Long-term trends in aquatic pollutants: Chloride and phosphorus dynamics in lakes embedded in urban and agricultural watersheds

by

Amy Marie Kamarainen

A dissertation submitted in partial fulfillment of the requirements for the degree of

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ABSTRACT

Long-term trends in aquatic pollutants: Chloride and phosphorus dynamics in lakes embedded in urban and agricultural watersheds

Amy Marie Kamarainen

Under the supervision of Professor Stephen R. Carpenter

At the University of Wisconsin, Madison

Aquatic ecosystems are increasingly affected by human activities such as land use change in the watershed. Changes in land use affect the delivery of non-point source loads of nutrients and pollutants. I explore long-term trends and drivers of two aquatic pollutants, chloride and phosphorus, associated with changes in land use and land cover. Comparison of these two pollutants provided an opportunity to explore simple and complex models for solute transport and processing in lakes embedded in changing landscapes.

Excessive chloride loading has become pervasive due to increases in road miles and rates of road salt application associated with urbanizing watersheds in northern climates. In the first chapter, I examined the relationship between road salt application and chloride dynamics in an urban watershed, Lake Wingra. Using a model calibrated with long-term data, I explored scenarios for changes in road salt management. I found that, under current conditions, the lake should quickly respond to changes in road salt application and projected mean concentrations are unlikely to exceed guidelines for
aquatic organisms. However, trends in chloride concentrations of the groundwater underlying the Wingra watershed suggested a need to mitigate road salt application.

In the second portion of my dissertation, I explored phosphorus dynamics in Lake Mendota to assess the relative importance of external loading and recycling of this limiting nutrient. Using a combination of field sampling, long-term data analysis and biological and physical modeling, I assessed the contribution of three different mechanisms of phosphorus recycling: biotic recycling, entrainment and sediment release. Both biotic recycling and entrainment provided important sources of P to primary producers during the stratified season. Entrainment was spatially and temporally variable, but could be reasonably represented using both a 3-D hydrodynamic model and sampling based on a single central location. Finally, although long-term P dynamics were primarily driven by external loading, P in the hypolimnion increased over time. This change was driven by changes in the stability of the water column and increased length of stratification. Changes in the physical condition of the lake held implications for phosphorus recycling and water clarity during the summer.
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It was a pleasure to interact with the members of the Long-Term Ecological Research (LTER) Project throughout my tenure. The breath of people and fields...
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instead of finding a "real job". I am so grateful for their love and support and their frequent offers to help out where they could. Weekly conversations with my sister Jen and brother Steve helped me stay grounded – and family vacations were the highlight of each winter. I appreciate all the times they came to visit me when I felt too busy to travel. Chiana and Megan are source for laughs and shoulders should I ever need them. It was and is so comforting to have such good friends.

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INTRODUCTION

Aquatic ecosystems are increasingly affected by human activities. Among the most significant pathway of influence is through runoff of nutrients and pollutants from the surrounding landscape. The influence of watershed composition on lake characteristics has long been recognized (Dillon and Kirchner 1974, O'Sullivan 1979). Extreme changes in land use and land cover result in changes in hydrology and solute export from the landscape (Bormann and Likens 1967, Likens et al. 1970). Nonpoint pollution – runoff of nutrients and toxins through diffuse landscape pathways rather than isolated discharge points – is now the principal driver of freshwater eutrophication in developed countries (Carpenter et al. 1998). Extensive changes in land use and land cover are occurring and will continue to occur globally in order to meet the food and housing needs of a growing global population (Meyer and Turner 1994, Millenium Ecosystem Assessment 2005, Foley et al. 2005).

Agriculture and urban land use have become the principal endpoints of land use change. According to a United Nations report, 2008 was the first year in which over 50% of the world’s population lived in urban areas, and this trend is projected to continue (UN-HABITAT 2008). Conversion of native land to residential and commercial use is associated with an increase in roads and impervious surface in the watershed (Arnold and Gibbons 1996). Additionally, urban roadways are generally underlain by extensive stormwater drainage networks that efficiently convey runoff to nearby retention basins or natural aquatic ecosystems (Smith et al. 1998, Hatt et al.)
The net effect of urbanization is a dramatically altered hydrologic regime that may readily transport pollutants to urban lakes and streams (Paul and Meyer 2001, Brabec et al. 2002).

The impact of urbanization on aquatic ecosystems is surpassed by that of agriculture, which is the single most significant cause of impaired waters in the United States (USEPA 2002). The negative influence of agriculture on aquatic resources is primarily driven by the redistribution of nutrients, due to use of synthetic fertilizers and manure, and subsequent runoff of nutrient-rich waters and sediment into lakes and streams (Bennett et al. 1999, Tilman et al. 2001). Over the past 40 years there has been a 12% increase in global cropland, and a 700% increase in fertilizer use (Foley et al. 2005, Tilman et al. 2001). The number of acres of land in agricultural production is projected to increase in developing nations by at least 23%, but may decrease in the developed world (Balmford 2005).

This dissertation is motivated by a need to better understand processes driving long-term trends in aquatic pollutants associated with changing landscapes. I focused on two very different solutes, chloride and phosphorus, which are important nonpoint pollutants in the Madison area. I used a combination of field sampling, modeling and long-term data analysis to assess the rates and dominant pathways of in-lake processing of phosphorus coming from the predominantly agricultural watershed of Lake Mendota. I also used long-term data analysis and modeling to explore scenarios for road salt management and chloride dynamics in the highly urbanized watershed of Lake Wingra.
In the 1950s, many municipalities began applying rock salt to roads during the winter to improve driving conditions. The long-term effects of road salt application are now being recognized due to an increase in chloride and sodium concentrations in lakes, streams and groundwaters across northern latitudes (Kaushal et al. 2002, Jackson and Jobbagy 2005, Howard and Maier 2007, Novotny et al. 2008). A number of studies document increasing chloride concentrations over time, yet few offer assessment of how chloride levels may respond to mitigation efforts (Novotny et al. 2008). In Chapter 1, I use a long-term dataset from the Lake Wingra watershed to characterize the drivers of chloride dynamics, build a model to represent changes in chloride concentration, and assess how the system may respond to changes in road salt management. Chloride is a conservative tracer, meaning that the mass added to a water body stays constant and is not altered by reactions with other chemical species or biotic uptake or release. Because of its conservative nature, I was able to represent the long-term changes in chloride concentrations using a simple model. Using this simple model I show that Lake Wingra should respond quickly to changes in chloride load and that current loading rates are not likely to exceed toxicity limits for aquatic organisms. However, the capacity of the lake to respond quickly to changes in load may be dramatically altered by accumulation of chloride in shallow groundwaters. Accumulation of chloride in groundwaters raises a number of concerns for aquatic resources in the Madison area, which I explore fully in Chapter 1.

Whereas chloride is a conservative pollutant, the second pollutant of interest, phosphorus, is biologically and chemically reactive, and its concentrations are
affected by uptake and release within aquatic ecosystems. Phosphorus (P) is frequently the macronutrient that limits primary production in freshwater ecosystems, so that biologically available P (PO$_4^{3-}$) is quickly taken up by plankton (Schindler 1977). Additionally, P readily forms complexes with iron, aluminum or calcium in the sediments of a lake (Golterman 1973, Baccini 1985). These complexes may render the P biologically inactive, effectively trapping P in lake sediments, until redox conditions become favorable for the chemical release of P into the water column (Mortimer 1941). The term “P recycling” has been used to describe processes by which bound P is made available for biological uptake. Mechanisms of recycling may include: 1.) recycling among biotic components through a cycle of consumption, excretion and uptake (Vanni 2002), 2.) release of phosphorus within the hypolimnion (from the sediments or sedimenting material) due to chemical or bacterial processes (Lee et al. 1977, Marsden 1989), or 3.) mixing of phosphorus-rich hypolimnetic water into the epilimnion, which is also called entrainment (Soranno et al. 1997, Stauffer 1987) (Figure 1). Of course, a build-up of P in the hypolimnion via mechanism #2 is a prerequisite for mechanism #3. Recycling mechanisms may contribute significantly to the annual P budget and may be responsible for delayed lake recovery following mitigation of external loading (Soranno et al. 1997, Nurnberg and Peters 1984, Jeppesen et al. 1998, Sondergaard et al. 2001, Jeppesen et al. 2005). Given the complex chemical and biological interactions that are relevant to phosphorus cycling in lakes, I needed to use a more complex, multi-faceted approach to explore the
importance of P recycling relative to external loading in Lake Mendota (Chapters 2, 3 and 4).

Lake Mendota is situated in an agricultural watershed where excessive phosphorus loading has led to a perpetual eutrophic state, yet during the summer, biologically available phosphorus falls below detection limits and is assumed to be limiting primary production in the epilimnion. Despite extremely low concentrations of bio-available P, phytoplankton communities maintain positive rates of primary production (Kamarainen et al. 2009a). In Chapter 2, I explored whether external load, entrainment from the hypolimnion, or biotic recycling within the epilimnion was most likely providing the P necessary for the observed rates of primary production. To do so, I combined a model of whole ecosystem metabolism with empirical measurements of the major components of the phosphorus budget during the summer of 2007. Findings suggest that biotic recycling and entrainment both contribute P necessary to sustain primary production (Kamarainen et al. 2009a).

Having confirmed the importance of entrainment in biological production, I combined an intensive field sampling campaign with a calibrated 3-D hydrodynamic model of Lake Mendota to assess the spatial and temporal variability in phosphorus entrainment (Chapter 3). Using this approach, I found that entrainment was spatially variable. Nonetheless, sampling at a single location could estimate the mean magnitude of the process (Kamarainen et al. 2009b). Also, the 3-D model successfully represented the spatial variation in phosphorus concentrations, thus
supporting the use of this model as a tool to accurately represent the physical
dynamics relevant in the transport of solutes within the basin.

In Chapter 4, I examined long-term changes in ice cover, physical
characteristics, phosphorus dynamics and water quality metrics in Lake Mendota
over thirty years. There was a significant decline in the ice cover and increase in the
strength and duration of stratification. At the same time phosphorus concentrations
increased and dissolved oxygen concentrations decreased in the hypolimnion of the
lake. The temporal synchrony between P and oxygen conditions in the hypolimnion
was likely driven by a common relationship with increasing stability and length of
stratification over time. Changes in the physical and chemical features of the lake
were tied to changes in water quality. We observed a significant improvement in
water clarity over time and a direct relationship between mean phosphorus
concentrations in the epilimnion and stability of the water column. While hypolimnetic
P concentrations increased, metrics of internal loading were, at best, weak predictors
of residual variation in April P concentrations predicted by the Vollenweider model.
Therefore, long-term P dynamics in the system were driven primarily by external
loads. In conclusion, water quality and phosphorus dynamics in Lake Mendota have
been affected by changes in ice cover and the strength and duration of stratification.
Yet, reductions of external loading, not further climate change, are the key to
restoration of water quality.

In summary, this thesis combines long-term data, short-term field campaigns,
and ecosystem models to analyze the dynamics of a conservative tracer, chloride,
and a highly reactive substance, phosphorus, in lakes. A relatively simple model successfully explained chloride dynamics. However, ongoing chloride enrichment of groundwater, which was not addressed by my model, could complicate chloride dynamics while greatly increasing year-round chloride concentrations in Lake Wingra in the future. Phosphorus dynamics, in contrast, were more complicated because of high rates of uptake and release within Lake Mendota. To understand phosphorus dynamics, I used statistical models of a 30-year time series in combination with sub-annual models of phosphorus uptake and recycling, including a detailed 3-D hydrodynamic model. Taken together, my analyses showed that recycling of phosphorus in Lake Mendota is biologically important during the stratified season and is related to recent P inputs (on a time frame of 1-2 years) as well as physical stability of the water column.
References


Figure 1. Conceptual diagram of the potential mechanisms of phosphorus recycling within lakes. Biotic recycling (1) refers to cycling of phosphorus among biotic components within the epilimnion. Release from sediments (2) represents the release, by chemical or bacterial means, of phosphorus derived from the sediments or freshly sedimented organic material. Entrainment (3) refers to mixing of phosphorus-rich hypolimnetic water across the thermocline into the epilimnion.
CHAPTER 1
Road salt management and chloride dynamics of an urban lake

by

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Abstract

Chloride concentrations have been increasing in freshwaters across the United States and Canada. These increases are widely attributed to the use of rock salt as a de-icing agent. In a given watershed, changes in rock salt application could be related to changes in urbanization, length and width of roads, weather, or road management practices. The roles of these factors must be assessed in order to predict or manage future changes in chloride concentrations. Here we develop a model based on road salt application rates, weather and hydrology to explain long-term (1973 – 2006) chloride dynamics in a shallow urban lake, Lake Wingra, Wisconsin. We use this model to explore consequences of different road salt application rates for chloride concentrations in the lake. A relatively simple model satisfactorily represented monthly chloride dynamics in Lake Wingra, but tended toward conservative estimates of extreme values. Simulations demonstrated that Lake Wingra responds rapidly to changes in chloride loading. Reductions in road salt use can mitigate chloride concentrations in the lake within ~5 years. Mean steady-state chloride concentrations are not projected to exceed the limits for health of humans and aquatic organisms, however, seasonal peak concentrations in excess of the United States Environmental Protection Agency chloride guidelines already occur. Groundwater contamination could increase chloride loadings to the lake and decrease the lake’s capacity to respond to reductions in road salt use. Uncertainty, especially in the rate of increase and time for recovery of chloride concentrations in
groundwater, highlight the need for detailed monitoring of road salt application and pathways of interaction between surface and groundwater resources.
Introduction

Road salt use is positively correlated with chloride concentrations in surface and groundwater across Canada and northern parts of the United States (Schindler 2000, Interlandi and Crockett 2003, Kaushal et al. 2005, Howard and Maier 2007). Increasing chloride concentrations have been most prevalent in urban and suburban watersheds with a high incidence of impervious surface (Siver et al. 1999, Novotny et al. 2008, Kelly 2008). Kaushal and others (2005) identified an exponential relationship between mean chloride concentrations and the percent of impervious surface in the watershed. Elevated chloride concentrations are not confined to urban areas, but have also been identified in rural areas where road salt is applied to major roadways during the winter (Schindler 2000). It is clear that the application of rock salt to roadways in northern climates is affecting chloride concentrations of water resources.

While the relationship between urbanization (as quantified by the number of road miles or percent of impervious surface) and increasing chloride concentrations is clear, there remains substantial variation in observed chloride concentrations that cannot be explained by changes in land use alone. Variation among lakes has been attributed to the watershed area:lake volume ratio, which serves as a proxy for the flushing rate of the lake (Novotny et al. 2008). Also, land-cover permeability and mode of storm water management within the watershed affect delivery of chloride to a lake. For example, in the Toronto area, up to 55% of road salt applied may enter the shallow groundwater system rather than being directly transported to surface
waters. Meanwhile, Smith and others (1998) show that drainage by storm sewers (as opposed to combined sewers or roadside swales) provides the most direct route for pollutant transfer to surface waters. Thus, the hydrogeology of the watershed is an important determinant of the fate and transport of chloride to surface and groundwater (Lindstrom 2005).

Detailed accounts of chloride dynamics within watersheds show seasonal peaks in chloride concentrations associated with snowmelt and spring rains (Koryak et al. 2001, Novotny et al. 2008). Also, inter-annual variation in weather conditions affects both road salt application rates and the water balance (Lindstrom 2005, Thunqvist 2003). If we hope to improve management of road salt and curb the rise in chloride concentrations, we need to better understand the drivers of seasonal and inter-annual variation of chloride concentrations within and among lakes, streams and aquifers.

Here we aim to improve understanding of drivers of inter-annual variation in chloride concentration using twenty-four years of monitoring data from an urban watershed. In this watershed there has been little change in road density since the early 1970s, yet road salt application and chloride concentrations in the lake have been steadily increasing. Thus, the effects of meteorological factors, road salt management practices, and hydrological variables may be viewed independently from changes in road density in the watershed. This provides an opportunity to study a system that represents a possible future for many currently urbanizing watersheds. We first assessed which combination of meteorological, hydrological and road salt
application variables could best describe observed chloride dynamics in the lake. Then, using the best-fitting model, we explored how changes in road salt management are likely to affect chloride dynamics and we quantified the rate of lake response to these changes.

**Materials and methods**

Lake Wingra is a small lake (area = 1.3 km$^2$, mean depth = 2.7 m) situated in an urban watershed (area = 14 km$^2$) underlain by an extensive storm water sewer network. The watershed is almost exclusively under the jurisdiction of the City of Madison, Wisconsin, USA (43.053° N, 89.425° W).

The number of roads in the watershed did not change substantially over the period of the study (see Results section), yet we were interested in whether other characteristics of the land cover within the watershed had changed over time. To explore this, we used historical land use/cover data for the watershed that had been synthesized previously for 1962 and 1995 (Wegener 2001). The original interpretation of land use/cover was based on ortho-rectified aerial photography. The United States Department of Agriculture (USDA) captured black-and-white panchromatic photographs in 1962, and Dane County provided digital orthophotos for 1995. The data for 1962 and 1995 were digitized into a GIS database using ESRI ArcView (v. 3.1) and on-screen digitizing techniques. Mixed land use/land cover classes were designated in order to best account for the influence of land-water interactions.
We also analyzed current land use/cover patterns using data from 2006. The aerial photographs (1-2m resolution) for 2006 were acquired through the National Agricultural Imagery Program made available through the USDA Wisconsin Farm Service Agency. These aerial photographs were digitized in a similar fashion using ESRI ArcView (v. 9.2) and on-screen digitization techniques. The same land use/cover designations were used for the 2006 data as were assigned to the 1962 and 1995 photographs.

The land area identified as high-intensity development was assumed to be completely impervious, while that identified as low-intensity development was primarily residential. The impervious surface within residential areas was quantified based on a focused analysis of the proportion of impervious surface (road, driveway, or rooftop) within land categorized as “low-intensity development”. Specifically, ten sub-set areas each measuring 250 x 250 m were randomly selected within the area identified as low-intensity development. The exact percent of impervious area (road, driveway, or rooftop) of each sub-set area was quantified. The mean percent impervious surface within these ten sub-set areas was then multiplied by the total surface area classified as low-intensity development to arrive at an estimate of the total impervious surface within low-intensity development. The high-intensity development and proportion of the low-intensity development were summed to arrive at an estimate of the total proportion of the watershed that could be classified as impervious.
The lake is currently monitored by the Madison Public Health Department (MPHD) and the University of Wisconsin North Temperate Lakes Long-term Ecological Research Program (NTL-LTER) on a monthly and quarterly basis, respectively. MPHD records began in 1962, though consistent monthly monitoring did not begin until 1973, and data were not collected between 1974 and 1984. NTL-LTER monitoring of the lake began in 1995 and continues today (http://lter.limnology.wisc.edu). Therefore, our analysis relies on monthly estimates of chloride concentrations in 1973 and 1974, 1984 to 1993, and 1995 to 2006. Each monitoring program collects one or two grab samples from the surface water of the lake, and chloride samples are analyzed on an ion chromatograph using standard laboratory methods (USEPA standard method 300.0). During periods when both MPHD and NTL-LTER records were available for the same month, these estimates were combined into a single estimate of mean monthly chloride concentration for the lake. Field replicate samples collected from each monitoring effort indicate that the natural and analytical variation was low (coefficient of variation < 0.07 in all cases and < 0.03 in most).

Total road salt applied during each winter has been recorded by the city of Madison since 1959, and road salt applied specifically to the Lake Wingra watershed was monitored from 1969 – 1973. While the majority of the watershed is within the limits of the City of Madison, there are four other municipalities/government agencies responsible for road management in the Wingra watershed. The City of Madison maintains 19.3 lane miles (1 lane mile = 1.61 km x number of lanes) (Table 1). The
city limits salting efforts to intersections, hills, bus routes and routes to schools and hospitals. The Wisconsin Department of Transportation maintains salting on the Beltline Highway (US Hwy 12/18, 14 and 151, 23.4 lane miles), Dane County maintains Fish Hatchery Road (6.2 lane miles), the Town of Madison and the Town of Fitchburg maintain a total of 4.9 lane miles within the watershed (Table 1). Because road salt applied to the Lake Wingra watershed was not monitored over the entire period of record, we used three approaches to approximate the application rates in the watershed based on the observed application rates for the entire city. These three estimates were then used as candidate predictors in the model fitting procedure to determine which approximation best explained the observed patterns in the lake.

The first approach (Approach 1) was to use the ratio of the number of miles of roads in the Lake Wingra watershed compared to road miles for the whole city (ROAD\textsubscript{w}/ROAD\textsubscript{M}) (Table 2). The ratio was then multiplied by the total road salt applied in the city (SALT\textsubscript{M}) to estimate the total salt load for the Wingra watershed for each winter. The second approach (Approach 2) was to use the number of lane miles in the Wingra watershed (LaneMiles\textsubscript{w}) multiplied by the road salt application rate (AppRate\textsubscript{A}) and the total number of applications for the winter (TimesApplied\textsubscript{M}, as recorded by the City of Madison) (Table 2). A mean application rate of 68 kg lane-mile\textsuperscript{-1} (150 pounds lane-mile\textsuperscript{-1}) was used based on a common set of road salt application guidelines used across all municipalities and government agencies. In all cases, we assumed that the number of road miles or lane miles in the watershed has not changed significantly since the 1970s. This assumption is supported by public
records of roads on the "salt route" during 1972 and 1973 compared to roads included in the salt routes today (City of Madison Street Division 1973). The final approach (Approach 3) was to use a regression relationship based on the period during which there were salt application records for both the City of Madison (SALT_M) and the Lake Wingra watershed (SALT_W). The observed relationship between total road salt applied in Madison and that applied in the Wingra watershed was used to predict the Wingra-specific application rate in years when Wingra-specific data were not available. Only five years of data were available for the comparison of Madison to the Lake Wingra watershed (1969 – 1973), so results of this approximation were interpreted with care. These three approximations all resulted in an estimate of the total amount of road salt applied to the watershed during the winter.

These annual estimates were then apportioned into monthly estimates of road salt application based on three approaches: 1) equal application during winter months (November – April), 2) application rate proportional to mean observed monthly application from 1969 – 1973, 3) application rate proportional to the observed cumulative precipitation during each month. Thus, in the end we had nine different estimates (3 monthly apportioning methods x 3 estimates of Wingra-specific loading) of the amount of road salt applied to the Lake Wingra watershed for each month. Each monthly estimate of road salt application was converted to an estimate of chloride applied based on the relative molecular weights of sodium and chloride, which are the primary components of rock salt applied to roadways (0.607 of the total road salt applied is chloride).
Along with data on chloride concentrations in the lake and road salt applied in the watershed, we compiled data on meteorological and hydrological variables that may help to explain chloride dynamics in Lake Wingra. We assessed monthly mean air temperature, cumulative precipitation between sampling events, estimated monthly discharge from the lake, estimated Cl outflow (based on mean observed Cl concentrations multiplied by estimated hydrologic discharge), days between sampling events (these were limited to between 21 and 35 days in order to approximate a monthly time-step for analysis) and the nine different estimates for chloride application in the watershed. These variables were all used as candidate predictors in a chloride model at a monthly time step. In addition to data collected/aggregated to a monthly time step, we collected annual measures of the winter severity index as calculated and recorded by the Wisconsin Department of Transportation. This index is based on the incidence of snow events, freezing rain events, total snow amount, and total storm duration during the winter of interest (Adams, 2009).

All model assessment of monthly data was carried out using the R statistical and modeling package (http://www.r-project.org/). We first evaluated models to predict chloride concentrations one time step (month) ahead. These models correspond to process-error fits as discussed by Hilborn and Mangel (1997). Initial assessment of candidate predictors was completed using the “regsubsets” function within the leaps package and initial predictors were selected on the basis of Mallow’s Cp. The top three models from each size class (size class = model set with the same number of parameters) were then compared using Akaike Information Criterion (AIC).
The best fitting model was then used to produce a predicted time series of monthly chloride concentrations based on model parameters and each month's chloride load. These predicted values were used in model analysis, but were not used in the simulation exercise.

The monthly data were also fitted to an observation-error method by least squares (Hilborn and Mangel 1997). The best-fit observation-error model and parameter values were used in simulation exercises to produce a deterministic trajectory of future monthly chloride concentrations based on starting conditions (from 2006) and model parameters. We used the observation-error model in the simulation exercise because we had an estimate of the initial conditions (Cl mass in the lake in 2006) and this approach allows prediction of the next time step based on estimated values rather than observed values (as in the process-error model).

Simulations explored different strategies for road salt management in the Lake Wingra watershed. We investigated different loading rates ranging from 0 – 60,000 kg month$^{-1}$ over the next forty years. The initial conditions for the simulations equaled the current observed mass in the lake (227,910 kg). In each simulation, loading rate was stochastic with a constant mean and monthly deviations drawn from a normal distribution with standard deviation equal to the loading rate during the most recent 10 years of observation. Time series plots showed that simulated data became stationary (constant mean and standard deviation) after approximately 7 years. Therefore, we allowed each simulation to run for 10 years before recording data in order to ensure that the model had reached stationarity. We then recorded the
minimum, maximum and mean chloride concentration in the lake over the next 40 years of simulation.

In a second round of simulations, we examined the response rate of the lake to changes in road salt application practices. In these simulations, we ran the model for 25 years at a given load, then decreased the load to half the original load, and ran the model at the reduced load for an additional 25 years. The onset of lake response was defined as the point at which the chloride concentration decreased below the minimum value observed over the 10-year period prior to manipulation. Similarly the termination of lake response was defined as the point at which the chloride concentration fell below the maximum CI concentration observed within the final 10 years of the simulation. The response rate was the number of months between the onset and termination of lake response.

Results

General trends

Since 1962, the amount of road salt applied each winter season has increased, with the exception of a short period during the early 1970s when the Madison city council first adopted management policies focused on reducing total road salt application in the watershed (Figure 1a). These efforts at reduction were effective until the late 1970s. Concurrently, chloride (Cl) concentrations in the lake have risen over the period of record (Figure 1b). The mean annual Cl concentrations
tended to be more variable than the observed road salt application rate (coefficient of variation = 0.18 and 0.04, respectively).

Estimates of road salt application rates differed among approaches (Figure 2). Difference between Approach 1 and 2, though statistically significant (Student's paired t-test, p < 0.001 in all cases), were not grossly different. However, Approach 3 differed greatly from the other approaches. In all cases, the estimates were not significantly different based on different methods for allocating total load over the winter months. All nine estimates of road salt application were used as predictors in the model, and Approach 1.1 (in which road salt application was proportional to the number of roads in the Wingra watershed compared to all of Madison, and application was distributed equally among months) was identified as the best predictor of patterns observed in the lake.

Despite changes in land use and land cover in the watershed over the past forty years and accompanied increase in the percent of impervious surface (Figure 3), there has not been a substantial change in the number of road miles maintained within the Lake Wingra watershed since the 1970's. In 1974 there were approximately 18.1 lane miles maintained by the city (salt route documented by City of Madison Street Division 1973), while today there are approximately 19.3 (City of Madison Engineering Department 2009). Therefore, changes in road salt application cannot be explained by changes in the total number of roads maintained in the watershed. Instead, road salt application rates are significantly related to the winter severity index for Dane County as calculated by the Wisconsin Department of
Transportation (Figure 4) \((p = 0.003, R^2 = 0.22)\). There remains a large amount of unexplained variation around this relationship. Because the impervious surface estimates and winter severity index values were only available at decadal or annual scales, these variables were not included as potential predictors in the monthly modeling exercise.

**Model results**

The chloride mass in the lake was best explained by a simple model that included terms for chloride loading to the watershed and proportional loss from the lake.

\[
\Delta Y = L_{t-1} - bY_{t-1}
\]

Where: 
- \(\Delta Y\) = change in chloride mass in the lake
- \(L_{t-1}\) = chloride load during the previous time period
- \(Y_{t-1}\) = chloride mass in lake during previous time period
- \(b\) = chloride loss coefficient

The load term was based on Approach 1.1 for estimating road salt application, in which the road salt applied in the Lake Wingra watershed was equal to the road salt applied by the City of Madison multiplied by a correction factor proportional to the number of roads in Wingra compared to all of Madison. This model was able to predict the chloride mass in the lake for each month based on observations of loading and chloride mass from the previous month (Figure 5a and Figure 6a). There is evidence, however, that this model tends to over predict low values and under
predict high chloride concentrations. The model was used to predict the entire time series based on the initial mass in the lake and observed monthly loading (Figure 5c). Based on this simulation approach, the model was able to represent seasonal and long-term trends in the data (Figure 5b and Figure 6b).

The above model was then used to examine the effect of different road salt application practices on the expected equilibrium concentration of Cl in Lake Wingra. The results of the 40-year simulations are summarized as the minimum, mean and maximum chloride concentration observed in the lake during the 40-year period of constant loading. The mean Cl concentration in the lake increased linearly with an increase in the mean loading rate used in the simulation (Figure 7). The variation around Cl estimates also increased slightly with an increase in loading rate, as shown by the increase in the range of simulated values (represented by the error bars in Figure 7). The mean loading rate (27,442 kg month$^{-1}$) observed over the last ten years is represented by a bold line in Figure 7. If this rate of loading continues into the future, we can expect to witness Cl concentrations in the lake over a range of 80 – 150 mg L$^{-1}$. Observed Cl concentrations over the last ten years have ranged from 71.6 – 105.7 mg L$^{-1}$ (represented by the bold line in Figure 7). Thus, if loading patterns remain the same, we can expect to see a further increase in Cl concentrations in the lake.

Alternatively, managers may aim to reduce road salt application and thus Cl loading to the lake. A reduction to a constant load equal to 50% of the original loading rate would result in an eventual 50% decrease in Cl concentration in the lake relative
to the starting concentration (Figure 8). The response rate of the lake varied from 45 to 54 months. Variation in response rate was due to the stochastic nature of the simulations, and did not differ systematically depending on the initial loading rate or concentration in the lake. Cl is not expected to be retained by the lake, but instead is removed in proportion to the flushing rate of the lake, which has been estimated to be \( \sim 0.75 \text{ yr}^{-1} \). The relatively fast flushing rate and the short response time of the model suggest that Lake Wingra could recover within 5 years from excessive loads, within the range of chloride loads observed to date.

**Discussion**

Chloride dynamics in Lake Wingra are primarily driven by the application of road salt in the watershed. The results of our empirical analysis combined with modeling efforts suggest that Lake Wingra is sensitive to changes in road salt application and that the lake responds to changes in road salt management within a time frame on the order of 45 – 54 months (\( \sim 4 – 5 \text{ years} \)). However, loading of chloride associated with road salt application has begun to affect the shallow and deep groundwater aquifers in the Madison area, and these subterranean resources will be much slower to respond to mitigation efforts (Kelly 2008). As groundwater transport of chloride to the lake increases, the lake may become less responsive to reductions in road salt application rate to the watershed. Current and short-term projected mean concentrations for the lake are not above the limit of concern for health of humans and aquatic organisms (discussed below), yet periodic seasonal
peaks in chloride concentrations do exceed these limits and should be a focus of further monitoring efforts. A similar model could be applied to other watersheds in order to explore the repercussions of various road salt management strategies.

Challenges in estimating road salt application

Other studies have shown that the degree of chloride increase in a lake can be related to the amount of impervious surface in the watershed (Novotny et al. 2008). Similarly, in the Wingra watershed we see that impervious surface has increased throughout the period of record. However, in the Wingra watershed, the number of road-miles has not changed appreciably since the late 1970’s. Thus, in Lake Wingra, we were able to explore the effects of road salt management independent of changes in road density. It seems that changes in road salt application can be primarily attributed to changes in management practices that are tied to winter weather conditions, rather than changes in the length of roads serviced (Figure 4). It remains possible that an increase in impervious surface may promote more direct delivery of chloride from the Lake Wingra watershed into the lake. We were not able to directly examine this idea given the relatively coarse temporal resolution of the data on impervious surface.

Our model selection procedure consistently identified “Approach 1.1” as the best metric to represent road salt application; the best long-term metric was based on a proportion of the number of road miles in the Lake Wingra watershed compared to the City of Madison with application attributed equally among months of the winter.
Yet, there may certainly be variation among municipal and county managers in application practices, and temporal variation in how much road salt is applied during each month of the winter. If application practices are notably different between the City of Madison, Dane County, the Town of Madison and Fitchburg, then the monthly estimates of road application may be more variable than those presented here. Application rates may not differ significantly among management agencies because all road management agencies rely on the same set of salt application guidelines, but different management agencies may salt with greater frequency. For example, Dane County maintains road salt application on a 6-lane highway that serves as the junction of United States Highways 12, 18, 14 and 151. Given the large volumes of traffic that use this roadway, we may expect greater application frequency on this segment of road. It was difficult to assess differences in application rates among municipalities due to lack of long-term records or event-specific accounts.

Further, road salt estimates used in this study may underestimate the true application rate within the watershed because we were unable to estimate the application rate on commercial or residential pavement. Other studies in urban area have suggested that application to parking lots, sidewalks and driveways may account for approximately 10 - 15% of the total salt application (Howard and Haynes 1993). Overall, our estimates of the magnitude of road salt application in the watershed should be interpreted as conservative and future modeling efforts would be improved by a more detailed accounting of when, where and how much road salt is applied within the watershed.
Imprecise estimates of road salt application may partially explain the instances of over or under-estimation of chloride concentration that are apparent in Figure 5b. While the model generally follows the dominant trend of the long-term data, the model does not do as well in predicting extreme chloride concentrations. It is possible that during these time periods other factors, like precipitation and discharge, may be important, though these were not identified as significant predictors in the model selection procedure. The tendency of the model to under and over-predict extreme values should be considered in interpreting the results of the simulations because the range of simulated values may be conservative compared to the range that can truly be expected.

**Accounting for a changing environment**

A simple model adequately represents the past and current Cl dynamics in Lake Wingra. However, projections of future Cl concentrations are based on the assumption that the nature of the system will remain the same at higher loading rates that have not yet been observed in the system. An alternate possibility is that continued high loading rates could fundamentally change how the system functions, thus necessitating use of a different model. This will occur if groundwater, which may constitute up to 35% of the water budget for the lake, becomes further elevated in chloride.

Historical hydrologic budgets for Lake Wingra indicated roughly equal contribution from precipitation (31%), surface runoff (34%) and groundwater (35%)
(Novitzki and Holmstrom 1979). Recent simulated estimates of the hydrologic contribution of groundwater to the flow of Lake Wingra, however, suggest that groundwater input to the lake has declined by up to 64% from a historic rate of 3.3 cfs to a current rate of 1.2 cfs (Lathrop et al. 2005) due to municipal groundwater use and drawdown. Historically, groundwater, surface water and precipitation delivered freshwater to the system, with the exception of chloride loading via surface runoff during winter and spring months. However, recent monitoring of the shallow groundwater aquifer connected to Lake Wingra shows that chloride concentrations are variable and periodically very high (Figure 9a).

These monitoring data have been collected in conjunction with a groundwater recharge project within the Lake Wingra watershed. Monitoring wells were installed at the recharge site, up gradient from the recharge site (to serve as a background reading), and at two locations down gradient from the recharge site. It is estimated, based on the groundwater flow paths, that groundwater entering the system at the recharge site will reach the lake within 20 – 40 years. Increases in chloride concentrations in the shallow groundwater aquifer could translate into higher concentrations of chloride entering the lake through groundwater year-round. Under these conditions, Lake Wingra would take longer to recover following a decrease in road salt application. Also, the concentrations of chloride in the shallow aquifer would take much longer to decrease due to the typically low recharge rate and slow flow rate of groundwater resources (Howard and Haynes 1993, Arnold et al. 2000, Lindstrom 2005, McGinley 2008).
Lake Wingra is closely connected to the shallow unconfined groundwater aquifer underlying the watershed (Oakes et al. 1975, Lathrop et al. 2005). Meanwhile, Madison residents depend on a deep groundwater aquifer (the confined Mount Simon aquifer), which is used as a municipal drinking water supply. The shallow and deep groundwater aquifers had historically been characterized as distinct, yet recent evidence suggests that long-term pumping from the deep aquifer has resulted in accelerated downward flow of recharge water from the overlying shallow groundwater aquifer (Borchardt et al. 2007). Increased interaction between shallow and deep groundwater aquifers raises the possibility that chloride contamination of shallow groundwater can be conferred to deep groundwater used for drinking water. There is already evidence of elevated chloride concentrations in monitored drinking water wells in the Madison area (Figure 9b). The trend of increasing chloride concentrations in shallow and deep groundwater aquifers, along with the increase in hydrologic interaction between the two, indicate the need for caution in road salt application in the region.

Chloride limits for aquatic organisms

Mean model projections are within an acceptable range for health of humans and aquatic organisms, as current drinking water limits are set at 250 mg L\(^{-1}\) for human consumption (USEPA 1988). Yet, seasonal peaks in chloride concentrations in the bottom waters of the lake have been observed to be as high as 420 mg L\(^{-1}\) (Figure 10). A seasonal pattern in chloride concentrations is typical in north-
temperate urban systems because road salt may be flushed off of the landscape in a pulse and accumulate in the bottom waters of the lake until mixing occurs (Novotny et al. 2008). During this period, chloride concentrations may exceed the limits for chronic and acute toxicity for aquatic organisms.

Road salt has been shown to have negative effects on aquatic organisms, most notably on benthic organisms and larval stages of amphibians (Mayer et al. 2007, Snodgrass et al. 2007, Grapentine et al. 2008). While direct toxicity testing suggests chronic toxicity limits ranging from 735 – 4681 mg L\(^{-1}\) for specific organisms in the laboratory, logistic modeling of chronic toxicity indicates that approximately 5% of aquatic species may be adversely affected by chronic chloride concentrations as low as 213 mg L\(^{-1}\) (Nagpal et al. 2003). Current USEPA standards take seasonal variability into account and suggest that aquatic organisms should not be exposed to a 4-day average concentration of greater than 230 mg L\(^{-1}\) more than once every three years, and a 1-hour average chloride concentration exposure should not exceed 860 mg L\(^{-1}\) more than once every three years (USEPA 1988). Based on our calculations, chronic chloride concentrations in Lake Wingra could reach these harmful levels (exceeding 213 mg L\(^{-1}\)) if loading increases to a mean loading rate of 44,800 kg per month for a period of 4 years. During the winter of 2007-2008, a winter with high snowfall in the Madison area, this loading rate was exceeded when a mean of 49,700 kg of chloride was applied each month to the Lake Wingra watershed.

Conclusions
Synoptic studies reveal that road salt application in the United States has increased steadily since application began in the 1950's (Jackson and Jobbagy 2005, Kelly 2008). Here we demonstrate a simulation model that explores the response of an urban lake to changes in road salt management practices. Under current conditions, Lake Wingra is likely to respond quickly to mitigation efforts (within ~5 years). However, continued loading warrants monitoring of shallow and deep groundwater resources, due to increasing chloride concentrations, long residence times, and increasing interaction between shallow and deep aquifers. Similar patterns in increasing chloride concentrations in surface and groundwaters have been observed in both urban and pristine areas across northern climates, and similar modeling approaches may be applied to other systems.

While current mean concentrations of chloride in surface and groundwater in the Lake Wingra watershed are below the limits of concern for health of human and aquatic organisms, concentrations periodically exceed these limits. The magnitude and durations of peaks in chloride concentrations in the lake may not be effectively documented by current monitoring efforts (based on single grab samples from the surface of the lake). Response of native biota to periodically high chloride concentrations is still not clear, and this topic warrants further research.

The approach we present could be a useful tool for managers and decision makers who are interested in the potential response of surface waters to continued or increased loading of chloride associated with road salt application. Uncertainty, especially in the rate of increase and the lag time for recovery of chloride
concentrations in groundwater, highlight the need for more detailed monitoring of road salt application and the pathways of interaction between surface and groundwater resources.
References


McGinley, P. M. 2008. Modeling the influence of land use on groundwater chloride loading to lakes. Lake and Reservoir Management 24: 112-121.


Table 1. Summary of the number of lane miles maintained by different municipalities and agencies within the Lake Wingra watershed in 2007.

<table>
<thead>
<tr>
<th>Municipality/Agency</th>
<th>Portions Salted</th>
<th>Total Lane Miles Managed</th>
</tr>
</thead>
<tbody>
<tr>
<td>City of Madison</td>
<td>Intersections; hills; bus, school and hospital routes</td>
<td>19.3</td>
</tr>
<tr>
<td>Wisconsin Department of Transportation</td>
<td>Beltline Highway (US Hwy 12/18, 14, 151)</td>
<td>23.4</td>
</tr>
<tr>
<td>Dane County</td>
<td>Fish Hatchery Road</td>
<td>6.2</td>
</tr>
<tr>
<td>Town of Madison, Town of Fitchburg</td>
<td>Select streets within the watershed</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Table 2. Approaches used to estimate the total winter-time load of road salt to the Lake Wingra watershed. ROADS = the number of road miles (range represents the range of road miles in Madison between 1973 and 2006), SALT = the total mass of road salt applied during the winter, LaneMiles = number of lane miles (where a 4-lane road = 4 x length of road), TimesApplied = Number of times during the winter road salt was applied (data only available at city level), AppRate = Application rate for road salt (common guidelines are used across all agencies). Definition of subscripts: W =

<table>
<thead>
<tr>
<th>APPROACH</th>
<th>CONDITIONS</th>
</tr>
</thead>
</table>
| 1. \( \frac{\text{ROADS}_w}{\text{ROADS}_M} \times \text{SALT}_M \) | ROADS\(_w\) = 19.3 mi  
ROADS\(_M\) (range = 512 – 758 mi)  
SALT\(_M\) (range = 1379 – 16277 MT) |
| 2. \( \text{LaneMiles}_w \times \text{TimesApplied}_M \times \text{AppRate}_A \) | LaneMiles\(_w\) = 57 mi  
TimeApplied\(_M\) (range = 16 – 36)  
AppRate\(_A\) = 68 kg mi\(^{-1}\) |
| 3. \( \text{SALT}_w = b_0 + b_1 \times \text{SALT}_M \) | Observed for 1969 – 1973 only  
SALT\(_w\) (range = 238 – 459 MT)  
SALT\(_M\) (range = 2895 – 6071 MT)  
\( b_0, b_1 = \) coefficients used to predict SALT\(_w\) in other years |

Lake Wingra watershed, M = City of Madison, A = All agencies.
Figure 1. (a) Total road salt applied in the Lake Wingra watershed during each winter. (b) Mean annual chloride concentration observed in Lake Wingra based on monthly sample collection following 1973. Prior to 1973, estimates are based on 1 – 6 observations of chloride concentrations in the lake within the year. Error bars represent the standard deviation around the annual mean (only shown for years with more than 2 samples).
Figure 2. Estimates of road salt application rates based on three approaches for estimating the total load for the winter (Approach 1, Approach 2, Approach 3) and on three methods for allocating road salt application among months of the winter (methods are designated as 1, 2, 3). The approaches are fully described in Table 1. Solid lines represent the median of the data, notches represent a 95% confidence interval, the boxes represent the inter-quartile range, the whiskers and dots represent the full range in the data, with dots signifying potential outliers. Each Approach is significantly different from the other (Student’s t-test, p-values <0.001 in all cases), but within each Approach there was no significant difference among methods for allocating among months.
Figure 3. Changes in land cover in the Lake Wingra watershed over 44 years. Though the number of road miles in the watershed has not changed significantly in the period between 1995 and 2006, there has been an increase in impervious surface in the watershed.
Figure 4. Significant positive relationship between the winter severity index and the mean winter-time chloride load in the watershed ($p = 0.003$, $R^2 = 0.22$). The line represents the model fit to the data. Winter severity index values were available from 1993 – 2008.
Figure 5. Chloride mass in the lake that was observed and predicted by the best fitting model. Predictions were made for each month based on the previous observed chloride mass (process-error model) (a), and predictions were simulated based on the initial conditions and model parameters (observation-error model) (b). The amount of Cl applied in each month served as input to the model (c). Note the x-axis is not continuous.
Figure 6. Observed and predicted values for the model. The line represents a 1:1 relationship. Panel (a) presents the fit one-step ahead (process-error model). Panel (b) presents fit to whole time series (observation-error model).

Figure 7. Mean chloride concentration expected in Lake Wingra following forty years of loading at different loading rates. The error bars represent the minimum and maximum simulated concentration based on stochastic simulations of a constant load. The bold line represents the range in Cl concentrations observed over the past ten years at a mean winter loading rate of 27442 kg month$^{-1}$. 
Figure 8. Effects of a 50% reduction in chloride loading rate. The baseline loading rate was set to four different levels: 2 times the current load, 1.5 times the current load, the current load, and 0.5 times the current load. The simulated reduction in load was implemented at time step 110.
Figure 9. Chloride concentrations in wells that tap the shallow (a) groundwater aquifer and deep (b) groundwater aquifer (the Mount Simon aquifer). The horizontal line in panel a represents the EPA limit for chronic exposure for aquatic organisms. The deep groundwater aquifer is used as a drinking water source by the City of Madison. Note the difference in scales on the axes.
Figure 10. Chloride profile in Lake Wingra on March 18th, 2008. Depth represents the depth from the surface of the lake.
CHAPTER 2

Phosphorus sources and demand during summer in a eutrophic lake

by

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Keywords: ecosystem metabolism; entrainment; respiration; production; C:P ratio; phytoplankton bloom.

Abstract

In pelagic systems, phytoplankton biomass may remain abundant or near equilibrium while concentrations of the limiting nutrient are below detection. In eutrophic lakes, it has been thought that episodic algal blooms are due to mixing events that break down this equilibrium by adding nutrients to the mixed layer. Alternatively, rapid rates of biotic recycling among primary producers and heterotrophic consumers could maintain high phytoplankton biomass, yet the recycling process has been difficult to observe in situ. Here we use free-water oxygen measurements and an associated metabolic model to infer rates of phosphorus (P) uptake and biotic mineralization in the epilimnion of a eutrophic lake. The rates of uptake and mineralization were compared to "external" sources of P such as loading and entrainment. Also, model results were assessed using sensitivity analysis. We found that the majority of phytoplankton P demand during the period of low P availability could be accounted for by biotic mineralization, but that it was important to consider the effects of entrainment in order to account fully for P uptake. These general results were relatively insensitive to model parameterization, though the relative C:P ratio of material taken up versus mineralized was an important consideration. This study integrates modeling and measurement tools that monitor ecosystem processes at finer temporal resolution than has previously been possible, complementing other studies that use experimental incubation and elemental tracers. Extension of this approach could enhance models that aim to integrate biological and
physical processes in assessment of water quality and prediction of phytoplankton biomass.
Introduction

Phytoplankton in lake ecosystems may remain abundant under apparent nutrient limitation despite loss by sinking, grazing, natural mortality and bacterial- and viral-mediated mortality (Juday et al., 1927; De Pinto et al., 1986; Caraco et al., 1992). This paradox is particularly puzzling in eutrophic lakes where strong summer stratification and nutrient limitation would seem to favor phytoplankton loss over production and growth, yet phytoplankton blooms may occur during the period when phosphorus concentrations are below detection (De Pinto et al., 1986). A number of mechanisms may explain the provisioning of phosphorus (P) to nutrient-limited primary producers including biotic recycling, loading from external sources and entrainment of P-rich metalimnetic waters.

Biotic recycling of organic P compounds by heterotrophic zooplankton and microbes is highly variable, but field and laboratory research suggests that much of the P needed for phytoplankton production may be supplied by heterotrophic mineralization (Barlow and Bishop, 1965; Cole et al., 1988; Sterner, 1989; Poister et al., 1994) and that mineralization may be the dominant supply of nutrients during bloom formation (De Pinto et al., 1986). Excretion of inorganic P by zooplankton alone may account for 4-239\% of the P demand of primary producers, and this percentage varies among months (Gulati et al., 1995; Vanni, 2002). However, other analyses focused on rates of primary production that are corrected for loss of phytoplankton argue that biotic recycling is not sufficient to explain observed rates of production during the summer (Caraco et al., 1992). Thus, multiple lines of evidence
suggest a variable and important role of heterotrophic consumers in P recycling, yet this process has been difficult to observe and quantify in lake ecosystems (Lehman, 1980).

External loading and entrainment are dominant sources of nutrients to lakes at an annual time scale, yet their importance during the period of summer stratification and low nutrient availability is not clear. External loading is often thought to be unimportant during summer months due to lower seasonal flows into lakes. Similarly, entrainment, or transport of P from deep water, has been noted to be low due to strong stratification (Lean et al., 1987). Recent work, however, suggests that the flux of nutrients across the thermocline may be an important driver of epilimnnetic metabolism (MacIntyre et al., 2002; Staehr and Sand-Jensen, 2007). Another study shows that external P inputs fuel new production (Caraco et al., 1992). Notably, external loading and entrainment may be most important following storms (MacIntyre et al., 2006), but in these cases the event is difficult to monitor and the fate of nutrient influx can be difficult to trace. As such, the relationship between episodic storms, movement of P-rich waters, and blooms of phytoplankton is noisy and difficult to interpret (Soranno et al., 1997; MacIntyre et al., 2002).

The pathways of P supply are transient and occur at temporal and spatial scales that have been challenging to observe. This challenge has been met using light/dark bottle incubations with $^{14}$C as a proxy for metabolic P demand, $^{32}$P incubations as a measure of P uptake rates, and experimental isolation of heterotrophic organisms to estimate rates of mineralization (Ryther, 1956; Hargrave
and Geen, 1968; Lean et al., 1983; Lean et al., 1987; Sterner, 1986; Vanni, 2002). These approaches involve extended incubation times during which it is difficult to maintain representative environmental conditions. Additionally, there is unresolved debate about the relationship between rates of $^{14}$C fixation and gross versus net primary production (Peterson, 1980; Carignan et al., 2000). The challenges and limitations associated with these techniques are widely recognized (Bender et al., 1987; Smith and Prairie, 2004; Staehr and Sand-Jensen, 2007).

Here we explore a complementary free-water approach to estimate P uptake and mineralization. We derived estimates of in situ P uptake and heterotrophic mineralization using high-resolution oxygen data and an associated metabolic model. We then compared metabolically-inferred P uptake and mineralization rates to sources of P such as external loading and entrainment. Empirical estimates of uptake, mineralization, loading and entrainment were used to calibrate a model of P demand and supply and we used this model to explore the theoretical bounds of biotic and abiotic P transformation within the epilimnion of a eutrophic lake. Our goal was to examine the dynamic behavior of P demand and supply processes to elucidate the relative importance of biotic recycling and abiotic sources of P like external loading and entrainment, particularly during the period of low P availability.

**Materials and Procedures**

This study has four main components: empirical measurements of oxygen, carbon and P; integration of these empirical estimates into a whole-ecosystem
metabolism model to estimate P uptake and mineralization rates; comparison of metabolically-derived uptake rates to potential sources of P such as in situ heterotrophic mineralization, external P loading and entrainment of P from the metalimnion of the lake; and sensitivity analysis of model results to changes in our assumptions. Estimated uptake rates served as a proxy for P demand, and throughout the text we use “uptake” and “demand” interchangeably.

All data were collected during the summer of 2007 on Lake Mendota, a eutrophic lake in Madison, Wisconsin (43°06' N, 89°25' W, 39.1 km² surface area, 12.3 m mean depth). Lake Mendota stratifies during the summer and soluble reactive P (SRP) typically falls below the limits of analytical detection in the epilimnion (North Temperate Lakes Long Term Ecological Research program (http://lter.limnology.wisc.edu)). Because SRP is often used as a proxy for the concentration of bioavailable P in the system, we targeted our assessment on this component of the P budget. We focused sampling efforts on the epilimnion during the period of strong stratification and low concentrations of SRP (28 June 2007 until 8 September 2007) in order to explore how phytoplankton P demand during this period may be met.

Field and Laboratory Methods

During the summer of 2007 an automated buoy equipped with temperature and oxygen probes was deployed at a central location in Lake Mendota. A TempLine (Apprise Technologies, Inc.) thermistor array recorded temperature every minute at
0.5 – 1.0 m intervals from 0 – 20 m depth. Dissolved oxygen concentrations were monitored using a D-Opto (Zebra-Tech LTD, New Zealand) optical dissolved oxygen probe that was suspended from the buoy at 2 m. The dissolved oxygen probe was compared weekly to manual measurements and corrected, assuming linear drift. The high-resolution temperature data were averaged over 24 hour periods and used to identify the maximum depth of the mixed layer for each day. Diel mixed layer depth was around 8 m for the season, though on a number of days microstratification was apparent within the first 2 or 3 meters of the surface. In order to avoid incorrectly identifying shifts in depth of the mixed layer due to microstratification, we defined the depth of the mixed layer as the final depth (starting from lake surface) at which the temperature was within 1.5 °C of the mean temperature of the first 5 m.

Water samples were collected at least weekly in acid-washed polyethylene bottles at 1 – 4 m intervals throughout the water column using a peristaltic pump for determination of total P (TP) and soluble reactive P (SRP) concentrations. In the field, SRP samples were filtered through a 0.45-μm polycarbonate etched filter using in-line filtration, and stored on ice. TP samples were preserved using Optima HCl, while SRP samples were refrigerated and analyzed within 24 h. SRP samples were analyzed colorimetrically using the ascorbic acid method (American Public Health Association (APHA), 1995). TP samples were analyzed using a Technicon Auto Analyzer following persulfate digestion (APHA, 1995). All statistical analyses and model iterations were run using the mean P concentration of samples from the epilimnion.
Particulate carbon and P samples were collected from triplicate integrated epilimnetic samples. These samples were collected at least weekly from mid-June to mid-October at depths determined by concurrent temperature profiles. All samples were filtered onto glass fiber filters and stored for carbon or P analysis. Because there is no evidence that the C:P ratio of phytoplankton should differ markedly from that of the whole water seston (Healey and Hendzel, 1980; Sterner and Elser, 2002), particularly during the summer when phytoplankton dominate seston composition (Hecky et al., 1993; Elser et al., 1995), the C:P ratios for uptake and mineralization are derived from the C:P ratio of the entire seston. Carbon values used in the C:P ratio were based on determination of ash-free dry mass (AFDM). Three replicates of each sample were filtered onto pre-weighed glass fiber filters (Proweigh GF/F, 47 mm, 1.5 μm pore size). The filters with sample residue were placed in a drying oven for at least 48 h, transferred to a desiccator for at least 48 h, and weighed. The filters and samples were then combusted at 550 °C for 4 h, returned to the drying oven and desiccator, and weighed again. Combusted mass was subtracted from dry mass to determine AFDM. Seston carbon concentration was inferred as 48% of the AFDM (Round, 1965; Fogg, 1975). Whole seston particulate P concentrations used as the denominator in the C:P ratio were determined using the method described by Lampman et al. (2001). Integrated epilimnetic samples were filtered onto pre-combusted glass fiber filters and frozen until analysis. Samples, standards, and blanks were placed in 25 ml acid-washed serum vials and digested by adding 20.0 ml of 1% low N potassium persulfate (Fisher Scientific ID #P282-500). The vials were
sealed with aluminum rings crimped over butyl rubber septa and autoclaved for 2.5 h at 120 °C. The concentration of P in the liquid portion of each sample was analyzed colorimetrically using the ascorbic acid method and all samples were corrected for P content of the filter and of the digestion reagent (APHA, 1995).

Water samples for the determination of chlorophyll a concentration were collected twice per week at 2 m using a peristaltic pump or Van Dorn sampler. Water was collected in dark 3.5 L bottles and stored on ice in the field. Within three hours of collection, samples were mixed well, filtered under low light conditions onto glass fiber filters (Whatman GF/F, 47 mm, 0.7 μm pore size), and frozen until analysis. Chlorophyll a samples were extracted with methanol and analyzed fluorometrically on a Turner TD-700 fluorometer. The final concentrations were corrected for phaeopigments (Holm-Hansen and Riemann, 1978; Arar et al., 1997).

Metabolic Inference of Phosphorus Uptake and Mineralization

Estimates of gross primary production (GPP) were derived as follows from free-water oxygen measurements collected during buoy deployment. For each 1-minute measurement interval, t, we calculated net ecosystem production (NEPt) from the measured change in oxygen concentration, ΔO2 (mmol O2 m⁻³ min⁻¹), and atmospheric exchange, Dt (mmol O2 m⁻³ min⁻¹). To express metabolism in areal units (mmol m⁻² min⁻¹), we multiplied by the depth of the mixed layer, z (m).

(Eq. 1) \[ \text{NEP}_t = \text{GPP}_t - R_t = (\Delta O_2 - D_t) \times z \]
Atmospheric exchange can be positive or negative. We use positive values to indicate addition of $O_2$ to the lake and negative values for removal. Atmospheric exchange was estimated as

\[ D_i = \frac{k([O_2]_{\text{SAT},t} - [O_2]_t)}{z} \]  

(Eq. 2)

$[O_2]_{\text{SAT},t}$ ($\text{mmol m}^{-3}$) is the aqueous concentration of oxygen if the lake were in equilibrium with the atmosphere and was calculated from water temperature using the empirical equation of Weiss (1970). $[O_2]_t$ ($\text{mmol m}^{-3}$) is the measured concentration of dissolved oxygen in measurement interval $t$. We calculated the gas piston velocity, $k$ ($\text{m min}^{-1}$), using estimates of $k_{600}$ ($\text{m min}^{-1}$) as a function of wind speed (Cole and Caraco, 1998; Cole et al., 2000) and the water temperature dependent Schmidt number, $Sc$, (Wanninkhof, 1992).

\[ k = k_{600} \left( \frac{Sc}{600} \right)^{-\frac{1}{2}} \]  

(Eq. 3)

We measured wind speed every minute at 2 m above the water surface and converted these measurements to values at 10 m height assuming a neutrally stable boundary layer and the empirical equation of Smith (1985) to calculate values of $k_{600}$.
(m min\(^{-1}\)). In order to express atmospheric exchange in volumetric units, we divided by the depth of the mixed layer, z (m).

We used the values of NEP for each measurement interval (NEP\(_t\)) to obtain daily estimates of NEP, GPP and ecosystem respiration (R) (Eq. 1). During darkness, the NEP\(_t\) values are attributable solely to respiration. Therefore, we summed the nighttime NEP\(_t\) values and divided by the period of darkness to get the rate of ecosystem R at night. We followed the convention of assuming daytime R is equal to nighttime R and averaged the R rates obtained for the night preceding and night after each daylight period to estimate R for each day. Daily values of GPP were calculated by summing the interval measurement of NEP\(_t\) for the daylight hours and adding daytime R. We aggregated daily estimates of GPP and R to a weekly scale following the convention established by Cole et al. (2000) and justified by Staehr and Sand-Jensen (2007). Also, the weekly scale was most fitting for inference because P samples were collected at a weekly time step.

We used estimates of GPP and ecosystem respiration (R\(_{tot}\)) to estimate P demand and mineralization (assuming photosynthetic and respiratory quotients of 1.0). The assimilation of P into algal cells should occur at a rate proportional to the net primary production (NPP) observed in the system. NPP is equivalent to GPP (mmol O\(_2\) m\(^{-2}\) d\(^{-1}\)) corrected for the amount of oxygen used in autotrophic respiration (R\(_a\)) (mmol O\(_2\) m\(^{-2}\) d\(^{-1}\)). Thus, to determine the rate of NPP and convert the oxygen-based estimate to carbon we used the following equation:

\[
\text{NPP} = \text{GPP} - \text{R}\(_a\)
\]
NPP = 0.375 * (GPP - Ra)

Where:

NPP = net primary production (mmol C m\(^{-2}\) d\(^{-1}\))

Ra = autotrophic respiration (mmol O\(_2\) m\(^{-2}\) d\(^{-1}\))

0.375 = mass ratio of C to O\(_2\)

Autotrophic respiration is difficult to determine, but has been quantified in a number of studies with values generally ranging from 35 – 60% of total community respiration (del Giorgio and Peters, 1993; Duarte and Cebrian, 1996, Dodds and Cole, 2007). As a nominal value we assumed that Ra would be equal to 50% of total community respiration.

In order to infer the P uptake rate (P\(_{\text{uptake}}\)), we assumed that over the short period of the study the in situ C:P ratio of phytoplankton serves as an adequate estimate of the C:P ratio at which inorganic materials are assimilated during photosynthesis. Thus, from estimates of NPP (mmol C m\(^{-2}\) d\(^{-1}\)) and seston molar C:P, we calculated rates of P uptake based on the following:

(Eq. 5) \[ P_{\text{uptake}} = \frac{\text{NPP}}{1/(\text{C:P})} \]

Mineralization of P (P\(_{\text{min}}\)), a measure of biotic recycling, was assumed to occur under conditions of heterotrophic metabolic equilibrium (i.e. growth ~ loss). Bacterial
Biomass is relatively constant during this period of the summer in Lake Mendota (epilimnetic bacterial biomass ranged from 130.3 – 177.8 mg C m$^{-2}$ in 1979 and 84.7 – 167.0 mg C m$^{-2}$ in 1980; Pedros-Alio and Brock, 1982) and it is likely that overall heterotrophic growth rates are approximately balanced by loss. Under a scenario of zero net heterotrophic growth, we infer that the C:P of mineralization is equivalent to the C:P ratio of the substrate. Therefore, the C:P ratio of mineralization was assumed to be equal to the C:P ratio of whole epilimnetic seston. This value was multiplied by the proportion of total respiration due to heterotrophs ($R_h$) (mmol C m$^{-2}$ d$^{-1}$) according to the following equation:

(Eq. 6) \[ P_{min} = R_h \times (1/(C:P)) \]

Where:

\[ R_h = R_{tot} - R_a \]

Estimating non-metabolic sources of phosphorus

In addition to quantifying the metabolic processing of P, we also assessed alternate SRP sources to the lake during the period when SRP was below detection. Estimates of external load were based on an approach used previously (Lathrop et al., 1998; Carpenter and Lathrop, 2008). There are four streams and two storm water inlets that enter Lake Mendota. Two streams (Pheasant Branch and Yahara River) and one storm water inflow (Spring Harbor) are continuously monitored for hydrologic and chemical inputs into the lake by the United States Geological Survey (USGS).
Loading was determined for these three inlets and these data were used to infer loading from other inlets based on previous estimates of the relative load entering the lake from each source (Lathrop et al., 1998). Baseline P loads were measured as input of total P, but data were also available to determine the approximate proportion of P entering the lake in the soluble form. For most inflows (Six Mile Creek, Pheasant Branch, Spring Creek, Spring Harbor and Willow Creek), the proportion of P entering as SRP was 24-52% of TP and did not depend on discharge. However, for the largest inflow, the Yahara River, the proportion entering the lake as SRP differed systematically based on flow rates (SRP = 0.045 (± 0.024) x TP when discharge < 5.7 m³ s⁻¹; SRP = 0.56 (± 0.028) x TP when discharge > 5.7 m³ s⁻¹) due to a wide river estuary immediately upstream of the lake. Therefore, when discharge > 5.7 m³ s⁻¹, the “high flow” proportion (0.523 x TP) of SRP was attributed to the input, while during “low flow” SRP input was equal to 0.186 x TP, based on flow-weighed mean SRP:TP ratio of all inflows. This rate was used to convert estimates of TP loading from all inflows to areal estimates of SRP loading. Similarly, we were interested in accounting for any significant loss of SRP to downstream systems through the outlet of the lake. The hydrologic outflow was multiplied by the mean SRP concentration of the epilimnion during the periods when SRP was detectable, however the total mass of SRP lost through this pathway was negligible (mean outflow < 0.0001 mg SRP m⁻² d⁻¹).

Entrainment of SRP into the epilimnion from lower strata of the lake was also considered. Entrainment events were identified using the high-resolution temperature
profiles, and entrainment was defined as an increase in the maximum depth of the mixed layer by 0.5 m or more. When an additional mass of water was incorporated into the epilimnion we quantified the associated SRP flux based on the volume of water incorporated and the mean SRP concentration of that water mass. This flux includes SRP derived from hypolimnetic and benthic remineralization.

We also considered the input of P from rain water using total weekly precipitation, as measured at a weather station associated with the Dane County Truax airport, multiplied by a TP concentration of 0.032 mg P L\(^{-1}\), an average used in previous budget calculations for the lake (Lathrop, 1979; Soranno et al., 1997). The mean estimate we derived (0.19 mg P m\(^{-2}\) d\(^{-1}\) ± 0.26) is likely an overestimate of the input of SRP because SRP makes up only a portion of total P input through precipitation.

Release of SRP from epilimnetic sediments in contact with the mixed layer was also considered as a source. The mean weekly depth of the mixed layer was used to calculate the area of the sediment surface that was in contact with the epilimnion, and this value was multiplied by an average SRP release rate for Lake Mendota of 2.4 mg P m\(^{-2}\) d\(^{-1}\) (Stauffer, 1987; Soranno et al., 1997). These estimates amounted to a mean release rate of 0.72 mg P m\(^{-2}\) d\(^{-1}\) (± 0.04) for the sediments in contact with the epilimnion, as the sediment area in contact with the mixed layer is approximately 30% of total lake sediments. Average inputs from sediment release and from precipitation were consistently low, hence we focused on external loading and entrainment, which can be episodic and important during summer months.
Sensitivity Analysis

In order to assess all variables on a common temporal scale, the mean weekly values of each input variable (GPP, $R_{tot}$, C:P, external load, entrainment) were cast into the model to compare the relative magnitude of SRP uptake and mineralization, and assess their magnitude in comparison to other sources of P (Fig. 1a). Rather than rely solely on mean values to summarize the trends in P demand and supply, however, we explored the feasible range of values that served as input to the model through sensitivity analysis. The full suite of mean weekly values observed for each variable was incorporated into the analysis through a bootstrapping procedure (Fig. 1b). The model was run for 2000 iterations by drawing values randomly with replacement from the observed dataset. Because GPP and $R_{tot}$ were positively correlated (Pearson's correlation analysis, $r = 0.83$, $p = 0.002$), these two variables were drawn concurrently from the dataset, meanwhile C:P values were not correlated with GPP and $R_{tot}$, therefore the C:P ratio for uptake (C:P$_{up}$) and mineralization (C:P$_{min}$) were drawn independently and randomly from the pool of observed weekly mean seston C:P ratios.

While we lack evidence that the C:P ratio of natural phytoplankton populations differs significantly from that of overall seston, one might think of scenarios of high detrital content or low phytoplankton biomass in which such a difference could occur. Also, while difference in the C:P ratio among components of the seston may be imperceptible based on current seston separation techniques, it is certainly possible
that different trophic groups (bacteria versus zooplankton) are differentially using
seston components in metabolic processes. Thus, there is likely to be an imbalance
between the C:P ratio taken up by phytoplankton and the C:P ratio of substrate that is
metabolized and subsequently mineralized during respiration. We explored the
sensitivity of the model results to the influence of an imbalance between the C:P ratio
of uptake and mineralization. Such exploration was based on the observed range in
weekly C:P ratios (180.1 – 483.8), which was comparable to sestonic C:P ratios that
had been previously documented for temperate lakes (range = 122 – 441) (Hecky et
al., 1993; Dobberfuhl and Elser, 2000).

Sensitivity analyses were used to explore the full range of values that may
feasibly be observed for the photosynthetic quotient (PQ), respiratory quotient (RQ)
and Ra. PQ and RQ vary depending on the biochemical composition of the molecules
produced or broken down during the metabolic process. Many researchers assume a
baseline value of 1.0 for both PQ and RQ in aquatic ecosystems (del Giorgio and
Peters, 1993; Hanson et al. 2003), and empirical estimates support this assumption
(Bender et al., 1987), yet reported values may range from 0.8 – 1.2 (del Giorgio and
Peters, 1993). We explored uncertainty in the quotients by running the model using a
range of PQ and RQ values from 0.8 – 1.2.

Another variable with potentially high uncertainty was the percent of total
community respiration (R_tot) that could be attributed to autotrophs (Ra) and
heterotrophs (Rh). Total respiration tends to increase with lake trophy, and respiration
by autotrophs becomes an increasing part of total respiration as lakes become more
eutrophic (del Giorgio and Peters, 1993; Biddanda et al., 2001; Roberts and Howarth, 2006). A literature review by del Giorgio and Peters (1993) suggests that autotrophic respiration may contribute 35% in oligotrophic systems and over 60% in eutrophic systems. As a conservative estimate of the range expected in natural lakes, we used $R_a$ values that ranged from 30-70% of total community respiration in the sensitivity analysis.

**Results**

$P$ concentrations followed a seasonal trend typical for Lake Mendota (Stauffer, 1987; North Temperate Lakes Long Term Ecological Research program (http://lter.limnology.wisc.edu)). Mean epilimnetic SRP concentrations declined through the spring and reached the limit of analytical detection by week 27 (1 July 2007 – 7 July 2007) (Fig. 2a). During spring and early summer (week 16 – 25, 15 April 2007 – 23 June 2007), SRP and TP concentrations were correlated ($r = 0.97$, $p < 0.001$). In contrast, TP was closely related to the particulate $P$ concentration after week 25 (24 June 2007 – 8 September 2007) ($r = 0.75$, $p = 0.008$), while SRP fell below detection. Following week 25 (24 June 2007), the majority of $P$ mass in the epilimnion was bound within the particulate pool ($TP = 0.032 \pm 0.002$ mg P L$^{-1}$, Particulate P = 0.025 ± 0.002 mg P L$^{-1}$). At the same time, the SRP concentration in the bottom waters of the lake increased (Fig. 2b). Our analysis was focused on the period of the summer between weeks 26 and 34 (24 June 2007 – 25 August 2007) when the lake was strongly stratified and SRP concentrations were below the limit of
detection (<0.003 mg L\(^{-1}\)). Despite a decline in biologically available P, phytoplankton biomass remained relatively high. Chlorophyll \(a\) concentration reached a peak in week 29 (15 July 2007 – 21 July 2007) (52.9 ±1.9 ug L\(^{-1}\)), and thereafter centered around a mean of 16.8 ± 5.8 ug L\(^{-1}\) for the remainder of the summer (Fig. 2c). The molar C:P ratio of seston in the epilimnion was generally high early in the summer (275.1 – 370.9) (20 June 2008 – 4 August 2008) and was lower during the later part of the summer (108.7 – 221.2) (5 August 2008 – 6 October 2008) (Fig. 2d). Gross primary production (GPP) ranged from 0.86 – 2.30, with an average of 1.52 g C m\(^{-2}\) d\(^{-1}\). Total community respiration (\(R_{\text{tot}}\)) ranged from 0.32 – 1.56, with an average of 1.08 g C m\(^{-2}\) d\(^{-1}\).

TN:TP ratios in the epilimnion ranging from 25.2 to 84.7 (on molar basis) suggested that phosphorus was limiting. Similarly, DIN:SRP ratios in the metalimnion (8 – 10 m) during the period of interest ranged from 15.4 – 30.7, suggesting that water entering the epilimnion through entrainment would be relatively rich in bioavailable N (based on Redfield’s N:P ratio of 16:1). Thus, P was considered the limiting nutrient during our study.

During the period that P was below the detection limit (24 June 2007 – 25 August 2007), weekly rates of SRP uptake were relatively constant (Fig. 3). While uptake rates were relatively low in weeks 28 – 30, rates were not significantly different among weeks 28 – 33. In most weeks, uptake exceeded the amount of P supplied by any single source, with the exception of weeks 28 and 33 (8 July 2007 – 14 July 2007 and 12 August 2007 – 18 August 2007). Rates of P supply via
mineralization were more variable than rates of uptake during the period of interest. Mineralization ranged from 23 – 109% of uptake, thus meeting an average of 57% of documented phytoplankton P demand. Mineralization represented a roughly consistent source of SRP to phytoplankton throughout the summer (mean = 4.5 ± 0.94 mg SRP m$^{-2}$ d$^{-1}$), while entrainment (mean = 2.59 ±1.41 mg SRP m$^{-2}$ d$^{-1}$) occurred during irregular pulses. During such events, the SRP flux via entrainment was comparable to observed rates of mineralization. P loading from external sources was consistently low during this mid-summer period and did not satisfy a significant portion of phytoplankton P demand (0.28 ± 0.03 mg SRP m$^{-2}$ d$^{-1}$, 3.5% of demand).

These trends taken together showed that on average the mean daily uptake rate (7.83 ± 0.66 mg SRP m$^{-2}$ d$^{-1}$) was met by the sum of documented sources (7.38 ± 2.38 mg SRP m$^{-2}$ d$^{-1}$) (t-test, p = 0.39); note that these two groups are independent over this period so a t-test was appropriate (Fig. 4). However, no single source of P was sufficient to explain the variation in P uptake. The mean rate of mineralization was not significantly different than that of entrainment (t-test, p = 0.41).

**Sensitivity Analysis**

Model iterations using combinations of low, nominal and high values for PQ, RQ and Ra demonstrated that the rate of uptake and the sum of all sources of P were not significantly different (by t-test) in any of the model scenarios (Fig. 5). The large error bars around the sum of sources in figure 5, representing the standard deviation around the mean, can be partly attributed to variation in estimates of entrainment and
external loading. External loading and entrainment estimates were independent of the metabolic parameters of the model, thus the effect of changes in model parameters may be best explored by comparing the differences between P uptake and mineralization.

In comparing P uptake to mineralization alone, high PQ/low RQ scenarios showed that uptake was significantly greater than mineralization in all cases (Fig. 5c). Given nominal PQ/RQ values, we found the relationship between uptake and mineralization was mediated by the value of $R_a$. When autotrophic respiration ($R_a$) was low, uptake was more likely to be balanced by mineralization (Fig. 5b). When PQ was low (0.8) and RQ (1.0) was high, however, model results showed that mineralization could feasibly meet the demands of phytoplankton P uptake under any $R_a$ scenario. Model results were most clearly affected by changes in the relative values of PQ and RQ, while model results were less sensitive to changes in the proportion of total community respiration attributed to autotrophs ($R_a$).

Given the difficulty in measuring C:P ratios of different sestonic components, we explored the sensitivity of model output to the C:P ratio used in calculating uptake and mineralization rates. We found the relative C:P ratio ($C:P_{up}/C:P_{min}$) was a critical factor in determining the magnitude of the difference between uptake and mineralization rates inferred from the model (Fig. 6). Results of all model iterations (2000) are presented in figure 6 as the difference between uptake and mineralization. For this sensitivity analysis, GPP, $R_{net}$, external loading and entrainment were integrated into the model as a dependent dataset, while the C:P ratios for uptake and
mineralization were randomly and independently chosen from the entire pool of observed C:P ratios of seston. Thus, the results presented in figure 6 demonstrate the effect of our assumption that the C:P ratios of uptake and mineralization are equal. As long as C:P_{up} was smaller than C:P_{min} (C:P_{up}/C:P_{min} < 1.0) the rate of P uptake exceeded that of P supplied through mineralization. We found that if C:P_{min} and C:P_{up} are significantly different in nature (which is possible, but hard to measure), then these differences could affect our estimates of the relative balance between P_{uptake} and P_{min}.

We were primarily interested in how P demand was met during periods of low P availability, yet we also had data to investigate patterns in P uptake and supply during the later period of the summer when P was available. An expanded time series showed the influence of a large storm with significant precipitation (and runoff, not shown) that occurred between week 33 and week 34 (Fig. 7). This storm event resulted in input of SRP from both external loading and entrainment (Fig. 8). Likely in response, mean uptake rates increased during week 35 (Fig. 8). During weeks 37 and 38, progressive deepening of the mixed layer at the end of the summer season resulted in significant entrainment and subsequent increases in the observed uptake and mineralization rates during weeks 38, 39 and 40.

When these results were averaged over the extended 14-week period, mineralization and uptake became statistically indistinguishable (t-test, p = 0.29) (Fig. 9). This was largely due to higher variation in uptake and mineralization represented in the larger data set (CV increased from 0.46 to 0.64 and from 0.55 to 0.91 for
uptake and mineralization, respectively). The sum of sources, though not statistically different from uptake, indicated that P was supplied in excess of what was needed by primary producers. The availability of P at the end of this period was also apparent in the epilimnetic P trends presented in figure 2a.

Discussion

We explored the mechanics and magnitude of P demand and supply using a combination of empirical data and modeling. Results indicated that the amount of P used by primary producers during the period of low P availability was predominantly supplied via biotic mineralization. P demand, however, cannot be met by mineralization alone and the relative balance among P sources (mineralization, external loading and entrainment) varied over the summer. Entrainment was also an important pathway of P transport, and the episodic input of P occurred during a period of higher than average wind speeds (week 27). While these results were generally insensitive to model conditions (i.e. independent of changes in Ra, PQ and RQ), the balance between P uptake and mineralization was mediated by the relative C:P ratios of uptake and mineralization. Thus, our results, which showed that patterns of P demand and supply were dictated by the relative C:P ratio of producers and consumers, support the importance of stoichiometric relationships in foodweb interactions and ecosystem processes (Elser et al., 1988; Elser et al., 1995; Dobberfuhl and Elser, 2000).
Our finding that entrainment was necessary to account for observed uptake suggests that entrainment can be important not only in annual budgets but also as a contributor to meeting P demand at a weekly scale during the stratified P-deficient season. Thus, part of the variation observed in patterns of gross primary production (GPP) and net ecosystem production (NEP) may be attributed to exchange of material across the thermocline (Staehr and Sand-Jensen, 2007). Also, entrainment occurred during a period of higher than average wind speeds (5.3 m s\(^{-1}\) during week 27, compared to June-September average of 4.5 m s\(^{-1}\)), but this entrainment event was independent of other storm indicators (precipitation, changes in solar flux). Such observations may help explain why the relationship between phytoplankton blooms and storm events are exceedingly noisy (Soranno et al., 1997).

Interestingly, peaks in phytoplankton biomass occurred approximately one week after significant P fluxes from entrainment and external loading (weeks 29, 35 and 38). The initial chlorophyll a peak (week 29), however, occurred soon after depleted P conditions were apparent. It is possible that the bloom we witnessed during week 29 was due to growth of the phytoplankton population that began under SRP replete conditions, possibly sustained by luxury uptake. Given our observed average uptake rate of 10 mg m\(^{-2}\) d\(^{-1}\) during week 26 and 27 and a mean mineralization of approximately 5mg m\(^{-2}\) d\(^{-1}\), we can come to a net P demand of approximately 5mg m\(^{-2}\) d\(^{-1}\), which translates to a daily uptake rate of 196 kg d\(^{-1}\). Meanwhile, the observed epilimnetic SRP concentration in week 26 was 0.0046 mg L\(^{-1}\), equaling an estimated 955 kg of SRP in the epilimnion. Given the conditions in
week 26, we would expect the SRP available in the epilimnion to have been taken up within approximately 5 days. This uptake may also have included luxury uptake under nutrient replete conditions. Given that phytoplankton may sustain three or four cell-doublings without taking up additional phosphorus (Reynolds 2006), a growth rate of 0.2 d\(^{-1}\) (or a doubling time of ~3.5 days) may allow phytoplankton to persist for an additional 14 days on luxury uptake. Based on the above assumptions, we can conclude that a bloom beginning in week 26 may have grown and persisted over a maximum of 19 days without a new source of phosphorus.

Later peaks in chlorophyll \(a\) concentration (weeks 35 and 38), though, demonstrate that entrainment and external loading can induce peaks in phytoplankton biomass that are accompanied by increases in the rates of uptake. It seems that mineralization generally provides sufficient P to sustain production during periods of low P availability, but that an external pulse is required to induce higher-than-average chlorophyll \(a\) concentrations. Our results corroborate other work showing that physical processes, including entrainment, are linked to external drivers (meteorological variation, evaporative cooling, temperature of inflow) in complex ways and can play an important role in nutrient cycling and ecosystem processes (Maclntyre et al., 2002; Fragoso et al., 2008). Our approach based on free-water metabolism estimates can be used to assess the relative importance of biotic recycling, entrainment and external loading among systems, and to reduce uncertainties in the relationship between P supplies and phytoplankton biomass during summer months.
We explored uncertainties in the model using alternative sets of model conditions (i.e. a range in values for Ra, PQ and RQ); in all cases inferred P uptake was equal to the sum of sources to the epilimnion during the period of low P availability. Under scenarios of unbalanced photosynthetic and respiratory quotients (PQ = 0.8, RQ = 1.2, all Ra) or low Ra (PQ = 1.0, RQ = 1.0, Ra = 0.3), mineralization alone was sufficient to account for total P demand, these model scenarios, however, are relatively unlikely to occur. Theoretical calculations and empirical observations suggest that PQ values are likely to be > 1.0 (Ryther, 1956; Williams and Robertson, 1991). The PQ was estimated to be 1.34 for a typical algal cell comprised of 40% protein, 40% carbohydrate, 15% lipid, and 5% nucleic acid (Williams and Robertson, 1991). Meanwhile, best estimates of RQ, while variable, tend to be < 1.0 (Hutchinson and Edmondson, 1957; Lampert and Bohrer, 1984). Thus the conditions represented by the PQ = 0.8 and RQ = 1.2 scenario are unlikely in aquatic ecosystems, while the conditions of our PQ = 1.2 and RQ = 0.8 scenario are more plausible. The results of our sensitivity analysis demonstrate that different values of Ra may affect the magnitude of uptake and mineralization, yet the difference between uptake and mineralization is relatively insensitive to changes in the proportion of total community respiration attributed to autotrophs (Ra) versus heterotrophs (Rh). When PQ and RQ are unbalanced, the pattern of uptake and mineralization will be dictated by the PQ:RQ relationship rather than the balance between autotrophic and heterotrophic respiration.
While model output was generally insensitive to changes in PQ, RQ, and Ra, the relative balance between uptake and mineralization was sensitive to the stoichiometric relationship between primary producers and organisms contributing to heterotrophic mineralization. Transfer of carbon and nutrients through foodwebs is mediated by stoichiometric relationships among foodweb components and trophic patterns may be structured by the stoichiometry of primary producers at the base of the foodweb (Sterner and Elser, 2002). There is variability in the C:N:P ratios of seston in lakes, and many organisms at the base of the foodweb have some plasticity in maintenance of tissue C:N:P ratios (Hecky et al., 1993; Sterner and Elser, 2002; Diehl et al., 2005). While we were not able to empirically distinguish among sestonic foodweb components (bacteria, phytoplankton, micrograzers), we were able to explore the influence of variation in C:P ratios within the modeling framework.

Our model results help constrain expectations of the patterns of P supply and demand likely in natural systems. Given the relationship presented in figure 6 and previously published stoichiometric relationships, we argue that P demand is likely to outweigh P supplied via mineralization alone. There is no conclusive evidence that the C:P ratio of seston, the component available as substrate for mineralization, should differ from the C:P ratio of phytoplankton, the component that represents the ratio of uptake (Healey and Hendzel, 1980; Sterner and Elser, 2002). Yet, there is evidence that mineralization of organic matter by zooplankton can exacerbate P limitation due to excretion at relatively high C:P ratios (Elser et al., 1988; Sterner, 1990). Also, measured C:P ratios of bacteria and zooplankton tend to be lower than
those documented for whole-water seston (Goldman et al., 1987; Fagerbakke et al., 1996; Dobberfuhl and Elser, 2000; Hochstadter, 2000). As such, retention of P in bacterial and zooplankton pools likely results in C:P ratios of mineralization that are greater than the C:P ratios of primary producers (Elser et al., 1995), and thus the relative ratio of $C:P_{up}:C:P_{min}$ is likely to be $< 1.0$. Under such conditions, our model results indicate that natural lake ecosystems are likely to cluster within the upper, left-hand portion of figure 6, and it may not be possible to explain the mid-summer rate of primary production by P supplied through mineralization alone.

Bacteria have been highlighted as dominant decomposers and mineralizers of organic material, yet they may also compete with phytoplankton for uptake of bioavailable P (Rigler, 1956; Currie and Kalff, 1984; Cotner and Wetzel, 1992). If bacteria are significant contributors to rates of heterotrophic respiration and these bacterial populations are net consumers of P, then our model would underestimate the true ecosystem demand for bioavailable P, and overestimate the rate of mineralization. While we do not have data to address this possibility directly, previous estimates of bacterial populations in Lake Mendota during late summer demonstrate relative consistency in bacterial biomass (Pedros-Alio and Brock, 1982). Given this consistency, it is likely that growth in the bacterial population is closely mirrored by loss and that the net population growth and rate of P uptake are close to zero. Also, Cotner and Wetzel (1992) suggest that P taken up by bacteria does not represent net uptake because they generally lack the capacity for P storage, thus bacterial uptake is comparable to the amount lost from internal pools. In light of the small influence of
heterotrophic versus autotrophic respiration on model results, we do not expect changes in our assumptions about the influence of bacteria on uptake and mineralization to have large effects on the results of the analysis.

Our approach and findings contribute to understanding of the relationship between primary production and nutrient cycling in aquatic ecosystems and complement other studies conducted using experimental incubation and elemental tracers. Using an approach that relies on free-water estimates, we can explore ecosystem processes in natural ecosystems, instead of under laboratory, light/dark bottle, or microcosm conditions. Our work integrates modeling approaches and monitoring data enhanced by tools for high-frequency data acquisition that can allow monitoring of processes at finer temporal resolution than has previously been possible. The assumptions of our approach are different from those inherent in previous analyses and therefore, this approach could be used to corroborate or question results from other modeling, experimental and observational approaches. Also, our work highlights an application for the emerging area of research related to whole-ecosystem metabolism (Hanson et al., 2003; Staehr and Sand-Jensen, 2007).

As our estimates of whole-ecosystem metabolism improve, we stand to gain a better understanding of ecosystem processes like nutrient cycling. Further application and refinement of this approach could also enhance models that assess water quality and predict phytoplankton biomass through integrated representation of biological and physical processes (Hamilton and Schladow, 1997; Fragoso et al., 2008).
References


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Figure 1. Flow chart depicting the steps taken in the baseline model run and in the sensitivity analysis.
Figure 2. Summer trends in epilimnetic phosphorus concentration (a), selected hypolimnnetic soluble reactive phosphorus (SRP) concentration (b), phytoplankton biomass (as measured by chlorophyll a concentration) (c) and seston C:P ratio (d). Values are mean estimates for each week, error bars represent one standard deviation. The dotted box delineates the focal period for this study.
Figure 3. Mean weekly estimate of rates of soluble reactive phosphorus (SRP) uptake, mineralization, external loading and entrainment for the period when SRP was below the limit of detection during summer 2007. Error bars represent one standard error around the mean and account for the daily variation in estimates of GPP and $R_{tot}$. 
Figure 4. Overall mean rate of phosphorus uptake compared to estimated magnitudes of possible sources of phosphorus. Sum Sources represents the sum of all documented sources of SRP input during the P-deficient stratified period. The components of Sum Sources (mineralization, external load, and entrainment) are shown to the right. Error bars represent one standard error around the mean (n = 7 weeks). Input of SRP from precipitation and epilimnetic sediment release were less than 1 mg SRP m\(^{-2}\) d\(^{-1}\) and are not shown here.
Figure 5. Results of sensitivity analysis based on alternate values (0.8, 1.0, 1.2) for the photosynthetic quotient (PQ) and the respiratory quotient (RQ) as well as alternate values for the percent of total respiration that is autotrophic ($R_a = 0.3, 0.5, 0.7$). Error bars represent the standard deviation around the mean. Asterisks (*) indicate a significant difference between mean uptake and mineralization (t-test, $\alpha = 0.05$). The difference between uptake and the sum of sources was not significant in any of the scenarios tested (t-test, $\alpha = 0.05$).
Figure 6. The relationship between the relative difference between uptake and mineralization and the ratio of C:P for uptake relative to mineralization. When the relative C:P ratio is close to one, as was the case in the baseline portion of our results, the difference between uptake and mineralization is slightly positive. When the C:P ratio of mineralization is less than C:P of uptake (C:P_{up}/C:P_{min} > 1.0), then the difference between uptake and mineralization approaches a mean of zero. However, when C:P of mineralization is greater than uptake (C:P_{up}/C:P_{min} < 1.0), the difference between uptake and mineralization is always positive.
Figure 7. Meteorological data for the summer of 2007. All data were monitored at the Atmospheric and Oceanic Sciences Building at University of Wisconsin – Madison, located 0.8 km south of Lake Mendota. Data available at: http://rig.ssec.wisc.edu/.
Figure 8. Mean weekly estimate of rates of soluble reactive phosphorus (SRP) uptake, mineralization, external loading and entrainment for an extended period during summer 2007 (n=14 weeks). Error bars represent one standard error around the mean and account for the daily variation in estimates of GPP and $R_{tot}$. 
Figure 9. Overall mean rate of phosphorus uptake compared to estimated magnitudes of possible sources of phosphorus. Sum Sources represents the sum of all documented sources of SRP. The components of Sum Sources (mineralization, external load, and entrainment) are shown to the right. Error bars represent one standard error around the mean. (n = 14 weeks). Input of SRP from precipitation and epilimnetic sediment release were < 1 mg SRP m$^{-2}$ d$^{-1}$ and are not shown here.
CHAPTER 3

Estimates of phosphorus entrainment in Lake Mendota: A comparison of one-dimensional and three-dimensional approaches

by

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Abstract

Entrainment of phosphorus across the thermocline can be an important nutrient source for phytoplankton in stratified lakes. In eutrophic stratified lakes, seasonal entrainment can be responsible for delayed recovery following a decrease in external phosphorus load. We compared seasonal estimates of entrainment derived from single- and multi-location thermocline migration approaches. Entrainment estimates from these methods were similar. A sampling approach based on a single centralized location produced whole-lake entrainment estimates in line with the mean value from the multi-location approach (the single-location approach reasonably reproduced patterns at a weekly and seasonal time scale). In this study, it was not essential to account for spatial variation in estimating annual rates of entrainment. We also estimated entrainment based on a three-dimensional (3-D) hydrodynamic model over a short period of significant thermocline migration. The 3-D model was most useful in exposing spatial and temporal variation in temperature and phosphorus profiles that are otherwise difficult to observe. Spatial variation in phosphorus profiles was associated with upwelling of metalimnetic water represented by the 3-D model. These transient dynamics, though a relatively small portion of an annual phosphorus budget, may supply nutrients to epilimnetic phytoplankton during periods of nutrient limitation. There is a need for further research that combines 3-D hydrodynamic modeling with field collection of biological and chemical data.
Introduction

Entrainment, herein defined as the turbulent exchange of water and solutes across the lower boundary of the epilimnion, is a significant component of biogeochemical fluxes to the epilimnion in many stratified lakes. Research on entrainment has often focused on phosphorus (P) because of its role as a limiting nutrient for phytoplankton and its importance in eutrophication. The relative contribution of entrainment towards the total P supply to the epilimnion can vary considerably from year to year (Effler 1986; Stauffer 1987; Soranno 1997).

Entrainment is one of the primary mechanisms by which P is recycled within the water column of stratified lakes and explains some of the inter-annual variation in the occurrence of algal blooms (Lathrop et al. 1999). Also, in some systems, entrainment provides a substantial source of phosphorus to phytoplankton during the growing season (Larsen et al. 1981; Kortmann et al. 1982; Hejzlar et al. 1993) and entrainment at the end of the summer has been identified as a mechanism for delayed recovery following restoration efforts aimed at decreasing external loads of P (Effler et al. 1986; Jeppesen et al. 2005; Søndergaard et al. 2007).

Estimates of entrainment have often relied on the simplifying assumption that temperature and P concentrations are homogeneous along a horizontal plane (Soranno et al. 1997; Franke et al. 1999; Baehr and DeGrandpre 2004). This assumption allows the monitoring of variables at a single location and substantially simplifies the sampling and analysis. Previous publications address the limitations of (Stauffer 1985; Stauffer 1993) and justifications for (Patterson et al. 1984) this
assumption. A number of recent studies, however, show spatial heterogeneity in turbulent events (Etemad-Shahidi and Imberger 2001; Saggio and Imberger 2001; MacIntyre et al. 2002; Boegman et al. 2003; MacIntyre et al. 2006; Na and Park 2006); and yet others connect dynamic physical processes to spatial heterogeneity in biological and chemical variables (Ivey and Boyce 1982; Stauffer 1985; MacIntyre and Melack 1995; MacIntyre and Jellison 2001; Eckert et al. 2002; Chao et al. 2006; Marce et al. 2007).

While spatial heterogeneity has been demonstrated, transience is often used as a rationale for averaging over spatial variation in field studies. Researchers interested in seasonal averages and annual P budgets may justifiably average over spatial heterogeneity at much shorter time scales. If one is interested in transient phenomena such as algal blooms, however, accounting for temporally and spatially heterogeneous nutrient fluxes likely becomes important. Eckert et al. (2002) revealed changes in stratification patterns over a six-hour period and found the changes differed among locations within the lake. These changes in physical properties were reflected in changes in the dissolved oxygen, redox intensity, and hydrogen sulfide profiles among locations.

Spatial and temporal variability in physical processes could have important effects on estimates of P entrainment, and new modeling approaches may better capture this variability compared to customary methods for estimating entrainment. To evaluate this possibility, we used a spatially explicit sampling design to compare single-location and multi-location estimates of seasonal P entrainment. We also
applied a three-dimensional (3-D) hydrodynamic model to a six-day period of high entrainment rates to assess the utility of this model in quantifying entrainment.

Materials and Procedures

Field and Laboratory Methods

Throughout the stratified portion of the summer of 2005 (23 June - 29 September), temperature, total phosphorus (P) profiles were collected over multiple locations in the lake (Figure 1). Samples were taken at approximately two-week intervals, and were collected more frequently following periods of strong wind. Samples were consistently collected at the central station (in the deepest area of the lake) throughout the summer, while an additional four sampling locations were chosen in accordance with different wind patterns. All locations that were sampled at least once are depicted in Figure 1.

Manual temperature profiles were collected at 0.5 – 1.0 m intervals using a YSI Dissolved Oxygen and Temperature probe (instrument model 58, probe model 5739, YSI Incorporated). Whole-water samples were collected in acid-washed polyethylene bottles at 1m – 4 m intervals using a peristaltic pump for determination of total P concentrations, and stored on ice. P samples were preserved using Optima HCl, while SRP samples were refrigerated and analyzed within 24 hours.

P samples were analyzed using a Technicon Auto Analyzer following persulfate digestion (American Public Health Association et al. 1995). Complete profiles at 1m resolution were constructed for each sampling date and location using
linear interpolation to estimate P concentrations for un-sampled depths. Interpolated profiles were used in all analyses.

Conventional thermocline movement analysis

Total P transport across the lower boundary of the epilimnion may be attributed to two processes 1) bulk P entrainment occurs episodically when P is transported during thermocline migration and 2) P flux occurs continuously due to turbulent diffusion across the epilimnetic boundary (molecular diffusion is considered negligible). Bulk entrainment was quantified as the mass of P transported from the metalimnion to the epilimnion when the thermocline deepened, computed as the product of estimated volume of water entrained and the measured concentration of P in entrained water prior to entrainment. The thermocline served as an estimate of the boundary between the epilimnion and deeper waters. Therefore, we used the position of the thermocline before and after entrainment to estimate the volume of water entrained. We used manually collected temperature profiles to compute entrainment so that our analysis would represent an approach customarily applied in both research and management contexts (Effler et al. 1986; Stauffer 1987; Stauffer 1993; Soranno et al. 1997).

The thermocline was defined as the depth in the profile at which the maximum temperature change occurs (Hutchinson and Edmondson 1957). A strong temperature gradient, or diurnal thermocline, within five meters of the lake surface (due to microstratification) was not considered in defining the depth of the
thermocline. When the thermocline depth changed, the volume of water transported was estimated from bathymetric data for the lake. This volume was multiplied by the P concentration at depth at each sampling location to obtain the bulk mass of P transported through entrainment at each location.

Additional transport of P across the thermocline boundary may occur due to turbulent diffusion. This flux was quantified based on the following equations, which represent an application of Fick's law where turbulent diffusive flux is directly proportional to the concentration gradient and the eddy diffusion coefficient ($K_z$) (Powell and Jassby 1974; Stauffer 1992, Stauffer 1993):

$$J_{pz} = -K_z C'_z A_z \Delta t$$

And

$$K_z = \left( \sum_{j=z+1}^{j=z-1} A_j (T_j(t_2) - T_j(t_1))) \times (\Delta t \frac{dT}{dz})^{-1} \right)$$

Where: $J_{pz}$ = the mean flux of phosphorus (p) in the z direction
$K_z$ = eddy diffusion coefficient (cm$^2$ s$^{-1}$)
$z$ = indicates the depth of the thermocline
$A$ = Lake area at surface (o), or at depth 1 m above or below the thermocline (j)
$T$ = temperature (°C)
$t$ = time step, period between sampling events

A single eddy diffusion coefficient and P gradient were defined at each location based on a 2 m temperature gradient centered at the depth of the thermocline. The mass of P transported through turbulent diffusion was estimated for the entire period between sampling events, and this cumulative mass was added to the bulk
entrainment estimated from thermocline migration to arrive at an estimate of the total P mass transported across the thermocline boundary at each location. Total entrainment was estimated at each location as though the location may be considered representative of the entire lake (i.e. estimates of bulk volume transported were based on total lake volume at depth). Estimates at each location were then averaged to derive a lake-wide mean entrainment rate over the period between sampling events.

We evaluated entrainment rate estimates by comparing these to the change in epilimnetic TP mass. During time intervals when sedimentation is constant and net inputs are small, changes in epilimnetic TP mass should be positively correlated with entrainment rates. As presented below, these conditions were satisfied in Lake Mendota over the summer of 2005. Mean epilimnetic TP concentrations were calculated at all locations, multiplied by the volume of the epilimnion over the whole lake, and presented as lake-wide arithmetic mean TP masses. All locations were weighted equally in calculating the lake-wide mean value for entrainment and epilimnetic TP mass.

Estimates of wet and dry deposition of P on the lake surface are minimal during summer (mean = 8.7 kg d$^{-1}$, range = 6.6 – 43.8 kg d$^{-1}$). Estimates are based on observed precipitation and estimated P concentration in precipitation of 0.032 mg L$^{-1}$ measured in the nearby Lake Wingra watershed (Kleusener 1972), along with an estimated dry deposition rate of 0.62 kg TP ha$^{-1}$ yr$^{-1}$ from (Amy et al. 1974).
Over 90% of external loading from the landscape occurred between January and June during 2005, before the time interval analyzed here (Lathrop 2007). The external loading of P over the summer was on the order of 2,000 kg TP (20.4 kg d\(^{-1}\)), based on measured inputs scaled to the whole watershed according to methods used in Lathrop et al. 1998. Meanwhile, monitored outflow data combined with the mean P concentration of the epilimnion show that loss through the outflow is approximately 15.8 kg d\(^{-1}\). Thus, net retention of P was approximately 4.6 kg d\(^{-1}\) during the summer of 2005.

Release of P from littoral sediments is another potential source of P that is small in comparison to variation in estimates of entrainment and changes in epilimnetic P mass. Previous studies show a mean epilimnetic P release rate for Lake Mendota ranging from 1.2 to 3.5 mg P m\(^{-2}\) d\(^{-1}\) (Stauffer 1987). The total contribution of littoral sediments should be between 17.4 and 51 kg P d\(^{-1}\), as approximately 37% of the total sediment surface area may be considered littoral (based on a mean thermocline depth of 9.5 m).

The total net input of P for 2005, considering aerial input, fluvial input and output, and release from littoral sediments was between 30.7 and 64.3 kg P d\(^{-1}\). The mean entrainment rate over the whole summer was 473 (± 281.2) kg P d\(^{-1}\). Thus, the other sources of P are about 10% of the mean daily entrainment rate we measured.

While the magnitude of sedimentation is great in Lake Mendota, sedimentation trap studies show that this flux is roughly constant over the summer period between July and September (Fallon and Brock 1980). If sedimentation is constant it would
have no effect on the correlation of entrainment with changes in epilimnetic P mass. We conclude that the correlation coefficient of entrainment and total epilimnetic P mass should be large and positive for an entrainment estimator that is accurate.

3-D hydrodynamic model

We accounted for the full suite of dynamic processes using a 3-D hydrodynamic model for six days over the period from the 23rd (day 266) to the 29th of September 2005 (day 272). The model could not be applied over a longer time period due to computational costs, and this period was chosen due to high rates of entrainment and observed spatial heterogeneity. The estimates of entrainment for this six-day period were then compared to the single- and multi-location conventional entrainment estimates derived for the same period.

The hydrodynamic model developed by Yuan and Wu (2004) employs the full Reynolds averaged Navier-Stokes equations, free of the hydrostatic pressure assumption that is commonly employed in other 3-D lake models (Hodges et al. 2000; Rueda and Schladow 2003). This allows for more accurate simulation of internal wave evolution and dynamics that are important to solute transport and energy transfer in the lake. The partial differential equations that govern mass and momentum conservation are solved by a generalized implicit method, by which all flow field components (such as three velocity components, pressure, free-surface elevation, and temperature) are solved simultaneously at each time step. The model employs a generic length scale approach for turbulence closure that explicitly
includes four popular turbulence schemes, offering the advantage of selectable parameterization to achieve an optimum result (Umlauf and Burchard 2003). Several flux-limiting schemes in combination with direction splitting techniques are used to calculate advection terms in scalar transport.

Following standard procedures (Dee 1995; Roache 1998), the model has been carefully verified and validated with several free-surface flow problems (Yuan and Wu, 2004; Yuan and Wu 2006; Yuan 2007). Also, we compared daily temperature profiles produced by the model to empirical temperature profiles collected by temperature loggers. Empirical temperature profiles were collected at one-minute intervals using HOBO Underwater Temperature Data Loggers (0.02 °C resolution, ±0.2 °C accuracy, MicroDAQ.com, Ltd.) at the same locations as P sampling. The data loggers were placed at 1m depth intervals through the metalimnion and at 2m intervals through the upper epilimnion and hypolimnion. Therefore, five thermistor chains were positioned at different locations during the 3-D model focal period from the 23rd (day 266) to the 29th of September 2005 (day 272). Our intent is to present an assessment of the 3-D model as a tool in studying the physics of P recycling in a natural lake, rather than demonstrate validation of the model. Therefore, further technical details of the model and its verification and validation can be found in Yuan and Wu 2004, Yuan and Wu 2006, and Yuan 2007.

In model simulations, the horizontal grid size was 100 m; grid-refinement tests showed that such a resolution gives grid-independent results. At this resolution there are approximately 7,200 horizontal “sampling locations” within the lake. A subset of
the 7,200 locations was used, however, because at depths shallower than 12m the water column may not have been stratified and the thermocline could not be defined. In model simulations, 15 vertical layers were used and a time step of 100 seconds was chosen. Such a set of numerical parameters lead to a ratio of simulation time to real time of approximately 1:10.

The model was driven by meteorological data, including: wind speed and direction, air temperature, solar radiation, barometric pressure, and relative humidity (Figure 2). Those data were obtained from the database of the Rooftop Instrument Group measured on the Atmospheric, Oceanic and Space Science Building at University of Wisconsin – Madison (approximately 0.5 km south of Lake Mendota, http://rig.ssec.wisc.edu/).

The model was initialized at 0000 hours on day 265 (allowing for a 24-hour burn in period before use of model output), with a null velocity field and a temperature profile obtained by averaging the five empirical temperature profiles. Coefficients for the surface and bottom drag were selected according to Wuest and Lorke (2003). A zero flux boundary condition was specified at the lake bottom for temperature calculation. The attenuation coefficient was specified according to the Secchi depth (approximated 3 m, measured during the study period), following the method of Beeton (1958).

Assessment

Study Site
Lake Mendota is a stratified, dimictic lake in southern Wisconsin with a surface area of 39.1 km\(^2\), mean depth of 12 m and maximum depth of 24 m. P inputs are primarily associated with runoff from the agriculturally-dominated watershed (Lathrop et al. 1998). The lake is stratified from the middle of June until the middle of October. P builds up in the metalimnion and hypolimnion of the lake each summer, while SRP concentrations in the epilimnion often fall below detection limits.

**General Outcome of Conventional Analysis**

Entrainment over the stratified period between late-June (day 174) and mid-September (day 266) resulted in the total gross transport of approximately 5,296 kg TP. There was considerable spatial heterogeneity in the estimates of entrainment, with the greatest spatial heterogeneity following periods of windy weather (day 206-207, day 266-272) (Figure 3). Entrainment was negative on a number of occasions; this indicates that the lower boundary of the epilimnion became shallower due to still wind conditions and high solar insolation. The magnitude of entrainment was positively correlated with mean wind speed ($r=0.79$, $p=0.012$, Pearson’s Correlation) and negatively correlated with the mean solar flux over the period between sampling events ($r=-0.93$, $p<0.001$, Pearson’s Correlation) (Figure 4).

The majority of entrainment occurred late in the season during a period of persistent winds. Over six days in late September (day 266-272) approximately 10,204 kg TP was entrained into the epilimnion, resulting in a mean daily rate of 1,701 kg TP day$^{-1}$ (Figure 3). As the thermocline degraded prior to fall mixis, a further
12,482 kg TP was incorporated into the epilimnion between 29 September 2005 (day 272) and 15 October 2005 (day 288). In total, conventional analyses indicate that entrainment accounted for the vertical flux of approximately 27,982 kg TP during the summer season (day 174 – day 288). Because spatially explicit sampling did not continue after 29 September 2005, entrainment through the October period was not considered in the remainder of the assessment.

Despite significant spatial heterogeneity in estimates of entrainment, the samples collected at the central location generally coincided with the mean estimate of entrainment for each sampling event. The entrainment observed at the central station tended to be less extreme than estimates at other locations (Figure 3). When summed over the entire summer (174 – 272), the total estimate of entrainment based on the central location (15,653 kg P) was close to the multi-location estimate (15,500 kg P). These results provide support for the idea that sampling at a single central location provides an acceptable estimate of the mean annual entrainment rate.

The validity of conventional entrainment estimates was supported by comparison with estimates of the change in epilimnetic TP mass (Figure 5). We did in fact find a significant positive correlation between estimated entrainment and the observed change in the epilimnetic TP mass (r = 0.6, p < 0.001, Pearson's Correlation). Note that estimates of entrainment tended to be greater than observed changes in epilimnetic TP mass (i.e. most entrainment values fall above the 1:1 line). This indicates that sedimentation is in fact a significant flux, and the amount lost from
the epilimnion through sedimentation was, at times, greater than that supplied through entrainment.

**Sensitivity Analysis**

Several definitions have been used to characterize the boundary between the mixed layer and deeper waters, and we explored the effect of boundary definition on the estimate of entrainment derived from the conventional approach. The boundary is most often defined as the thermocline, or the depth at which the maximum temperature change occurs (Max_Change) (Hutchinson and Edmondson 1957). Yet, this approach may lead to spurious changes in thermocline and epilimnetic depth (Soranno et al. 1997; Fee et al. 1996). Therefore we used three additional approaches to define the epilimnetic boundary, including the depth of the primary isotherm (Isotherm). The isotherm is estimated as the mean seasonal temperature at the thermocline when the thermocline is defined by the Max_Change method (Soranno et al. 1997; Robertson 1989, Marce et al. 2007). This approach tends to limit the spurious changes in thermocline depth that may be observed with other approaches (Soranno et al. 1997). In our study the primary isotherm was 18.3 °C for the summer season. The second approach used was the Mid-point method, in which the thermocline depth is halfway between the base of the epilimnion and the top of the hypolimnion (Mid_Point) (Soranno 1995). Here, the base of the epilimnion and top of the hypolimnion are both defined as the first depth at which the temperature change is greater than one degree Celsius per meter, starting at the lake surface or
lake bottom respectively. Finally, we also used a more conservative measure of P flux based on changes in the maximum depth of the mixed layer (Within_One). In this case, the mixed layer was defined as the mass of water with a uniform temperature (i.e. temperature differential within one degree Celsius) (Nagai et al. 2005).

Estimates of entrainment differed slightly depending on the approach used for defining the boundary of the mixed layer. Mean rates and the range of estimates were similar in all cases (Figure 6). Further, the different approaches resulted in entrainment estimates that were positively correlated with one another ($r > 0.72$, $p < 0.01$, in all cases). Within One was typically smaller in magnitude than the others, which would be expected because it is the most conservative definition. Yet, the Max Change thermocline definition matched best with observed changes in the epilimnetic P mass, therefore, the Max_Change definition was used to summarize conventional estimates of entrainment over the stratified season.

We also examined whether spatial variation in entrainment observed during the 206-207 and 266-272 periods may be exclusively local and therefore lead to overestimation of lake-wide entrainment when scaled to the whole lake. To do so, we used Thiessen polygons (delineated using ArcGIS) to define the area of influence around each sampling point. Entrainment estimates were then weighted by the relative contribution of each site to the total lake estimate (weighting = surface area of Thiessen polygon/total surface area of lake). We found no difference between estimates derived on a whole-lake basis compared to those derived using the Thiessen polygon weighting.
Hydrodynamic Modeling Approach

We used the model to estimate the volume of water associated with thermocline migration during the period from 23 September (day 266) until 29 September (day 272). During this period the thermocline migrated over 2 m to a lake-wide mean depth of 13 m. In particular, a storm occurred on day 271 into 272. During this storm, cool air temperatures and high wind speeds (mean ~ 10 m/s) from the west and northwest contributed to thermocline deepening (Figure 7).

The hydrodynamic model reasonably reproduced thermal profiles for the period of interest (Figure 8). The model results do show slightly warmer temperatures in the hypolimnion than those observed in the temperature profile. This may be because we used a zero flux boundary condition in the model. Our assumption that heat flux at the lake bottom was zero over this six-day period may be erroneous, yet the hypolimnetic warming in the model did not appear to affect thermocline definition (defined as the depth of max rate of temperature change (Max Change)). The six-day range in the depth of the thermocline defined by the 3-D model (11.1 – 13.6 m) conformed reasonably well with the beginning (day 266) and ending (day 272) thermocline depths defined by the conventional method (10.8 – 13 m). Thus, we determined that the thermal structure of interest was indeed captured by the 3-D model, and the thermal structure defined by the model was used to estimate entrainment over the six-day period.
In order to compare the 3-D model output with the conventional approach (both single- and multi-location approaches), all approaches were used to estimate entrainment from 23 September 2005 until 29 September 2005 (day 266 – day 272). Estimates for this period using the single-location conventional method resulted in an estimate of 10,836 kg TP, the multi-location conventional method resulted in an estimate of 10,204 (± 3340) kg TP, while the 3-D model provided an estimate of 12,550 kg (± 1176) TP (Figure 9). The estimates of entrainment based on conventional and 3-D model calculations resulted in slight, though not statistically significant (t-test, p > 0.4, d.f. = 9), overestimation of the change in TP mass that was observed in the epilimnion (7,806 (± 1087) kg TP) over the 23 September – 29 September period (single-location results not included in statistical test due to small sample size (n=1)) (Figure 9).

The 3-D model captures upwelling dynamics likely responsible for spatial variation in P entrainment observed on dates associated with storm conditions. Representation of the lake thermal structure in the model demonstrates that under high wind speeds (~10 m s\(^{-1}\)) spatial variation in water temperatures is directly related to spatial variation in P concentrations across locations in the lake (Figure 10). The constant westerly winds blowing from days 270 through 273 resulted in upwelling of metalimnetic water in the western basin of the lake. Spatial heterogeneity in TP and SRP concentrations at depth, likely caused by upwelling, is apparent along the boundary between epilimnetic and metalimnetic water (11 – 13 m) (Figure 10). Similarly, a horizontal cross-section across the 12 m depth plane (Figure 11b)
demonstrates that the thermal structure of the lake responds to wind speed and direction, and this spatial variation in temperature is reflected in P concentrations at specific locations (Figure 11). Such spatial variation in temperature and P profiles may give rise to variation in estimates of entrainment. Congruence between thermal structure represented in the model and observed spatial variation in P profiles demonstrates that the model is capturing dynamics relevant to the distribution of P over short time scales.

While gross entrainment rates derived from all three approaches did not differ significantly during this six-day period, we were interested in whether the three different approaches converged on similar estimates of entrainment at a daily time scale. We used the P profile on day 266 along with daily temperature profiles from the temperature loggers to quantify daily P flux as the thermocline eroded. We found there were marked differences in daily entrainment rates among the three approaches, and daily entrainment rates were not correlated with one another. Given that we sampled P profiles less frequently than temperature profiles, we were not able to assess which of these approaches most closely approximated changes in epilimnetic P mass at a daily time step.

**Discussion**

Studies of P entrainment have shown that 1.) entrainment may represent a significant contribution to the annual P budget of the photic zone in many lakes and 2.) entrainment may provide a source of P to P-limited planktonic organisms during
the summer growing season (Søndergaard et al. 2003). Our study suggests that single and multi-location approaches deliver comparable estimates of seasonal entrainment. The 3-D model represented thermal structure and hydrodynamic patterns relevant to P distribution and transport over a short period of thermocline deepening. Also, 3-D model estimates of gross entrainment over a six-day period showed general agreement with the conventional estimates, though total entrainment quantified using the 3-D was slightly higher. Estimates of daily entrainment differed among conventional and 3-D approaches and were not correlated. The incongruence among daily estimates based on three approaches suggests validating a P entrainment model at a daily time scale requires more intensive measurements.

Our results corroborate earlier findings that suggest horizontal variation in P concentrations is a relatively small source of overall variation in estimates of P stored in the metalimnion (Stauffer 1985). Our seasonal estimate of entrainment captured at a single central location is consistent with estimates based on the multi-location conventional sampling method. These results generally hold true even when the definition of the thermocline is modified. In this study, sampling locations were distributed on either side of the node of the internal seiche such that we typically captured both inflated and deflated P concentrations during thermocline tilting. The effective averaging of these values canceled out the effects of thermocline displacement on the estimates of entrainment for a single date. Because estimates of entrainment at the central station correspond with spatially explicit estimates, and the central station is less prone to the confounding effects of thermocline tilt, we suggest
that sampling at a single location is effective in characterizing lake-wide amounts of P entrainment into the epilimnion. Thus, previous efforts to estimate mean annual entrainment based on a single centralized sampling location are likely justified, particularly in lakes with little morphometric variation.

Entrainment predominantly occurs in large pulses concurrent with atmospheric cooling and the passage of storms (Stauffer and Lee 1973; Stauffer 1993; Imberger and Patterson 1990; Soranno et al. 1997). Consistent with these findings the largest entrainment rates in our study occurred during periods of windy weather (Figure 4). Our sampling approach (regular sampling combined with increased sampling frequency following high wind speeds) was designed to capture the majority of entrainment events. The general thermal trend over the summer suggests that big changes in the depth of the thermocline were not frequent during the summer of 2005 (Figure 2). Instead thermocline migration could be characterized as gradual, and we believe our sampling routine was sufficient to capture entrainment associated with this gradual progression of the thermocline.

At the same time, our seasonal analysis demonstrates that entrainment is not limited to large storm events but that a significant flux also occurs during relatively calm periods due in large part to turbulent diffusion across the thermocline (Figure 12). It is difficult to account for this flux because $K_z$ values can be highly variable and tend to increase when entrainment intensifies. Thus, it may be difficult to capture short-term changes in $K_z$ using a weekly monitoring approach, but such short-term changes in $K_z$, and the associated P flux, can be accounted for by the 3-D model.
Therefore, though mean seasonal estimates of entrainment can be accomplished using the single-location conventional approach, many of the physical dynamics responsible for variation in entrainment estimates are better represented using a 3-D modeling technique.

The three-dimensional approach is most useful in understanding the connection between physical processes and the lateral distribution of P. 3-D hydrodynamic modeling lends insight into timing of delivery of P over short time scales and can identify local regions of upwelling responsible for transient spatial variation in P concentrations. During periods of upwelling, transient supplies of P can become available at specific locations within the lake (Western basin of Lake Mendota, day 272 – day 273, Figure 8). Due to high uptake rates for SRP and high rates of lateral movement of solutes within the epilimnion it is extremely difficult to observe local, transient changes in P concentrations. Yet, these discrete fluxes of P may supply P-limited phytoplankton with needed nutrients. The 3-D hydrodynamic model effectively captures the physical dynamics likely responsible for transient P fluxes.

While we observed spatial heterogeneity in P profiles during the period between 266-272, one limitation of this sampling design was that we were not able to more closely examine the contribution of fluxes near the lateral boundaries of the lake. All of our sampling locations were positioned in water that was at least 12 m deep, and thus any contribution of P to the epilimnion through mixing at the lateral boundaries could only be recognized following advection of dissolved and suspended
material to our sampling locations. Recent work suggests boundary mixing is important to scalar transport in lakes ((Etemad-Shahidi and Imberger 2001, MacIntyre et al. 2002). Our 3D hydrodynamic model is capable of simulating internal wave dynamics (Yuan 2007), and provides a platform to study turbulent mixing in benthic boundary layer and its interaction with internal waves. With a sediment transport subroutine added, the present 3D hydrodynamic model can be used to further study P transport due to lateral boundary mixing.

Our finding that a single-location thermocline migration approach is sufficient to capture the seasonal trend in entrainment will be useful in a management context. Meanwhile, our observations of the relationship between physical processes and spatial heterogeneity in P profiles will be of interest to researchers who study transient dynamics associated with bloom formation and phytoplankton patchiness. While it may be possible to use a single-location conventional approach to achieve a reasonable accounting for the total entrainment at a seasonal scale, a more complex model is required if one wishes to understand the mechanisms responsible for the transport of P. The non-hydrostatic nature of our 3D hydrodynamic model allows for more accurate simulation of a variety of physical processes such as flow over steep topography, upwelling, deep water convection, dynamics of short surface waves, degeneration of basin-scale waves, and evolution of nonlinear internal waves. All of these processes affect (to differing degrees) P transport in lakes. Thus, the 3-D model is a useful tool for representing physical processes that generate mixing and transport of biologically important solutes over intra-seasonal time scales.
Comments and Recommendations

While our results suggest that sampling at a single central location is sufficient for capturing a seasonal estimate for entrainment, readers should keep in mind the morphometric complexity of the lake when applying this conventional method to other systems (Robarts et al. 1998). Lake Mendota has a relatively simple basin shape. Yet, studies have shown that the shallow sill, which forms some separation between the main lake basin and the western arm of the lake, is sufficient to impose some bias in solute concentrations between the two basins (Stauffer 1985). Therefore, morphometric complexity could lead to greater spatial variation in entrainment estimates. The 3-D model could be useful in exploring the spatial variation in entrainment estimates in lake basins with greater morphometric complexity.

Time-dependent, three-dimensional computer models are capable of resolving the high degree of spatial and temporal variability inherent to lake dynamics, such as nutrient entrainment. Due to computational costs, however, the application of 3-D models to real lakes is restricted to coarse grid simulations, and the associated numerical issues must be carefully addressed to ensure the quality of model results. Further, even the coarse-grid simulation is fairly time intensive, and sometimes becomes impractical for the long-term (e.g. seasonal or annual time scale) application in large lakes. Therefore, we recommend a combined approach, including field measurements, conventional limnological methods, and 3-D modeling to investigate entrainment over multiple spatial and temporal scales. At the same time,
we recognize opportunities to improve the efficiency of the 3-D model (e.g. through code parallelization), and to broaden its applicability through explicit coupling with chemical and biological models.

In conclusion, the 3-D hydrodynamic model agrees with conventional estimates of entrainment and both generally agree with observed changes in epilimnetic P mass over a short period of late-summer thermocline migration. The simplest approach involving sampling at a single central location, near the deepest part of the lake, resulted in sufficient estimates of mean annual entrainment. The hydrodynamic model, however, can provide fine-scale information about the spatial and temporal variation in P concentrations that is not achievable in other ways. In this regard, further research and development to expand the use and applicability of 3-D hydrodynamic models would be productive.
References


Figure 1. Bathymetric map of Lake Mendota. Bathymetric lines are labeled with depth in meters. The twelve sampling locations are designated by dots, with the central station location designated by a star. Coordinates: 43°06' N, 89°25' W
Figure 2. Season-long air temperature, wind speed and water temperature for Lake Mendota for the summer season 2005.
Figure 3. Daily entrainment rate for total phosphorus (TP) based on one to five locations. Negative entrainment values indicate that the thermocline was shallower at the end of the time period.
Figure 4. Correlation between entrainment rates and mean wind speed or mean solar flux over the period between sampling events. $r =$ Pearson's product moment correlation coefficient, $p =$ p-value based on $\alpha = 0.05$. 
Figure 5. Positive correlation between the observed change in epilimnetic phosphorus mass at each location and the estimate of the mass of phosphorus entrained ($r = 0.6$, $p < 0.001$).
Figure 6. A comparison of mean entrainment rates based on four definitions of the boundary of the mixed layer. WO = Within One, MC = Max Change, MP = Mid-Point, IT = Isotherm.
Figure 7. Meteorological conditions between 23 September 2005 (day 266) and 29 September 2005 (day 272). Wind direction is from the north at 0 degrees, east at 90 degrees, south at 180 and west at 270. Each color in the temperature graph represents a depth within the thermal profile. Air and surface water temperatures show a cooling trend. Entrainment can be observed in the temperature graph as the depths represented by orange, yellow, and green are incorporated into the epilimnion. Strong west winds on day 271 and 272 are accompanied by rapid deepening of the thermocline.
Figure 8. Model validation of temperature profiles. Dots represent measured temperatures. Lines represent model fit to the data.
Figure 9. Cumulative estimate of phosphorus flux during the period between 23 September and 29 September (Day 266 – 272). “Epilimnion” represents an estimate of the change in phosphorus mass in the epilimnion over the period of interest; 3D Model = the sum of phosphorus entrained according to the 3D hydrodynamic model; “Multi-loc.” = the sum of phosphorus entrained according to the multi-location conventional approach; “Single-loc.” = the sum of phosphorus entrained according to the single-location conventional approach where the single location is positioned near the center of the lake. Error bars represent the standard error around the mean of all locations (n=5 in all cases except Single-loc (n=1)).
Figure 10. Thermal representation of a west to east cross-section of Lake Mendota during a three day period in late September (28 September (day 271) – 30 September (day 273)) based on 3-D hydrodynamic model. The images depict the thermal structure at 0000 hours on each date. The colors represent temperature in degrees Celsius. The arrows represent direction and magnitude of water velocity. Upwelling (cool metalimnetic water reaches the surface) can be observed at the west end of the lake on day 272 and 273. Total phosphorus (TP) concentration profiles are depicted for the three sampling locations indicated by vertical lines on the day 272 color image. Horizontal lines indicate a subset of the depths at which phosphorus samples were collected. Spatial variation in phosphorus profiles is apparent, particularly near the depth of the thermocline (thermocline ~ 13 m on day 272).
Figure 11. Spatial variation in thermal structure at the surface (A) and at 12 m below surface (B). Colors represent temperature in degrees Celsius. Thermal images are based on a horizontal cross-section of Lake Mendota using a 3-D hydrodynamic model for a 24-hour period on the 29th September 2005 (day 272). Numbers in the graphics represent the SRP concentration (mg/L) at each depth and location on day 272.
Figure 12. Relative contribution of turbulent flux and bulk entrainment toward the total estimate of entrainment for each sampling period.
CHAPTER 4

Long-term trends in ice cover, stability, phosphorus and water quality in
eutrophic Lake Mendota

by

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Abstract

Effects of climate warming are apparent in lake ecosystems evidenced by rising water temperatures and shorter duration in ice cover. Modeling exercises, studies of anomalous weather years, and examination of lakes across latitudinal gradients suggest that changes in temperature will result in changes in the physical structure of lakes, nutrient cycling, phenology, water quality and habitat availability. Yet, few studies can empirically document the effects of warming trends on physical, chemical and biological aspects of the system. Here we present a long-term record from Lake Mendota of changes in ice cover, physical characteristics, phosphorus dynamics and water quality metrics that provides evidence of the link between changes in chemical and biological variables and changes in the physical characteristics of the lake. We also examine the effects of changes in physical and chemical variables on the general water quality characteristics of the lake. Temporal trends show a decline in ice cover and correlated increases in strength and duration of stratification. At the same time, we observed significant increases in phosphorus concentrations and anoxic conditions in the hypolimnion. The trends in phosphorus and oxygen conditions were likely due to a common relationship with increasing stability and length of stratification over time. Change in the physical and chemical features of the lake were tied to changes in water quality in that we also observed a significant improvement in water clarity over time, and a significant relationship between mean phosphorus concentrations in the epilimnion and stability of the water column. Thus, our study provides empirical evidence of changing physical conditions
in a deep dimictic lake and demonstrates that these physical changes have implications for the distribution of solutes and the trajectory of water quality in lakes.
Introduction

The effects of global warming are evident in lake ecosystems and lakes may serve as a harbinger of further change at local and regional scales. Records of the duration of ice cover show consistent and significant trends toward earlier ice break up and later freeze dates across North America (Magnuson et al. 2000, Jensen et al. 2007). Also, recent lake ice cover records (since 1975) show an increasing rate of change compared to historical changes in ice duration (Jensen et al. 2007). Changes in the duration of ice cover are anticipated to have dramatic effects on stratification and mixing patterns, on phenology and seasonal succession, on evaporation and hydrology, and on the behavior and distribution of organisms that depend on these systems.

Potential effects of climate change on aquatic ecosystems have been largely explored through modeling exercises (Magnuson et al. 1997, Elliot et al. 2005). Simulations of water temperature and dissolved oxygen characteristics in lakes of different morphometries suggest that surface water temperature and the duration of stratification can be expected to increase along with a lengthening of the period of hypolimnetic anoxia (Stefan et al. 1996, DeStasio et al. 1996). From projected changes in temperature and oxygen characteristics we can infer changes in the distribution of fish species and biotic interactions within lakes (DeStasio et al. 1996, Magnuson et al. 1997). Other modeling studies suggest likely changes in the timing and species succession associated with the spring phytoplankton bloom (Elliot et al. 2005)
In addition to modeling exercises, some studies have been able to use anomalous weather years (Jankowski et al. 2006, Wilhelm and Adrian 2008) or a latitudinal gradient (Weyhenmeyer 2004, Kosten et al. 2009) in lakes to explore the potential influence of climate change on aquatic systems. These studies provide empirical support for dramatic changes in thermal structure and concomitant changes in oxygen distribution within lakes (Jankowski et al. 2006). Notably, Kosten et al. (2009) found that an interaction between climate and nutrient concentrations determined the vegetation structure within lakes across a climate gradient.

Although we have a number of models and long-term records of water temperature (Livingstone 2003, Arhonditsis et al. 2004) that support the idea that climate change will result in significant changes in the physical structure of lakes, there are few studies that provide empirical evidence for the effects these physical changes will have on the biology and chemistry of aquatic systems. Here we present a thirty-year record from Lake Mendota of changes in ice cover, physical characteristics, phosphorus dynamics and water quality metrics which provides evidence for changes in internal processes resulting from changes in the physical characteristics of the lake. We also examine the implications of changes in physical and chemical features for the general water quality characteristics of the lake.

Materials and methods

All data were collected on Lake Mendota, a eutrophic dimictic lake in Madison, Wisconsin (43°06' N, 89°25' W, 39.1 km² surface area, 12.3 m mean depth). This
lake has been monitored using consistent methods since 1975. The program began under auspices of the Wisconsin Department of Natural Resources (WIDNR) (1975 – 1995) and more recently has been monitored jointly by the WIDNR and the North Temperate Lakes Long-Term Ecological Research program (NTL-LTER, http://lter.limnology.wisc.edu). We compiled information on ice duration, water temperatures, Secchi depth, phosphorus loading and dissolved oxygen and phosphorus concentrations within the lake. We used these data to calculate metrics related to lake stability, phosphorus dynamics, annual and summer-time phosphorus mass balances, and the duration of stratification and anoxia.

Metrics related to the physical conditions of the lake included a metric related to the duration of anoxia as a measure of the number of days that the lake was strongly stratified. In each year we documented the first day on which oxygen concentration at any depth was < 1.0 mg L$^{-1}$ and documented the final day of the summer on which anoxic conditions were observed. The difference between these dates served as a proxy for the length of stratification. We also calculated the mean Schmidt stability index for the lake over the summer. This calculation is a measure of the total amount of energy that it would theoretically take to mix the entire lake (Imberger and Paterson 1990). This metric is calculated as:

$$SS = \frac{1}{A_o} \sum (z - z^*)(\rho_z - \rho^*)A_z \Delta z$$

Where: $SS = \text{Schmidt stability (g cm}^{-1} \text{)}$

$A_o = \text{surface area of the lake}$

$z = \text{depth of interest}$
\( z^* \) = depth of mean density \\
\( \rho_z \) = water density at depth \( z \) \\
\( \rho^* \) = mean water density \\
\( A_z \) = area of lake at depth \( z \) \\
\( \Delta z \) = depth interval of calculation (1m)

Total phosphorus (P) samples were collected in acid-washed triple-rinsed containers at 2 – 4 m intervals along the depth profile of the lake, and were generally collected on a monthly basis. Phosphorus profiles were consistently collected in mid-April and late October or early November in order to capture the P concentration in the lake during spring and fall mixis. Temperature and dissolved oxygen concentrations were recorded at every meter along a depth profile, and were sampled every two weeks. All samples and measurements were collected at the deepest point (~ 24 m) near the center of the lake. TP samples were preserved using Optima HCl (1 N), and later analyzed using spectrophotometric techniques following persulfate digestion, according to the most recent standard methods at the time (APHA et al., 1995).

Details of methods related to P input to and export from the lake have been reported previously in other studies (Lathrop et al. 1998, Lathrop 2007 and Carpenter and Lathrop 2008). Briefly, there are four streams and two storm water inlets entering Lake Mendota. Two streams (Pheasant Branch and Yahara River) and one storm water inflow (Spring Harbor) are continuously monitored for hydrologic and chemical inputs into the lake by the United States Geological Survey (USGS). Loading was determined for these three inlets and these data were used to infer loading from other inlets based on previous estimates of the relative load entering the lake from each
source (Lathrop et al., 1998). Outflow of P was determined using the hydrologic outflow of the lake multiplied by the mean epilimnetic P concentration.

Annual estimates of the phosphorus budget were based on calculations of the cumulative P load and P outflow from the lake between April 16th of one year and April 15th of the next. Annual estimates of load combined with hydraulic conditions for the water-year were used as input variables for prediction of April P concentrations in the spring based on the Vollenweider model (Vollenweider 1976):

\[
[P] = \left(\frac{L_p}{q_s}\right) \times \left(\frac{1}{1 + \sqrt[3]{z/q_s}}\right)
\]

Where: \( [P] \) = mean P concentration (mg L\(^{-1}\))
\( L_p \) = annual P load (g)
\( q_s \) = annual hydraulic load (m\(^3\))
\( z \) = mean depth (m)

Additionally, we calculated a budget for the changes in P during the summer of each year. Calculation of the P budget for the summer was based on observed April (\( P_A \)) and November (\( P_N \)) P mass. Inputs and outputs from the system were quantified using monthly estimates of P load and P outflow over the months between April and November (this period will be referred to as the "summer"). Between April and November of a given year, mass balance can be used to estimate November P mass as follows:

\[
P_N = P_A + \text{SUMMLOAD} - \text{SUMMOUT} + \text{Net_flux}
\]

where \( P_A \) and \( P_N \) are P mass in April and November respectively, \( \text{SUMMLOAD} \) and \( \text{SUMMOUT} \) are load and outflow, respectively, between April and November, and
Net_flux is the difference between sediment release and sedimentation between April and November, such that Net_flux is positive if recycling exceeds sedimentation, and negative if sedimentation exceeds recycling. All budget terms except Net_flux were measured directly. We estimated Net_flux by rearranging the equation as:

$$\text{Net\_flux} = (P_N + \text{SUMM}_{\text{OUT}}) - (P_A + \text{SUMM}_{\text{LOAD}})$$

In many lakes with anoxic hypolimnia, the rate of release of P from the sediments is associated with the extent and duration of anoxic conditions due to the release of P from chemical complexes in lake sediments under reducing conditions (Nurnberg 1984, Nurnberg 1987). Therefore, the Anoxic Factor (AF), an index of anoxic conditions, was explored as a potential predictor of hypolimnetic P conditions in our long-term study. The AF is a measure of the number of days during the summer that an area equivalent to the surface area of the lake is overlain by anoxic water (Nurnberg 1987). The AF was calculated based on periodic oxygen profiles collected between April and November in each year using the following:

$$\text{AF} = \sum \frac{\text{duration} \times \text{anoxic\_area}}{\text{lake\_area}}$$

Where: AF = Anoxic Factor (days)
Duration = number of days between oxygen profiles
Anoxic_area = sediment surface area (m²) exposed to anoxic conditions (DO < 1.0 mg L⁻¹) between sampling events
Lake_area = total surface area of the lake (m$^2$)

Other variables of interest included the rate of decline in dissolved oxygen (DO), the rate of accumulation of P, and the P concentration observed in the hypolimnion in each September. For determination of the decline of DO and accumulation of P, we quantified the total mass of DO and P in the hypolimnion, which for this purpose was defined as the depths between 14 m and 24 m in depth. As the mean thermocline depth is typically between 8 – 12 m, this definition of the hypolimnion avoids incidental inclusion of water from the mixed layer. We documented the DO or P in the hypolimnion at a number of sampling points during the summer and used the slope of the mass over time as a measure of the rate of DO decline or P accumulation. We excluded summers in which there were fewer than 3 observations of the P or DO profiles during the summer. Also, in order to identify a reasonable slope, we limited our observation of DO profiles to the period between May 1$^{st}$ and July 15$^{th}$, the period during which oxygen concentrations in the hypolimnion were observed to be changing. Similarly, observation of P mass in the hypolimnion was limited to the period between April 15$^{th}$ and September 1$^{st}$, the period during which a clear trend in hypolimnetic P mass could be identified. The maximum P concentration was observed at an index depth and date to facilitate comparison across years.

I used the P concentration at 20 m depth for the sampling date in closest proximity to September 1$^{st}$ (all sample dates fell between 25 August and 7
September). An examination of the September P concentration versus the day of year the sample was collected showed that the small variation in the timing of sample collection did not affect the concentration of P observed.

All variables were normalized to a common annual time step based on the mean of observed values. Analyses of the relationships among variables were conducted using Pearson’s Correlation, with an alpha significance of 0.05. All analyses were completed using the R statistical software program (http://www.r-project.org/).

Results

Metrics related to ice cover and the physical structure of the lake showed notable temporal trends over the approximately 30-year period of record. Ice duration showed a significant decline over time (p = 0.046, r = -0.37) (Figure 1a). Based on a five-year average, the duration of ice cover has declined from a mean of 109 days per winter to approximately 96 days of ice cover. The ice cover duration in 2001 (21 days) was identified as an outlier using Grubb’s test, so this value was not included in the reported five-year average.

The duration of stratification increased significantly over the last thirty years (p = 0.046, r = 0.37) resulting in an increase in mean length of stratification from approximately 122 to 139 days (again, based on a five-year average) (Figure 1b). The Schmidt stability index also provided a signal that the physical structure of the
lake has changed over time, yet this temporal trend was marginally significant (p = 0.053, r = 0.35) (Figure 1c).

Some phosphorus (P) metrics have changed significantly over time. April P mass and the mean concentration of P in the epilimnion, while temporally variable, show no consistent trend over the period of record (Figure 2a and 2b, respectively). On the other hand, the rate of P accumulation in the hypolimnion and the September concentration of P in the hypolimnion have both increased notably since the late 1970's (p = 0.003, r = 0.57; p < 0.001, r = 0.82, respectively) (Figure 2c and 2d, respectively).

We found evidence that the observed changes in hypolimnetic P dynamics are related to changes in physical characteristics of the lake. The concentration of P in the hypolimnion in September was positively correlated with the duration of stratification (p = 0.005, r = 0.54) (Figure 3a). Yet, there was no significant relationship between the September P concentration and the date of onset of stratification (p = 0.22, r = -0.26). The rate at which P accumulated in the hypolimnion was also weakly related to the duration of ice cover, but this trend was not statistically significant at an \( \alpha = 0.05 \) (p = 0.061, r = -0.38) (Figure 3b).

Hypolimnetic oxygen metrics also changed over thirty years and these changes were associated with the strength and duration of stratification. The Anoxic Factor increased significantly over time (p = 0.029, r = 0.41) (Figure 4) and these changes were correlated with changes in the Schmidt stability index (p = 0.007, r = 0.49) (Figure 5a). Similarly, the rate of dissolved oxygen decline in the hypolimnion
was negatively correlated with the date of onset of stratification (p = 0.009, r = 0.48). Therefore, when the lake stratifies early in the season, dissolved oxygen is lost from the hypolimnion at a faster rate (Figure 5b). The oxygen metrics, however, were not correlated with changes in P in the hypolimnion (rate of P accumulation or September P concentration) (p > 0.05, r < 0.2, in all cases). This indicates that the temporal synchrony between P and oxygen conditions in the hypolimnion was driven by a common relationship with increasing stability and length of stratification over time.

These changes in the physical structure of the lake along with changes in the phosphorus and oxygen dynamics in the hypolimnion have resulted in significant changes in the water quality characteristics of the lake. The mean summer Secchi depth reading has improved significantly over the period of study (p = 0.004, r = 0.52) (Figure 6). The improvement in water clarity is positively related to an increase in the stability of the water column (p = 0.016, r = 0.44) (Figure 7a). Additionally, the stability of the water column is correlated with the mean P concentration in the epilimnion (p = 0.015, r = -0.46) (Figure 7b). The mean epilimnetic P concentration tends to be lower during summers with a high Schmidt stability index.

Given that we observed a significant temporal trend in characteristics associated with internal loading (rate of P accumulation in the hypolimnion and increasing late-season P concentrations in the hypolimnion) we wanted to explore the potential effects of these changes on the annual phosphorus dynamics of the lake. The summer season was bracketed by measurements of the P mass in the lake in
April and November, during spring and fall turnover (Figure 8a). In many cases, fall and spring values were quite similar and this relationship was reflected by a significant positive correlation ($r = 0.64$, $p < 0.001$). Generally, the $P_N$ was greater than $P_A$, but there were notable exceptions in 1993 and 1998. Summertime P loads ($SUMM_{LOAD}$) were quite high in some years, and peaks in summertime P loading appeared more frequent in recent years (Figure 8). Loss of P from the outlet ($SUMM_{OUT}$) of the lake was relatively constant, with the exception of 1993 when an unusually high summertime loading rate was associated with an unusually high export of phosphorus from the lake. $SUMM_{LOAD}$ consistently exceeded $SUMM_{OUT}$ (Figure 8b).

The balance of these input and output components was summarized as an estimate of Net_Flux within the lake (Figure 8c). Sedimentation is known to be a large component of the P flux within this eutrophic lake (Sonzogni et al. 1976, Soranno et al. 1997), so it is not surprising that in most years the downward flux of P via sedimentation outweighs the upward flux of internal loading from the sediments, thus the value of Net_Flux is negative. Conversely, years in which internal loading outweighs sedimentation are relatively rare. But, because positive peaks in the Net_Flux highlight instances in which the net balance is in strongly in favor of one component of the vertical flux, these peaks in net internal loading are particularly notable.

While there is no apparent temporal trend in the Net_Flux (Figure 8c), which serves as an index of net internal load, The residual of Net_Flux (after regression
against the mean P concentration of the previous year) was positively correlated with $P_{\text{accum}}$ ($p = 0.03$, $r = 0.45$) (Figure 9). Thus, phosphorus in the hypolimnion generally accumulated faster in years when sedimentation was relatively low. There appeared to be a saturation of the relationship between net flux and P accumulation, such that at high accumulation rates we didn't always see a further increase in the net internal load. However, this relationship was difficult to interpret because the net flux represents the relative balance between sedimentation and internal load. It is possible that in summers with high P accumulation, there may also be higher rates of sedimentation.

We explored whether any of the metrics related to internal loading could explain residual variation associated with the Vollenweider model. The P load to Lake Mendota has been variable, but shows no significant temporal trend (Figure 9a). Similarly, the April P mass and associated residual error from the Vollenweider model ($V_{\text{err}}$) show no significant temporal trend (Figure 9b and 9c). Variability in $V_{\text{err}}$ does seem to have decreased in recent years (Figure 9c).

The rate of accumulation of P in the hypolimnion, the maximum concentration of P observed, and the net flux metric from the previous year were not significantly related to the residual errors of the Vollenweider model ($V_{\text{err}}$). Instead, a display of the autocorrelation function for April P mass suggests that there is a 1-year time lag in the mass of P in the lake in April, indicating that some variation in observed April P mass can be explained by the previous April P mass in the previous year (Figure 11). In fact, we found a simple linear regression model based on April P mass from the
previous year and the total P load from the previous year could explain the April P
mass in the year of interest quite well ($p < 0.001$, $R^2 = 0.67$, AIC = 527.6). In this case,
adding net flux from the previous year to the model resulted in a marginally significant
improvement in model fit (coefficient p-value = 0.064, AIC = 525.4). Thus, there is
some support for the idea that release of phosphorus from the sediments (as a “new”
source of P) contributes to the April P mass in the lake.

We did observe a relationship between the rate of P accumulation in the
hypolimnion and the residual variation around the Vollenweider relationship. The
residuals from the Vollenweider model (an index of Spring P conditions) were
correlated with the net flux metric for the following summer ($p = 0.05$, $r = 0.39$) (Figure
12). Thus, when April P concentrations were higher than predicted by the
Vollenweider model (i.e. a negative residual) it was most likely that there would be
net sedimentation during the summer. Net recycling was most prevalent in years
when the Vollenweider model predictions were greater than the observed April P
concentrations.

Discussion

Changes in lake stability and length of stratification are associated with
changes in the duration of ice cover. Long-term records document a decrease in ice
cover on Lake Mendota and many lakes worldwide (Magnuson et al. 2000). Scenario
modeling exercises corroborate the relationship between the stability and duration of
stratification in lakes and climate change (Hondzo and Stefan 1992). Other long-term
studies indicate that surface waters warm at a higher rate compared to bottom waters, thus inducing changes in physical stability of the water column and duration of stratification (Livingstone 2003). Our study provides empirical evidence of changing physical conditions in a deep dimictic lake and demonstrates that these physical changes have implications for the distribution of solutes and the trajectory of water quality in lakes.

Changing physical conditions in the lake played a dominant role in determining the distribution of P and DO during the summer with implications for water quality. As length of stratification increases, we might expect P to build up in the hypolimnion over a longer period of time (Nurnberg 1998). However, our data suggest this is not the sole reason for the increasing trends in maximum P concentrations in the hypolimnion because $P_{\text{sept}}$ was consistently measured around September 1\textsuperscript{st} in all years and the magnitude of $P_{\text{sept}}$ was not significantly correlated with the date of onset of stratification. Instead we think that the increase in $P_{\text{sept}}$ may be partly attributed to a lower vertical flux rate of P to the epilimnion and higher rates of sedimentation from the epilimnion. During years with relatively low stability, the vertical eddy diffusivity would be higher, thus allowing higher rates of vertical diffusion through the hypolimnion and potentially reducing sedimentation (Stuaffer 1992). Thus changes in the P concentration in the hypolimnion of Lake Mendota are likely due to an increase in the period over which P may accumulate, increased sedimentation, and to effective containment of P within the hypolimnion.
The importance of physical conditions in vertical solute transport and water quality are in line with previous studies that show entrainment events and algal blooms are tied to changing weather dynamics at a daily scale (Soranno 1997, Stauffer 1992). Similarly, Lathrop and others (1999) found that interannual variation in Secchi depth could be explained by lake stability, along with Daphnia grazing and P availability. The effects of climate change, however, are not likely to have positive effects on water quality across lakes. An increase in strength and duration of stratification could have profound repercussions in shallow lakes with intermittent mixing. Polymictic lakes are often prone to short-term stratification, and as such may experience bouts of anoxia and internal loading (Riley and Prepas 1984, Kallio 1994, Wilhelm and Adrian 2008). If climate change can be expected to increase the incidence of these internal loading episodes, water clarity would likely decline.

Net_Flux was positively correlated with the rate of P accumulation in the hypolimnion ($P_{\text{accum}}$). It follows that $P_{\text{accum}}$ rates are relatively low when net sedimentation is high, which may imply that P accumulating in the hypolimnion is not derived from sedimentation in the same year. Instead, correlation between the September P concentration at 20 m ($P_{\text{sept}}$) and the mean epilimnetic P concentration ($P_{\text{epi}}$) of the previous year lend support to the idea that P accumulating in the hypolimnion is due to recycling of P from the previous year.

A short lag time between deposition of P in the hypolimnion and remineralization is further supported by the fact that none of the three metrics of internal loading (rate of P accumulation, September P concentration at 20 m, and the
net flux metric from the previous summer) could explain residual variation around the Vollenweider model predictions of April P mass. Additionally, the 1-year time lag in the autocorrelation function for April P mass suggests the memory term (via the mechanism of internal loading) for the system is relatively short-lived.

This interpretation is illustrated well by observations during the period between 1987 and 1992, which followed a drought in 1987-1988. During this period external loads were relatively low and consistent, if internal loading were a dominant process, we would expect to see evidence of net P release particularly during the summer months. However, we see that the November phosphorus mass very closely tracks the phosphorus mass observed in April, and the difference between the two can very nearly be explained by the difference between summer-time external load and P outflow (Figure 8). Thus, a number of lines of evidence from this long-term study suggest that mean P conditions in Lake Mendota are predominantly controlled by external loading to the system. This finding supports previous studies following the diversion of wastewaters from Lake Mendota which suggested that, overall, the sediments of the lake act as a sink rather than source of phosphorus to the system (Sonzogni and Lee 1974).

Changes in climatic patterns are already having noticeable effects on lake ecosystems. The resultant changes in water temperature and physical stability of a lake have the power to exact changes in oxygen dynamics and internal nutrient cycling. Using a long-term data set we provide empirical evidence for changes in the physical characteristics for Lake Mendota and show that changes in oxygen,
phosphorus and water quality have occurred at the same time. While there have been significant changes in internal phosphorus dynamics in the lake, the error around the Vollenweider model (which predicts April P conditions) could not be explained by these changes in internal P loading. Thus, P dynamics for the system remain driven by external loading, and reductions of external loading, not further climate change, are the key to restoration of water quality.
References


Figure 1. Temporal trends in ice cover (a), the duration of stratification (b), and the Schmidt stability index (c). Ice cover and duration of stratification show significant trends over time ($r = \text{Pearson's Correlation coefficient}, p = \text{p-value}$). Schmidt stability index shows a temporal trend which is marginally significant at an $\alpha = 0.05$. The ice cover value for 2001 (21 days) was identified as an outlier (Grubb's test)
Figure 2. Temporal trends in phosphorus dynamics in Lake Mendota. There is no significant temporal trend in the mass of phosphorus in the lake in April of each year (a) or in the mean epilimnetic phosphorus concentration (b). The rate of phosphorus accumulation in the hypolimnion (c) and the phosphorus concentration at 20 m depth in September (d) both showed significant increases over time (r = Pearson’s correlation coefficient, p = p-value).
Figure 3. Hypolimnetic P variables were related to changes in physical characteristics of the lake. The phosphorus concentration at 20 m depth in September was significantly correlated with the duration of stratification (a). There was a negative trend in the relationship between ice duration and the rate of P accumulation in the hypolimnion (b), but this relationship was not statistically significant ($r = $ Pearson's Correlation coefficient, $p = p$-value).
Figure 4. There was a significant increase in the Anoxic Factor over time ($r = 0.41$, Pearson's Correlation coefficient, $p = 0.029$).
Figure 5. Changes in the oxygen characteristics of the hypolimnion were significantly related to changes in the physical characteristics of the lake. The Anoxic Factor was positively correlated with the Schmidt stability index (a), while the rate of dissolved oxygen decline in the hypolimnion was significantly correlated with the date of onset of stratification ($r = $ Pearson's Correlation coefficient, $p = $ p-value).
Figure 6. The mean summer time Secchi depth reading has increased significantly over time ($r = Pearson's$ Correlation coefficient, $p = p$-value).
Figure 7. Changes in the Secchi depth are positively correlated with changes in the Schmidt stability index (a), while there is a negative relationship between the mean phosphorus concentration in the epilimnion and the Schmidt stability index ($r = -0.46$, $p = 0.015$).
Figure 8. Summer phosphorus metrics. Phosphorus mass in the lake at spring (April, $P_A$) and fall (November, $P_N$) mixis (a). Total phosphorus inputs (Load) and outputs (Outflow) during the period between April and November (b). The summer Net flux is a measure of the balance between inputs, outputs and the starting and ending P mass: Net flux = ($P_N + \text{SUMM}_{\text{OUT}}$) − ($P_A + \text{SUMM}_{\text{LOAD}}$).
Figure 9. There is a significant positive relationship between the rate of P accumulation in the hypolimnion during the summer and the Net_flux over that same summer. Rate of P accumulation is slightly higher in years when sedimentation is low.
Figure 10. Annual phosphorus metrics. Annual P load (a) represents the total external load that entered the system between April 16th of the previous year and April 15th of the year of interest. April P mass (b) represents the total P mass in the lake on April 15th of the year of interest. Panel (c) represents the error in the prediction of the April P concentration based on the Vollenweider model. When $V_{err}$ is positive, observed P concentration < predictions; when $V_{err}$ is negative, observations > predicted P concentration.
Figure 11. Autocorrelation function (ACF) (a) for the time series of P mass in Lake Mendota in April of each year. Note the significant autocorrelation (a) at a 1-year time lag. We also present the ACF of the first difference between successive April P mass observations (b).
Figure 12. There was a marginally significant positive relationship between the residuals of the Vollenweider model ($V_{err}$) and the residuals of the Net Flux metric (after regression against mean P in the epilimnion).