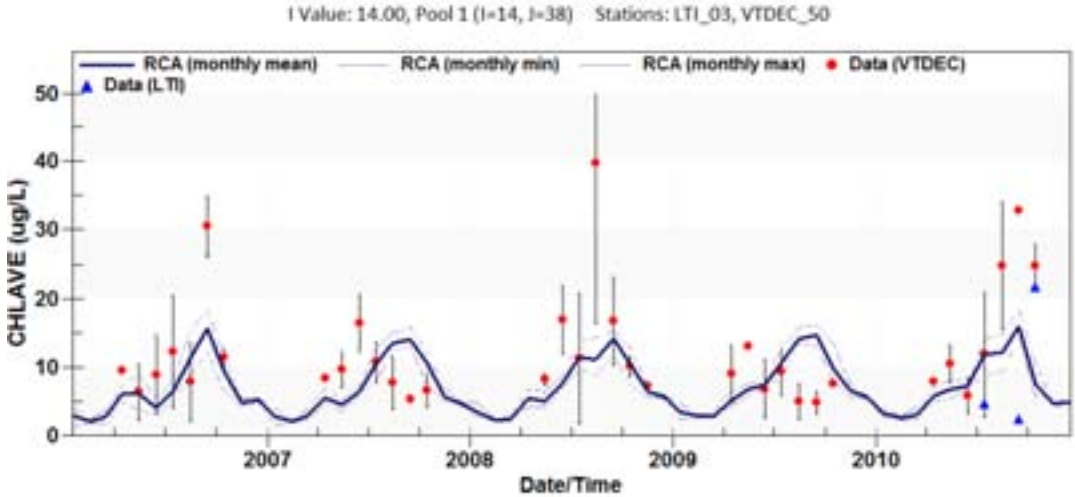


Figure A-1. Monthly average chlorophyll at VT DEC 50 from 2006 to 2010.

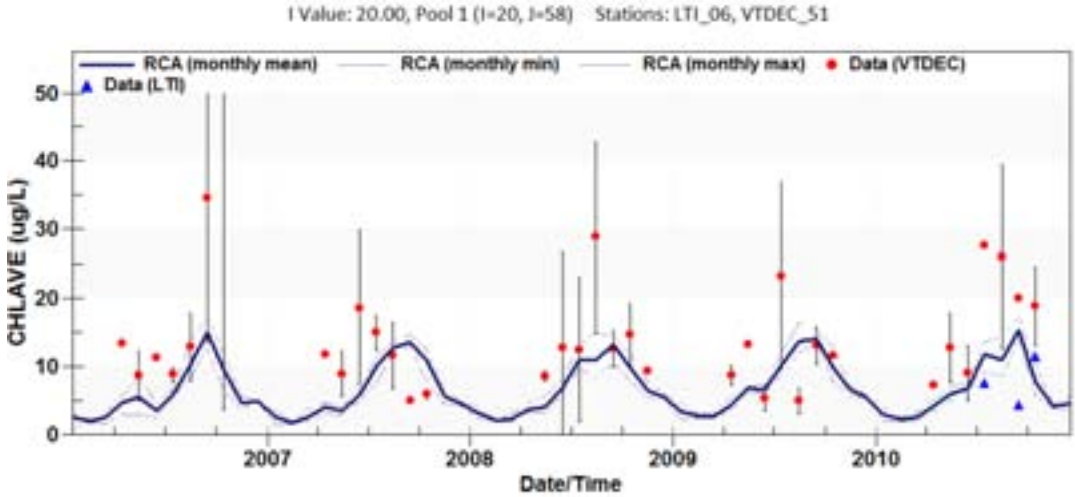


Figure A-2. Monthly average chlorophyll at VT DEC 51 from 2006 to 2010.

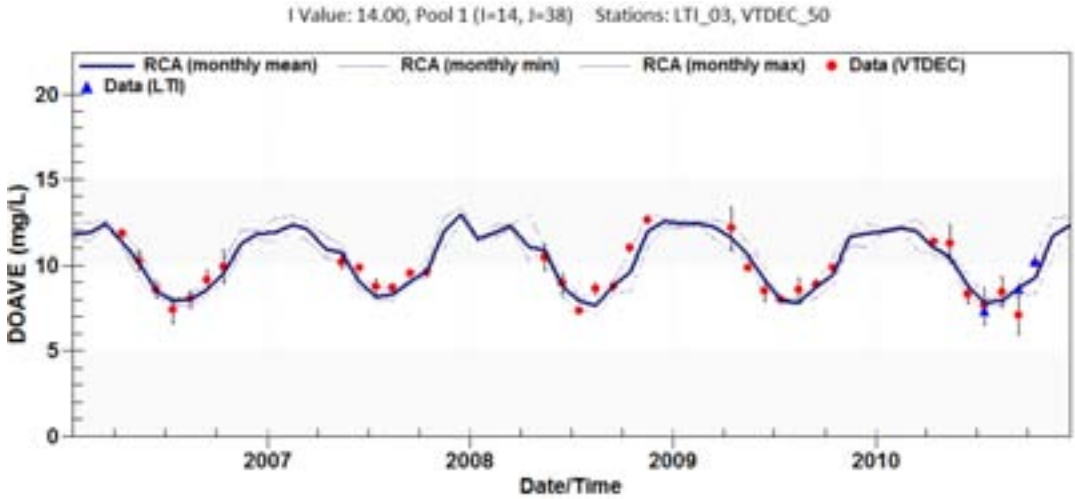


Figure A-3. Monthly average surface DO at VT DEC 50 from 2006 to 2010.

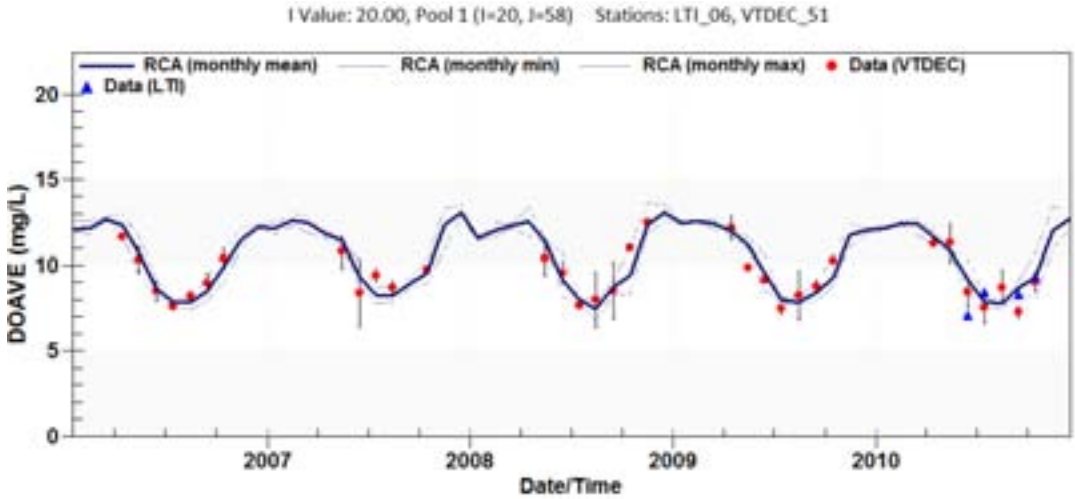


Figure A-4. Monthly average surface DO at VT DEC 51 from 2006 to 2010.

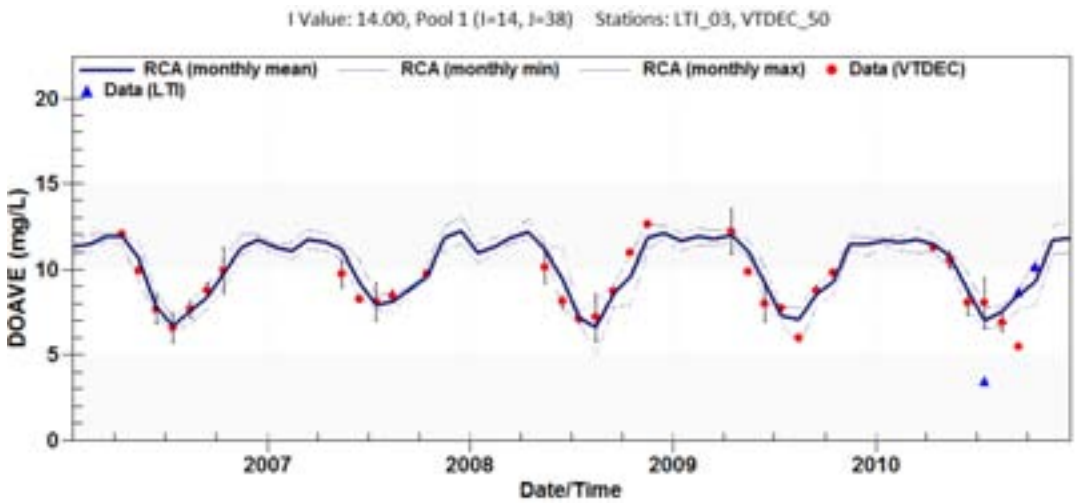


Figure A-5. Monthly average bottom DO at VT DEC 50 from 2006 to 2010.

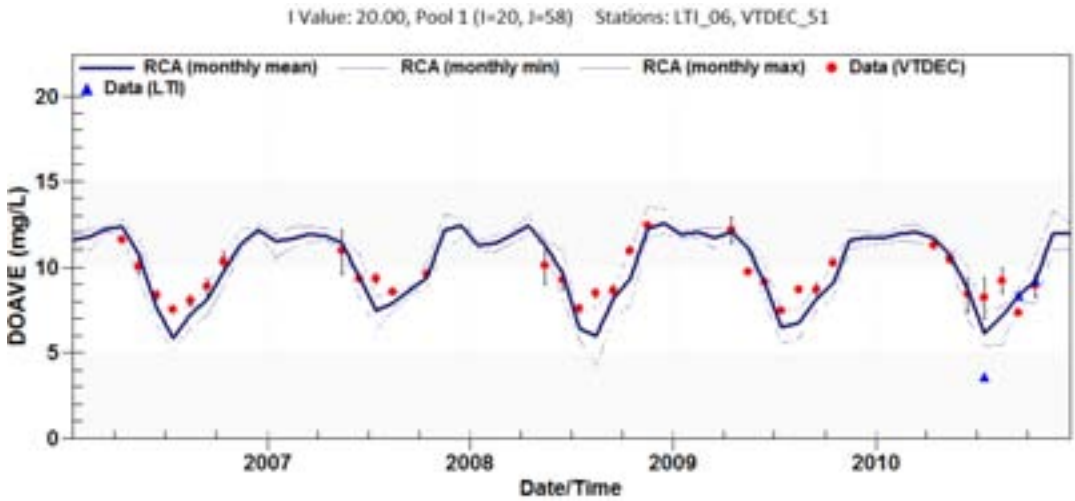


Figure A-6. Monthly average bottom DO at VT DEC 50 from 2006 to 2010.

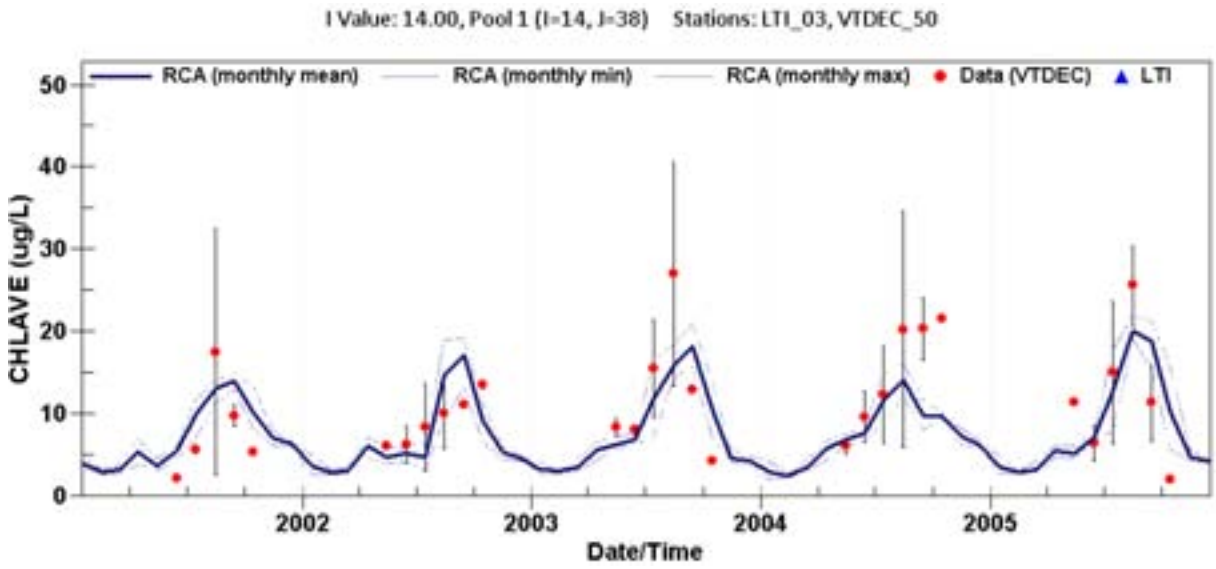


Figure A-7. Monthly average chlorophyll at VT DEC 50 from 2001 to 2005.

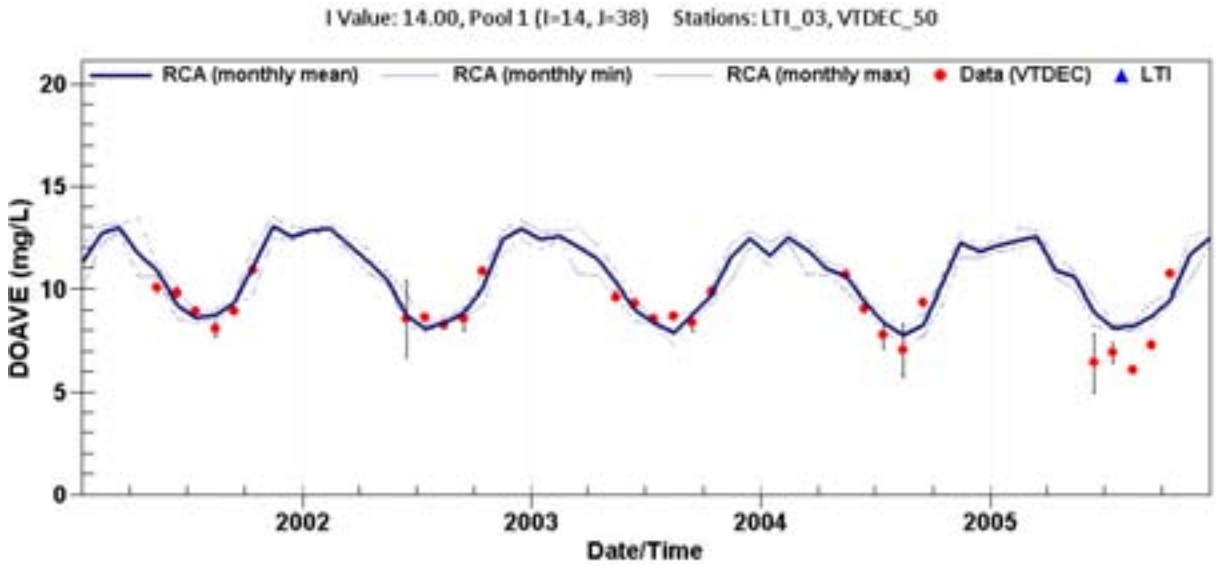


Figure A-8. Monthly average surface DO at VT DEC 50 from 2001 to 2005.

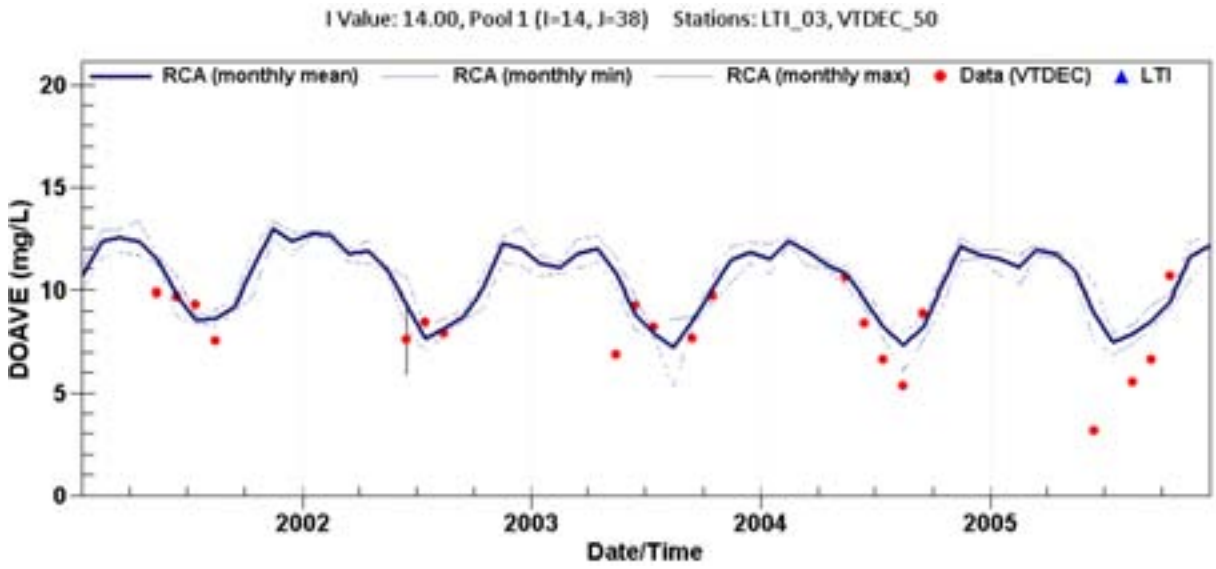


Figure A-9. Monthly average bottom DO at VT DEC 50 from 2001 to 2005.

10. APPENDIX B – 2010 FIELD DATA MEMORANDUM

[Attached separately]

Development of a Long-Term Phosphorus Mass Balance Model for Missisquoi Bay: Application to Assess the Contribution of Internal Phosphorus Loading

Data Memo Submitted to LimnoTech for Field and Laboratory Analyses
Conducted by the William H. Miner Agricultural Research Institute
Feb. 14, 2011

Stephen Kramer[1], Eric Young[1], Catherine Ballard[1], Laura Klaiber[1], and Lisa Klaiber[1]
[1]William H. Miner Agricultural Research Institute, Chazy, NY

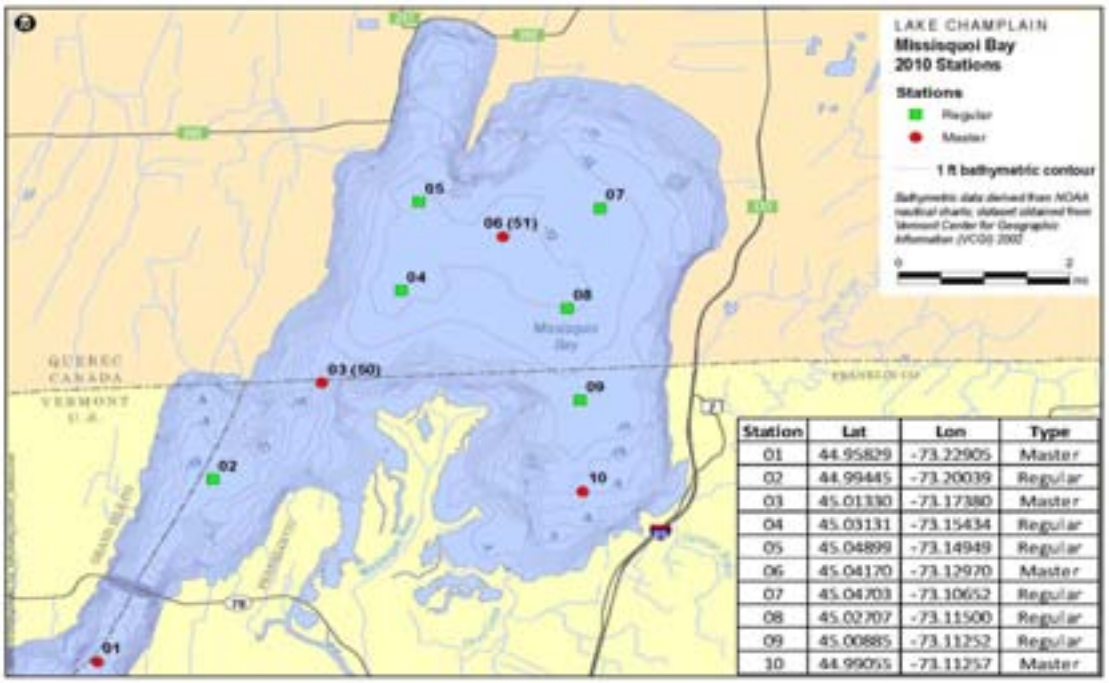
Objective

The objective of work reported here was to carry out the established field and laboratory procedures as defined in LimnoTech's research proposal submitted to the Lake Champlain Basin Program. Specifically, this included: (i) water and sediment sampling in Missisquoi Bay, (ii) a laboratory incubation experiment to quantify P release from sediment cores, and (iii) a sequential P extraction procedure to quantify different inorganic P pools in the sediment cores. Since detailed information on the methods and procedures utilized for this project has been previously reported, information on methods is given only where deemed appropriate.

Table 1. Date of sampling trips and approximate water conditions of Missisquoi Bay.

Cruise	Date	Conditions	Collector	Sample notes
1	6/3/10	**Pre-bloom**	*SK, EY, LBK	Initial cruise under extremely windy conditions. Sampled stations 5-9 only
2	7/15/10	**Pre-bloom**	SK, EY, LBK	Clear, calm conditions. Collected water column and first set of sediment core samples at all 10 stations.
3	9/3/10	**Bloom**	SK, EY, LMK	Clear, calm conditions. Collected water column samples at all 10 stations.
4	9/9/10	**Bloom**	SK, EY, LBK	Overcast, cool, 5-10mph W wind. Collected water column samples and second set of sediment cores samples at all 10 stations.
5	10/7/10	**Post-bloom**	SK, EY	Very cold, windy conditions. Collected water column samples at all 10 stations.

*SK = Stephen Kramer; EY = Eric Young, LBK = Laura Klaiber, LMK = Lisa Klaiber



Station	Lat	Lon	Type
01	44.95829	-73.22905	Master
02	44.99445	-73.20039	Regular
03	45.01330	-73.17380	Master
04	45.03131	-73.15434	Regular
05	45.04899	-73.14949	Regular
06	45.04170	-73.12970	Master
07	45.04703	-73.10652	Regular
08	45.02707	-73.11500	Regular
09	45.00885	-73.11252	Regular
10	44.99055	-73.11257	Master

Figure 1. Location of the ten sampling stations established in Missisquoi Bay.

Water Quality and Sediment Core Sampling

Water and sediment samples were collected using an 18ft Boston whaler (captain Bill Ryan, VT). Each site was located using a Garmin Vista HcX GPS. Once onsite, the boat was secured using a river anchor and pointed into the wind to remain on station. Water column samples were collected at the Master and Regular stations (see figure 1) using a Wildco 2.2-L Kemmerer Bottle (Model 1520-A42) at 1 meter depths and the bottom 1 meter of the water column. Once collected, water samples were transferred into a clean, acid washed 2-L Nalgene HDPE bottles. Water column samples were capped and stored on ice until returning to Miner Institute. Chlorophyll a samples were preserved by adding six drops of 1% $MgCO_3$ to each sample. Intact 2” diameter x 20” long sediment cores were collected using a Wildco Ogeechee Sediment Corer (Model 2424-B25) with attached slide hammer. This unit had a vacuum valve system that enabled the cores to be retrieved intact on board the boat. Sediment cores were collected, capped, and stored upright in coolers and placed in a refrigerator upon returning to Miner. Additional water samples were collected by members of the Vermont Department of Natural Conservation (VTDEC) throughout the summer. The VTDEC samples were analyzed for soluble phosphorus (SRP) and total Dissolved P (TDP) only. All of the water chemistry and chlorophyll a data is detailed in Appendix I- Table 1. A summary of this dataset has been compiled in Appendix I- Table 2.

Along with water sampling for chemical analysis, stations were vertically profiled by 1 meter (m) increments for water quality parameters, including dissolved oxygen (DO), pH, temperature, conductivity and oxidation/reduction potential (ORP) using a YSI 556 MPS multiparameter probe calibrated to NIST traceable standards. The probe calibrations were performed according to the manufacturer's guidelines, including barometric pressure.

Field analysis:

1. **Water quality**: Along with field sampling for water chemistry data, stations were vertically profiled by 1 m increments for water quality parameters, including dissolved oxygen (DO), pH, temperature, conductivity and oxidation/reduction potential (ORP) using a YSI 556 MPS multiparameter probe calibrated to NIST traceable standards. The probe calibrations were performed according to the manufacturer's guidelines, including barometric pressure. All of the water quality data from all stations in Missisquoi Bay can be viewed in Appendix I- Table 1. Appendix I-Table 2 shows the average 2010 water quality values for the water column and sediment pore region at each station.

Laboratory Analyses

1. **Water chemistry**: Water samples from Missisquoi Bay were stored at 39°F (4 °C) until they could be processed. Aliquots of water were filtered through a 0.45 um mixed cellulose ester membrane for Soluble P and total dissolved P analysis (APHA 4500-P). Total P and total dissolved P digests were performed using EPA 365.1 method using a Consolidated Stills autoclave for 30 minutes at 250 °F (121 °C). Phosphorus determination was determined using either a Seal AA3 Autoanalyzer with a MT-19 chemistry module, or a Spec 20 Genesys with a 5 cm pathlength cell as per Standard Methods. Total solids were performed on an aliquot of the raw water samples as per standard methods. Chlorophyll a samples were preserved in the field and then filtered at the end of each cruise day. The filters were frozen at -20°C and delivered on ice to Endyne Laboratories (Plattsburgh, New York) where the chlorophyll a content was determined by Standard methods (SM 10200H.3). All water chemistry data are listed in Appendix II-Table 3. Appendix II-Table 4 contains the averaged values for the phosphorus and chlorophyll a data. Appendix II-Table 5 contains the total solids data for the stations. The analyses were completed within the time frames set forth in Standard Methods, with the following exceptions: June 25, 2010 all river samples were processed on June 30, 2010; Sept 3, 2010 all bay samples were processed on Sept 6, 2010; Oct 1, 2010 all river samples were processed Oct 4, 2010. All experimental runs included two levels of Ultracheck standards (SRP and Total P accordingly). All standard values were within the accepted range on the certificate by lot from the Ultra Scientific

2. **Sediment flux analysis**: on the September 9, 2010 cruise multiple 2" diameter x 20" long sediment cores were collected at the four (4) "Master" stations: stations 1, 3, 6, and 10 (see figure 1) using a Wildco Ogeechee Sediment Corer (Model 2424-B25) with attached slide hammer. These sediment cores were brought onboard, capped and sealed with Parafilm, and stored upright in coolers full of ice until they were returned to the Miner Institute. Upon return to the Miner Institute, the cores were carefully drained. Then the top 10 cm portion of each core was transferred with a core extraction tool (Wildco) into a

clean 2” x 20” acrylic liner. Once the bottom was capped and sealed with Parafilm each core was covered with 300 mL of 0.45 um filtered bulk water sample obtained at each master station during the cruise. Duplicate cores were subjected to either anoxic (nitrogen gas) or oxic (compressed air) conditions for 2 weeks with aliquots of overlying water removed and analyzed for SRP and TDP on set intervals. An aliquot of the corresponding filtered bulk sample was then added to each respective core to maintain volume. The data derived from these experiments is listed in Appendix III- tables 6 and 7. The analysis was completed within the time frames set forth in Standard Methods. All experimental runs included two levels of Ultracheck standards (SRP and total P accordingly). All standard values were within the accepted range on the certificate by lot from the Ultra Scientific

3. **Sediment characterization analysis**: On the September 9, 2010 cruise single 2” diameter x 20” long sediment cores were collected at all 10 stations using a Wildco Ogeechee Sediment Corer (Model 2424-B25) with attached slide hammer. These sediment cores were collected, capped, and stored upright in coolers full of ice until they were returned to the Miner Institute. Upon return, the cores were carefully drained. Then the top 10 cm portion of each core was transferred with a core extraction tool (Wildco) into clean drying pans. All cores were dried in a 50ºC forced air drying oven (VWR). After drying was complete, the cores were crushed with a mortar and pestle and passed through a 1.4 mm sieve. The dried and sieved sediment were stored in air tight plastic bags until analyzed. All samples were sequentially analyzed for labile phosphorus (P) (ammonium chloride extractions), aluminum and iron bound phosphorus (sodium hydroxide extraction), and calcium bound P (hydrochloric acid extraction). All extractions were passed through a mixed cellulose 0.45 um filter and were analyzed for soluble phosphorus (SRP) using standards created in each of the three extraction matrices (ammonium chloride, sodium hydroxide and hydrochloric acid). The results for these characterizations are presented in Appendix IV- Table 8. The analysis was completed within the time frames set forth in Standard Methods. All experimental runs included two levels of Ultracheck standards (SRP and total P accordingly). All standard values were within the accepted range on the certificate by lot from the Ultra Scientific.

4. **Photo documentation:** Appendix V contains digital images taken during sampling

Appendix I- Water quality data for Missisquoi Bay in 2010

Table 1- all water quality data collected at various Missisquoi Bay stations during the summer of 2010. DO is dissolved oxygen (mg/L), SpCond is specific conductivity (uSiemens/cm), ORP is the Oxidation Reduction potential, Secchi depth (inches) and BP is the barometric pressure in psi. Data was collected at "1 meter" incremental depths and the "bottom" (1 meter) of the water column at all stations.

Station	Date	Depth (m)	DO (mg/L)	pH	Temp (C)	Cond. (uS/cm)	ORP	Secchi (inches)	BP (psi)
1	7/15/10	1	7.02	7.61	26.43	138	103	98	15.11
1	7/15/10	Bottom	6.78	7.49	26.26	138	87		15.05
1	9/9/10	1	8.79	7.92	20.00	137	151		14.91
1	9/9/10	2	8.87	8.00	20.01	136	151		14.90
1	9/9/10	3	8.91	8.02	20.01	137	150		14.90
1	9/9/10	Bottom	8.91	8.00	20.01	137	151		14.90
1	10/7/10	1	9.65	7.29	13.81	125	181	30	14.41
1	10/7/10	2	9.81	7.53	13.8	124	175		14.41
1	10/7/10	3	9.75	7.57	13.8	124	176		14.41
1	10/7/10	4	9.77	7.58	13.79	124	175		14.41
1	10/7/10	Bottom	9.75	7.56	13.77	123	174		14.41
2	7/15/10	1	6.98	7.68	26.65	137	133	143	15.05
2	7/15/10	Bottom	5.76	7.23	26.18	138	47		15.03
2	10/7/10	1	10.72	9.13	13.81	140	155	27	14.41
2	10/7/10	2	10.64	9.07	13.82	158	158		14.41
2	10/7/10	3	10.67	9.07	13.82	138	159		14.41
2	10/7/10	4	10.60	8.95	13.74	140	164		14.41
2	10/7/10	Bottom	10.41	8.95	13.83	138	-165		14.41
3	7/15/10	1	7.37	7.79	26.93	134	90	75	15.00
3	7/15/10	Bottom	3.45	6.87	25.90	133	95		14.97
3	9/9/10	1	8.59	7.76	20.11	148	157		14.91
3	9/9/10	2	8.64	7.77	20.11	149	157		14.91
3	9/9/10	3	8.67	7.76	20.09	147	157		14.91
3	9/9/10	Bottom	8.68	7.71	20.05	148	88		14.91
3	10/7/10	1	10.21	8.29	13.86	131	58	31.5	14.40
3	10/7/10	2	10.23	8.25	13.86	131	62		14.40
3	10/7/10	3	10.28	8.17	13.85	130	68		14.40
3	10/7/10	4	10.24	8.22	13.87	131	69		14.40
3	10/7/10	Bottom	10.18	8.20	13.87	131	12		14.40
4	7/15/10	1	7.75	8.02	26.89	138	146	103	15.05
4	7/15/10	Bottom	3.71	7.10	25.98	138	52		15.04
4	10/7/10	1	9.97	7.97	13.98	152	100	23.5	14.40
4	10/7/10	2	10.00	7.94	13.99	152	101		14.40
4	10/7/10	3	9.90	7.92	13.98	155	102		14.40
4	10/7/10	4	9.91	7.89	13.97	155	106		14.40
4	10/7/10	Bottom	9.88	7.88	13.96	156	107		14.39
5	6/3/10	1	7.34	6.54	20.58	133	183	73	14.80
5	7/15/10	1	7.20	8.06	27.11	142	120	124	15.03

5	7/15/10	Bottom	6.89	7.74	26.54	139	93		15.01
5	10/7/10	1	9.84	7.79	13.77	173	132	25	14.40
5	10/7/10	2	9.77	7.78	13.76	175	132		14.40
5	10/7/10	3	9.76	7.77	13.75	176	134		14.40
5	10/7/10	4	9.77	7.77	13.76	174	136		14.40
5	10/7/10	Bottom	9.73	7.71	13.75	176	1		14.40
6	6/3/10	1	7.09	6.86	20.50	134	198	122	14.82
6	7/15/10	1	8.42	8.58	27.06	146	79	101	15.12
6	7/15/10	Bottom	3.58	7.02	26.22	143	53		15.03
6	9/9/10	1	8.21	7.57	19.92	150	132		14.91
6	9/9/10	2	8.35	7.57	19.93	150	135		14.91
6	9/9/10	3	8.40	7.54	19.93	151	138		14.91
6	9/9/10	Bottom	8.38	7.49	19.93	150	-31		14.91
6	10/7/10	1	9.44	7.50	13.71	146	110	24	14.41
6	10/7/10	2	9.32	7.42	13.67	139	112		14.41
6	10/7/10	3	9.28	7.35	13.64	137	117		14.40
6	10/7/10	4	9.26	7.34	13.62	135	119		14.41
6	10/7/10	Bottom	9.22	7.34	13.60	133	107		14.40
7	6/3/10	1	7.79	7.61	21.23	140	165	80	14.83
7	7/15/10	1	8.06	8.38	27.26	144	104	113	14.99
7	7/15/10	Bottom	3.22	6.99	26.23	146	103		15.04
7	10/7/10	1	9.13	7.29	13.59	106	146	25	14.41
7	10/7/10	2	9.02	7.22	13.58	107	150		14.41
7	10/7/10	3	9.04	7.19	13.58	106	150		14.41
7	10/7/10	4	9.03	7.22	13.57	105	148		14.41
7	10/7/10	Bottom	8.99	7.17	13.59	106	25		14.41
8	6/3/10	1	7.17	7.56	21.38	137	166	72	14.82
8	7/15/10	1	8.51	8.33	26.83	136	123	90.5	14.93
8	10/7/10	1	9.81	7.64	13.96	172	104	24	14.41
8	10/7/10	2	9.77	7.66	13.97	172	108		14.41
8	10/7/10	3	9.73	7.67	13.97	173	114		14.41
8	10/7/10	4	9.73	7.66	13.98	174	117		14.41
8	10/7/10	Bottom	9.72	7.64	13.98	173	120		14.41
9	6/3/10	1	7.23	7.46	21.20	133	167		14.80
9	7/15/10	1	9.44	8.67	27.05	133	109	75.5	14.97
9	7/15/10	Bottom	2.87	6.78	25.16	117	56		15.01
9	10/7/10	1	9.64	7.71	13.89	168	140	26	14.41
9	10/7/10	2	9.65	7.71	13.88	168	141		14.41
9	10/7/10	3	9.66	7.68	13.88	168	144		14.41
9	10/7/10	4	9.65	7.67	13.88	167	145		14.41
9	10/7/10	Bottom	9.50	7.46	13.91	169	-50		14.41
10	7/15/10	1	9.37	8.51	26.59	123	56	70.5	15.00
10	7/15/10	Bottom	2.65	6.68	25.12	109	64		15.05
10	9/9/10	1	8.75	7.85	19.72	152	70		14.91
10	9/9/10	2	8.93	7.84	19.72	152	79		14.91
10	9/9/10	Bottom	8.95	7.84	19.72	151	83		14.91
10	10/7/10	1	9.99	7.66	13.60	119	100	22	14.42
10	10/7/10	2	10.00	7.68	13.60	119	100		14.41

10	10/7/10	3	9.99	7.61	13.59	120	102		14.42
10	10/7/10	4	9.95	7.60	13.59	120	106		14.41
10	10/7/10	Bottom	9.76	7.39	13.61	120	-22		14.41

Table 2- Missisquoi Bay water quality data averages for all water column depths, and the bottom 1 meter samples at each station. DO is dissolved oxygen (mg/L), SpCond is specific conductivity (uSiemens/cm), ORP is the Oxidation Reduction potential, Secchi Depth is the light penetration value in inches, and BP is the barometric pressure in pounds per square inch (psi).

Station	DO (mg/L)	pH	Temp (C)	SpCond (uS/cm)	ORP	Secchi Depth	BP (psi)
1	9.07	7.69	17.71	133.88	152.50	64.0	14.68
1-Bottom	8.48	7.68	20.01	137.33	132.67		14.79
2	9.92	8.78	16.37	138.60	153.80	85.0	14.54
2-Bottom	8.09	8.09	20.01	138.00	-59.00		14.72
3	9.28	8.00	17.84	137.63	102.25	53.3	14.67
3- Bottom	7.44	7.59	19.94	137.33	65.00		14.76
4	9.51	7.95	16.56	150.40	111.00	63.3	14.53
4- Bottom	6.80	7.49	19.97	147.00	79.50		14.72
5	8.95	7.62	17.12	162.17	139.50	74.0	14.57
5- Bottom	8.31	7.73	20.15	157.50	47.00		14.71
6	8.64	7.53	18.00	143.11	126.67	82.3	14.70
6- Bottom	8.80	7.42	16.77	141.50	38.00		14.66
7	8.68	7.49	17.14	118.00	143.83	72.7	14.58
7- Bottom	6.11	7.08	19.91	126.00	64.00		14.73
8	9.12	7.75	17.35	160.67	122.00	62.2	14.57
8- Bottom	9.72	7.64	13.98	173.00	120.00		14.41
9	9.21	7.82	17.30	156.17	141.00	33.8	14.57
9- Bottom	6.19	7.12	19.54	143.00	3.00		14.71
10	9.57	7.82	17.20	129.29	87.57	46.3	14.64
10- Bottom	7.12	7.30	19.48	126.67	41.67		14.79

Appendix II- Water chemistry data for Missisquoi Bay in 2010

Table 3- Missisquoi Bay 2010 water quality data collected by the W.H Miner Institute and Vermont Department of Environmental Conservation (VTDEC). Samples were collected at "1 meter" depths from the surface or the "bottom" (1 meter) of the water column. Duplicates were taken of the 1 meter deep samples ("Duplicate").

Station	Sample Type	Date	SRP (ug P/L)	TDP (ug P/L)	TP (ug P/L)	Chlorophyll a
1	1 meter	7/15/10	7.28	18.95	24.64	1.26
1	Bottom	7/15/10	6.29	8.44	45.49	
1	1 meter	9/3/10	0.99	3.74	4.99	2.70
1	Bottom	9/3/10	3.62	6.24	8.74	
1	1 meter	9/9/10	4.59	12.10	73.89	
1	Bottom	9/9/10	4.89	17.84	78.99	
1	1 meter	10/7/10	8.11	47.44	62.03	*17.53*
1	Bottom	10/7/10	11.82	34.56	61.35	
2	1 meter	7/15/10	7.61	11.85	25.9	1.18
2	1 meter	9/3/10	1.64	4.99	7.49	6.70
2	1 meter	10/7/10	7.43	54.89	77.02	33.33
3	1 meter	5/18/10	7.81			
3	1 meter	6/2/10	14.70	29.28		
3	1 meter	6/15/10	10.23			
3	1 meter	6/25/10	5.86	9.76		
3	1 meter	7/6/10	2.92	22.12		
3	1 meter	7/14/10	6.83	16.53		
3	1 meter	7/15/10	5.63	6.32	35.38	4.60
3	Bottom	7/15/10	9.93	14.21	55.6	
3	1 meter	7/20/10	15.55	30.35		
3	1 meter	7/29/10	4.81	18.71		
3	1 meter	8/23/10	4.32	18.98		
3	1 meter	9/1/10	5.32	14.65		
3	1 meter	9/3/10	1.64	3.12	4.99	2.40
3	Bottom	9/3/10	8.22	11.23	13.73	
3	1 meter	9/8/10	4.49	10.19		
3	1 meter	9/9/10	2.23	9.56	69.43	
3	Bottom	9/9/10	1.53	5.73	71.34	
3	1 meter	10/5/10	6.54	10.16		
3	1 meter	10/7/10	10.81	60.31	85.89	21.79
3	Bottom	10/7/10	13.85	48.79	64.07	
4	1 meter	7/15/10	7.94	16.58	43.59	4.80
4	1 meter	9/3/10	1.32	4.37	5.62	4.80
4	1 meter	10/7/10	14.86	59.64	74.98	21.79
5	1 meter	6/3/10	9.58	18.46	46.09	

5	1 meter	7/15/10	4.63	8.69	32.22	2.20
5	1 meter	9/3/10	0.66	8.11	9.36	5.60
5	1 meter	10/7/10	19.93	68.45	72.25	19.52
6	1 meter	6/2/10	9.22	20.37		
6	1 meter	6/3/10	13.35	27.37	40.59	
6	1 meter	6/15/10	3.63			
6	1 meter	6/25/10	6.18	11.71		
6	1 meter	7/6/10	4.5	11.71		
6	1 meter	7/14/10	7.18	21.82		
6	1 meter	7/15/10	5.63	11.06	37.91	7.80
6	Duplicate	7/15/10	4.96	11.06	63.18	7.20
6	Bottom	7/15/10	10.26	17.37	45.49	
6	1 meter	7/20/10	11.91	38.44		
6	1 meter	7/29/10	3.85	14.03		
6	1 meter	8/23/10	4.66	14.24		
6	1 meter	9/1/10	5.33	35.04		
6	1 meter	9/3/10	1.32	6.24	8.11	3.90
6	Duplicate	9/3/10	1.97	5.62	6.86	4.60
6	Bottom	9/3/10	3.95	4.37	4.99	
6	1 meter	9/8/10	5.46			
6	Bottom	9/9/10	7.06	10.83	67.52	
6	1 meter	9/9/10	7.05	17.84	80.26	
6	1 meter	10/5/10	25.17	43.35		
6	1 meter	10/7/10	25.33	60.31	71.57	12.41
6	Duplicate	10/7/10	23.64	61.67	72.25	10.42
6	Bottom	10/7/10	24.66	60.99	70.89	
7	1 meter	6/3/10	8.91	21.64	55.03	
7	1 meter	7/15/10	6.29	12.64	34.75	6.40
7	1 meter	9/3/10	0.66	4.99	6.24	5.20
7	1 meter	10/7/10	23.64	52.18	64.76	8.10
8	1 meter	6/3/10	10.90	33.73	53.66	
8	1 meter	7/15/10	5.29	17.37	27.8	3.60
8	1 meter	9/3/10	0.66	5.62	6.86	4.20
8	1 meter	10/7/10	20.94	71.16	87.25	19.79
9	1 meter	6/3/10	6.39	15.28	68.1	
9	1 meter	7/15/10	5.29	8.69	52.44	9.00
9	1 meter	9/3/10	0.66	2.50	3.74	4.20
9	1 meter	10/7/10	22.63	63.70	75.66	19.20
10	1 meter	7/15/10	4.63	9.48	37.27	10.2
10	Duplicate	7/15/10	4.69	11.06	111.82	7.80
10	Bottom	7/15/10	15.22	22.11	92.24	
10	1 meter	9/3/10	1.32	2.50	3.74	7.20
10	Duplicate	9/3/10	1.32	3.74	4.99	7.60
10	Bottom	9/3/10	1.97	6.24	7.49	
10	1 meter	9/9/10	1.00	11.47	56.06	

10	Bottom	9/9/10	1.10	8.92	101.28	
10	1 meter	10/7/10	5.07	46.76	59.98	17.16
10	Duplicate	10/7/10	4.73	48.79	60.67	18.42
10	Bottom	10/7/10	6.76	47.44	58.62	
Missisquoi River	1 meter	6/29/10	2.95	9.11		
Missisquoi River	1 meter	8/20/10	1.66	10.5		
Missisquoi River	1 meter	9/9/10	2.29	13.38		
Missisquoi River	1 meter	10/1/10	41.84	56.67		
Pike River	1 meter	6/29/10	27.92	39.69		
Pike River	1 meter	8/20/10	2.00	12.47		
Pike River	1 meter	9/9/10	47.84	54.15		
Pike River	1 meter	10/1/10	142.18	216.01		
Rock River	1 meter	6/29/10	39.45	48.15		
Rock River	1 meter	8/20/10	45.23	55.79		
Rock River	1 meter	9/9/10	6.56	97.46		
Rock River	1 meter	10/1/10	109.82	146.01		

Table 4- Summer 2010 average water chemistry data for Missisquoi Bay and tributaries. Samples were collected at "1 meter" depths and the "bottom" (1 meter) of the water column at the highlighted "Master" stations.

Station	Sample Type	SRP (ug P/L)	TDP (ug P/L)	TP (ug P/L)	Chlorophyll a
1	1 meter	5.24	20.56	41.39	7.16
1	Bottom	6.66	16.77	48.64	
2	1 meter	5.56	23.91	36.81	13.74
3	1 meter	6.86	18.57	48.92	9.60
3	Bottom	8.38	19.99	51.19	
4	1 meter	8.04	26.86	41.40	10.46
5	1 meter	8.70	25.93	39.98	9.11
6	1 meter	8.09	23.81	46.00	7.72
6	Bottom	11.48	24.83	43.58	
7	1 meter	9.87	22.86	40.19	6.57
8	1 meter	9.45	31.97	43.89	9.20
9	1 meter	8.74	22.54	49.99	10.80
10	1 meter	3.29	19.11	47.79	11.64
10	Bottom	6.26	21.18	64.91	

Missisquoi River	1 meter	12.19	30.06		
Pike River	1 meter	54.98	73.14		
Rock River	1 meter	50.26	77.09		

Table 5- All Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) data collected during 2010 trips on Missisquoi Bay. Samples were collected at "1 meter" depths and the "bottom" (1 meter) of the water column at the highlighted "Master" stations.

Station	July 15, 2010		Sept. 3, 2010		Oct. 7, 2010		Overall	
	TSS (mg/L)	VSS (mg/L)	TSS (mg/L)	VSS (mg/L)	TSS (mg/L)	VSS (mg/L)	TSS (mg/L)	VSS (mg/L)
1	*1.4*	*0.0062*	*11.2*	*0.0032*	*12.6*	*0.0086*	*8.4*	*0.0060*
1-Bottom	*4.0*	*0.0060*	*23.6*	*0.0076*	*7.6*	*0.0166*	*11.7*	*0.0101*
2	*2.6*	*0.0074*	*6.8*	*0.0052*	*3.4*	*0.0102*	*4.3*	*0.0076*
3	*2.4*	*0.0044*	*2.4*	*0.0024*	*18.2*	*0.0090*	*7.7*	*0.0053*
3-Bottom	*8.8*	*0.0144*	*5.6*	*0.0056*	*3.8*	*0.0100*	*6.1*	*0.0100*
4	*3.2*	*0.0204*	*4.0*	*0.0064*	*6.2*	*0.0102*	*4.5*	*0.0123*
5	*1.6*	*0.0306*	*6.0*	*0.0020*	*8.6*	*0.0070*	*5.4*	*0.0132*
6	*2.0*	*0.0062*	*5.8*	*0.0022*	*6.5*	*0.0059*	*4.4*	*0.0048*
6-Bottom	*6.4*	*0.0320*	*32.4*	*0.0764*	*5.8*	*0.0182*	*14.9*	*0.0422*
7	*1.4*	*0.0048*	*5.2*	*0.0040*	*5.2*	*0.0098*	*3.9*	*0.0062*
8	*3.0*	*0.0096*	*6.4*	*0.0028*	*9.4*	*0.0086*	*6.3*	*0.0070*
9	*4.0*	*0.0030*	*2.0*	*0.0080*	*8.0*	*0.0088*	*4.7*	*0.0066*
10	*3.1*	*0.0051*	*2.0*	*0.0036*	*8.4*	*0.0093*	*4.3*	*0.0065*
10-Bottom	*18.0*	*0.0994*	*22.8*	*0.0020*	*14.0*	*0.0262*	*18.4*	*0.0425*

Appendix III- Sediment Flux analysis for Missisquoi Bay Master stations

Table 6- Averaged Missisquoi Bay Master station sediment P flux analysis results for Soluble Phosphorus (SRP). Master stations are 1, 3, 6 and 10.

Station	Days after incubation	Average Anoxic SRP (ug P/L)	Anoxic Stdev	Average Oxic SRP (ug P/L)	Oxic Stdev
1	0	4.59	0.00	4.59	0.00
1	1	30.07	11.12	2.60	0.49
1	3	79.26	25.15	3.53	0.38
1	4	97.84	21.82	3.70	0.42
1	5	105.51	24.42	1.44	0.23
1	6	102.15	30.07	1.12	0.23
1	10	132.17	20.76	6.40	2.33
1	11	152.85	3.51	9.85	1.37
1	13	177.61	6.81	16.31	5.91
1	15	166.91	9.21	14.67	0.08
3	0	2.23	0.00	2.23	0.00
3	1	21.47	6.98	1.93	0.16
3	3	34.12	18.42	2.21	0.49
3	4	25.41	3.41	2.42	0.48
3	5	51.16	19.90	1.12	0.23
3	6	63.63	23.96	1.12	0.23
3	10	81.99	98.25	2.99	0.89
3	11	78.00	65.99	4.39	1.38
3	13	99.85	76.55	7.07	1.81
3	15	89.45	51.60	12.11	3.01
6	0	7.06	0.00	7.06	0.00
6	1	15.23	10.83	2.29	0.29
6	3	50.93	10.61	12.16	0.08
6	4	65.98	13.75	12.11	3.29
6	5	88.89	4.97	19.02	2.49
6	6	86.65	4.52	2.72	0.23
6	10	114.12	13.24	15.71	1.73
6	11	93.52	9.73	15.92	4.55
6	13	118.16	12.41	23.38	7.99
6	15	116.31	1.08	29.17	8.59
10	0	1.00	0.00	1.00	0.00
10	1	22.21	14.33	4.06	3.05
10	3	46.65	14.88	3.14	0.42
10	4	55.72	27.01	3.22	0.77
10	5	95.12	12.43	5.44	1.81
10	6	102.95	12.66	6.23	2.03

10	10	81.62	30.69	9.87	6.41
10	11	68.83	22.68	13.79	3.49
10	13	137.18	13.15	17.77	0.38
10	15	174.83	60.75	22.60	0.70

Table 7- Missisquoi Bay Master station Sediment P flux analysis results for Total Dissolved Phosphorus (TDP).

Station	Days after incubation	Average Anoxic TDP (ug P/L)	Anoxic Stdev	Average Oxic TDP (ug P/L)	Oxic Stdev
1	0	12.10	0.00	12.10	0.00
1	1	73.83	21.62	64.07	9.66
1	3	187.01	7.82	73.50	14.72
1	4	227.34	28.98	81.63	19.78
1	5	252.70	49.89	93.96	4.99
1	6	247.24	58.50	77.60	0.00
1	7	335.43	10.88	98.45	5.90
1	10	347.46	25.57	111.44	6.97
1	11	384.28	24.64	95.33	4.65
1	13	322.46	10.08	79.23	40.34
1	15	321.99	1.79	102.05	7.17
3	0	9.56	0.00	9.56	0.00
3	1	73.83	9.66	54.31	5.06
3	3	159.69	0.46	65.05	5.52
3	4	161.31	18.40	75.45	22.08
3	5	195.61	50.79	63.49	10.88
3	6	196.58	56.69	60.29	12.70
3	7	283.80	82.09	81.13	2.27
3	10	247.53	66.48	77.58	14.88
3	11	239.31	54.86	79.22	8.83
3	13	263.04	58.26	74.48	15.69
3	15	281.74	43.47	97.93	8.52
6	0	10.83	0.00	10.83	0.00
6	1	74.48	17.94	62.44	0.00
6	3	157.41	5.52	93.34	16.10
6	4	168.14	2.30	94.64	3.22
6	5	189.52	0.45	93.96	4.08
6	6	181.50	5.44	86.90	3.17
6	7	238.91	25.85	112.88	5.44
6	10	240.30	27.43	113.08	5.58
6	11	224.52	12.55	104.21	6.97
6	13	115.67	2.24	79.23	4.48

6	15	*242.44*	*16.58*	*122.33*	*8.07*
10	0	*11.47*	*0.00*	*11.47*	*0.00*
10	1	*85.21*	*21.16*	*78.06*	*11.96*
10	3	*136.27*	*64.85*	*122.61*	*24.38*
10	4	*210.75*	*4.60*	*95.29*	*24.38*
10	5	*256.86*	*1.36*	*98.13*	*28.12*
10	6	*257.18*	*2.72*	*89.15*	*29.93*
10	7	*372.63*	*32.65*	*117.69*	*21.31*
10	10	*314.26*	*26.03*	*121.63*	*34.40*
10	11	*323.46*	*2.79*	*123.27*	*30.22*
10	13	*347.02*	*33.61*	*164.80*	*94.12*
10	15	*323.46*	*2.79*	*123.27*	*30.22*

Appendix IV- Missisquoi Bay Sediment characterization analysis

Table 8 - Missisquoi Bay 2010 sediment characterizations for all stations sampled. Fractions include Labile-phosphorus (Labile-P), Aluminum and Iron bound phosphorus (Al-P and Fe-P), and Calcium bound phosphorus (Ca-P). No detectable Labile-P was detected.

Location	Fraction	Average Phosphorus (mg P/kg)	STDEV
Station 1	**Labile P**	< 0.03	
Station 2	**Labile P**	< 0.03	
Station 3	**Labile P**	< 0.03	
Station 4	**Labile P**	< 0.03	
Station 5	**Labile P**	< 0.03	
Station 6	**Labile P**	< 0.03	
Station 7	**Labile P**	< 0.03	
Station 8	**Labile P**	< 0.03	
Station 9	**Labile P**	< 0.03	
Station 10	**Labile P**	< 0.03	
Station 1	**Al-P and Fe-P**	*91.67*	*1.93*
Station 2	**Al-P and Fe-P**	*804.87*	*21.46*
Station 3	**Al-P and Fe-P**	*84.24*	*2.67*
Station 4	**Al-P and Fe-P**	*118.65*	*14.98*
Station 5	**Al-P and Fe-P**	*141.91*	*2.21*
Station 6	**Al-P and Fe-P**	*138.50*	*22.83*
Station 7	**Al-P and Fe-P**	*157.87*	*4.03*
Station 8	**Al-P and Fe-P**	*166.14*	*20.98*
Station 9	**Al-P and Fe-P**	*120.30*	*22.74*
Station 10	**Al-P and Fe-P**	*154.71*	*6.12*
Station 1	**Ca-P**	*494.31*	*6.86*
Station 2	**Ca-P**	*279.20*	*2.85*
Station 3	**Ca-P**	*516.93*	*13.21*
Station 4	**Ca-P**	*457.02*	*14.07*
Station 5	**Ca-P**	*469.11*	*10.94*
Station 6	**Ca-P**	*481.17*	*2.55*
Station 7	**Ca-P**	*520.32*	*19.25*
Station 8	**Ca-P**	*476.45*	*2.23*
Station 9	**Ca-P**	*493.22*	*14.84*
Station 10	**Ca-P**	*450.23*	*0.97*

Appendix V-Photo documentation of Missisquoi Bay field sampling.