EFFECT OF LAKE N FIXATION ON WATERSHED EXPORT
UNDER N LOADING REDUCTION SCENARIOS

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By

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Coastal eutrophication is an important global environmental problem, and nitrogen input from the watershed is a primary cause. Consequently, management efforts often focus on lowering watershed N export by reducing the N loading (e.g., fertilizer application). Simple quantitative models are needed to evaluate alternative scenarios at the watershed scale. Existing models generally assume that, for a specific lake/reservoir, the relationship between N loading and export is linear, which means a certain reduction in loading will result in a proportional reduction in export. However, reducing N loading will reduce the N/P ratio, and N fixation by cyanobacteria may increase, which may change the (effective) N export fraction. The hypothesis of this research is that lake and watershed N export is not reduced proportionally when N loading is reduced, because N fixation will counteract the reduction. The objective is to evaluate and quantify this effect. The hypothesis is tested by analysis of data from three approaches: microcosm lab experiments, lake field observations/budgets and lake ecosystem model applications. A simple model (Fixation and Export of Nitrogen from Lakes, FENL) is developed based on a steady-state mass balance with loading, output, loss/retention, and N fixation, where the amount fixed is a function of the N/P ratio of the loading. The FENL model is then implemented into a Chesapeake Bay watershed model and applied to predict watershed N export under three scenarios (baseline, 60% N reduction and balanced N+P reduction). The results suggest that lake and watershed N export will not be reduced proportionally with N loading. Results for the Chesapeake Bay watershed show that: (1) Under a 60% N
reduction scenario, the majority of lakes are pushed into the N-fixation regime and the added N by fixation in lakes counteracts the N loading reduction, thus, the watershed N export does not decrease proportionally. (2) The effect is significant at the watershed scale. Reducing 60% of N loading only will result in a 50% reduction in N export from the watershed. (3) A 60% N+P reduction will reduce the N export by 60%. The results of this research support a dual nutrient management strategy.
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Chapter 1 **Introduction**

Coastal eutrophication is an important global environmental problem that can result in degradation of water quality, hypoxia, fish kills and harmful algal blooms (HABs). A recent global survey of coastal eutrophication identified more than 400 systems as experiencing hypoxia (Diaz and Rosenberg 2008; Rabalais, Diaz et al. 2010). For example, the continental shelf along the northern Gulf of Mexico has become the second largest coastal hypoxic zone in the world (“The Dead Zone”) (Rabalais, Turner et al. 2002b). Another example is Chesapeake Bay on the eastern U.S. coast, where seasonal hypoxia has occurred for decades (Hagy, Boynton et al. 2004). The associated economic effects of coastal HABs in the U.S. are at least $82 million/year (in 2005 dollars) (Hoagland and Scatasta 2006).

Excessive nutrient input is a primary cause of coastal water eutrophication. Although there is some debate over which nutrient is limiting primary production in coastal waters (Smith 1984; Cerco 1995; Sylvan, Dortch et al. 2006; Paerl 2009), it is clear that N is an important factor, and its increased input is often considered to be the main cause of coastal eutrophication (Alexander, Smith et al. 2000; Rabalais, Turner et al. 2002a; Hagy, Boynton et al. 2004; Scavia and Donnelly 2007). Thus, in order to reduce coastal eutrophication, management plans often focus on the reduction of watershed N loading (Heathwaite, Sharpley et al. 2000).
The cost of nutrient reduction management actions at the watershed scale can be substantial. For example, the hypoxia in the Gulf of Mexico has been tied to agriculture in the upper Midwest and the cost to reduce this loading by 30% can be as high as US$1.4 billion/year (Rabotyagov, Campbell et al. 2010). It is clear that accurate estimates of the watershed N export under different management scenarios are of high societal relevance.

Watersheds are complex systems including numerous sources and sinks of N. Lakes and reservoirs may constitute a significant source and/or sink to the watershed N budget by the processes of sedimentation/burial, denitrification and fixation of atmospheric N (Horne and Goldman 1972; Harrison, Maranger et al. 2009). For example, 16% of N load to the Missouri River watershed is lost in lakes and reservoirs before entering the Mississippi River (Brown, Sprague et al. 2011). 43% of the annual N input to Clear Lake is contributed by N fixation, and this can be a significant source to the watershed and downstream San Francisco Bay (Horne and Goldman 1972). Thus, this source/sink needs to be considered when estimating/modeling N export from the watershed to the coastal area.

The N cycle of watersheds is complex and the available data are limited, so simple quantitative models are needed to evaluate alternative scenarios at the watershed scale. A number of models have been developed and applied at the watershed scale to estimate watershed N export. SPARROW (Spatially Referenced Regression on Watershed Attributes) predicts N point and nonpoint source loading to and transport and loss in the stream and lake/reservoir network (Smith, Schwarz et al. 1997). SPARROW has been
applied at the national scale and a number of higher resolution regional models are also available (Ator, Brakebill et al.; Moore, Johnston et al. 2011; Wise and Johnson 2013). A similar empirical regression model (RivR-N) was developed to predict N removal in streams and reservoirs and has been applied to watersheds in the northeastern U.S. (Seitzinger, Styles et al. 2002). The problem with the existing models is that they assume, for a specific lake/reservoir, a constant fraction of N loading is exported downstream, and they do not explicitly account for N fixation, which may change under N loading reduction scenarios. Specifically, reducing N loading will reduce the N/P ratio and favor cyanobacteria that can fix N (Findlay, Hecky et al. 1994; Hellström 1996; Vrede, Ballantyne et al. 2009).

We hypothesize that watershed N export will not be reduced proportionally with watershed N loading reduction, because N fixation will counteract the reduction (Figure 1.1). The objective of this research is to quantify the magnitude of this effect at the watershed scale. For example: if the N loading to the Chesapeake Bay watershed is reduced by 60%, how much reduction in the N export can be expected?
1.1 Overview of the research

This study has two main parts: (1) quantifying the relationship between lake N loading and export under varying N loading and developing a model for this process (Chapter 2), (2) improving the model, implementing it in a watershed model and applying it at the watershed scale to quantify how lake N fixation affects watershed N export to coastal waters (Chapter 3).

In Chapter 2, a simple model (Fixation and Export of Nitrogen from Lakes, FENL) is presented that explicitly accounts for N fixation in lakes and reservoirs. This model is developed based on a steady-state mass balance with loading, output, loss/retention and N fixation, where the amount fixed is a function of the N/P ratio of the loading (i.e. when N/P is less than a threshold value, N is fixed). The model is calibrated against data from three approaches: microcosm lab experiments, lake field observations/budgets and lake ecosystem model applications. The data and model results of the 17 individual systems suggest that N export will not be reduced proportionally when reducing N loading.

Figure 1.1. Effect of N fixation on lake budget under N loading reduction scenarios.
Chapter 3 focuses on quantifying the effect of lake and reservoir N fixation on watershed N export under different N loading reduction scenarios, using Chesapeake Bay as a case study. In this chapter, a modified version (FENL2) is presented. The difference between these two versions is that, for FENL1, it assumes that sufficient N will be fixed so that the input N to P ratio is at a threshold value. This is a conservative assumption (from a management perspective), but not very realistic, because N fixation is an energy expensive process subject to numerous environmental factors (Howarth, Marino et al. 1988a; Paerl 1990; Paerl 2009; Paerl, Xu et al. 2011a). Thus, in FENL2, the amount of N that can be fixed is limited by a factor. FENL1 and FENL2 are then parameterized and calibrated against the dataset consisting of laboratory experiments, lake field budgets and ecosystem models. The two models are then coded into the Chesapeake Bay SPARROW model. Three models: SPARROW with the original lake model (referred to as SPARROW), SPARROW with FENL1 and FENL2 lake models (referred to as FENL1 and FENL2) are calibrated and applied to the Chesapeake Bay watershed to predict watershed N export. From the management perspective, SPARROW, FENL1 and FENL2 can be considered “best case”, “worst case” and “best estimate”. The models were evaluated under three management scenarios: baseline, 60% N loading reduction and 60% N+P loading reduction. The results suggest that the watershed N export will not be reduced proportionally under an N only reduction scenario, but will be reduced proportionally under a balanced N+P reduction scenario.

Chapter 4 summarizes the conclusions and the contributions of this research and discusses future research in this area.
1.2 References


Chapter 2 Accounting for N Fixation in Simple Models of Lake N Loading/Export\textsuperscript{1}

2.1 Abstract

Coastal eutrophication, an important global environmental problem, is primarily caused by excess N and management efforts consequently focus on lowering watershed N export (e.g. by reducing fertilizer use). Simple quantitative models are needed to evaluate alternative scenarios at the watershed scale. Existing models generally assume that, for a specific lake/reservoir, a constant fraction of N loading is exported downstream. However, N fixation by cyanobacteria may increase when the N loading is reduced, which may change the (effective) fraction of N exported. Here we present a model that incorporates this process. The model (Fixation and Export of Nitrogen from Lakes, FENL) is based on a steady-state mass balance with loading, output, loss/retention and N fixation, where the amount fixed is a function of the N/P ratio of the loading (i.e. when N/P is less than a threshold value, N is fixed). Three approaches are used to parameterize and evaluate the model, including microcosm lab experiments, lake field

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observations/budgets and lake ecosystem model applications. Our results suggest that N export will not be reduced proportionally with N loading, which needs to be considered when evaluating management scenarios.

2.2 Introduction

2.2.1 Coastal water eutrophication

Eutrophication of coastal waters is an important problem that can result in degradation of water quality, hypoxia, fish kills and harmful algal blooms (HABs). A recent global survey of coastal areas found that 762 systems are eutrophic, of which 479 are experiencing hypoxia (Diaz and Rosenberg 2008; Rabalais, Díaz et al. 2010). For example, the continental shelf along the northern Gulf of Mexico has become the second largest coastal hypoxic zone in the world (“The Dead Zone”) (Rabalais, Turner et al. 2002b). On the eastern U.S. coast, hypoxia in Chesapeake Bay has been a recurring issue for decades (Murphy, Kemp et al. 2011). The economic impacts of coastal HABs in the U.S. are at least $82 million/year, of which public health costs of illnesses are $37 million/year (Hoagland and Scatasta 2006).

Nitrogen is generally believed to be the limiting nutrient for primary production in estuarine and coastal systems, and an increase of N input is considered to be the main cause of eutrophication. Thus, “The Dead Zone” is believed to be caused by an increase of N loading from the Mississippi River (Alexander, Smith et al. 2000; Rabalais, Turner et al. 2002a; Scavia and Donnelly 2007; Scavia, Evans et al. 2013). Similarly, the hypoxia in Chesapeake Bay has a positive correlation with the N loading (Hagy, Boynton et al. 2004). Management actions therefore focus on reducing N export from watersheds
(Heathwaite, Sharpley et al. 2000). The N cycle of watersheds is complex, but to evaluate management scenarios, simple models are needed that can be applied at the watershed scale given the available data. In lakes and reservoirs, N can be lost by sedimentation/burial and denitrification and gained by fixation of atmospheric N, which may constitute a significant source and/or sink in the watershed N budget (Horne and Goldman 1972; Harrison, Maranger et al. 2009). For example, N loads from the Missouri River Basin are 16% lower due to loss in lakes and reservoirs (Brown, Sprague et al. 2011). This source/sink needs to be accounted for when estimating/modeling N export from the watershed to the coastal area. The focus of this paper is on modelling the relationship between N loading and export to/from lakes and reservoirs in simple watershed models used to estimate N input to coastal systems.

2.2.2 Existing simple models

A number of simple models have been developed and used to evaluate management actions at the watershed scale. SPARROW (Spatially Referenced Regression on Watershed Attributes) predicts nutrient point and nonpoint source loading to and transport and loss in the stream and lake/reservoir network. For lakes and reservoirs, SPARROW assumes N is removed in a first-order fashion using a net loss rate or apparent settling velocity, which accounts for loss by sedimentation and denitrification and gain by N fixation (Alexander, Elliott et al. 2002; Schwarz, Hoos et al. 2006; Alexander, Smith et al. 2007; Preston, Alexander et al. 2011a). Consequently, a constant fraction is exported for a given system. This model has been applied to estimate N loading from the Mississippi River Basin to the Gulf of Mexico (Goolsby and Battaglin 2000; Alexander, Smith et al. 2007; Robertson, Saad et al. 2014) and from the Waikato
River Basin, New Zealand to the Tasmanian Sea (Alexander, Elliott et al. 2002). A number of applications to major regions in the U.S. are also available (Preston, Alexander et al. 2011b). A similar empirical regression model (RivR-N) was developed to predict N removal in streams and reservoirs and has been applied to watersheds in the northeastern U.S. That model also assumes that the fraction of N removed is constant for each lake/reservoir (Seitzinger, Styles et al. 2002). A summary of existing simple lake/reservoir N export models is provided in Table 2.1. The last column in the table shows the reduction in N export predicted for a 50% reduction in loading. Three of the models assume that the fraction of N exported does not change with N loading and the N export reduces by 50%. The empirical models by Fleischer, Gustafson et al. (1994) and Tomaszek and Koszelnik (2003) predict that the export fraction changes with the loading, but the effect is small and opposite to what would be expected considering N fixation (see below).
Table 2.1. Summary of simple lake/reservoir N export models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>$E_{50}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) SPARROW (Alexander, Elliott et al. 2002)</td>
<td>$Re = \frac{1}{1 + v_s(q_s)^{-1}}$</td>
<td>50</td>
</tr>
<tr>
<td>(2) RivR-N (Seitzinger, Styles et al. 2002)</td>
<td>$Re = 1 - 88.45 \times (q_s)^{-0.3677}$</td>
<td>50</td>
</tr>
<tr>
<td>(3) Tomaszek and Koszelnik (2003)</td>
<td>$Re = 1 - (1 + \tau_w)^{-0.957} \times W_{N,load}'^{(-0.043)}$</td>
<td>52</td>
</tr>
<tr>
<td>(4) Fleischer, et al. (Fleischer, Gustafson et al. 1994)</td>
<td>$Re = 1 - 10^{(0.069 \times (\log W_{N,load}')}^2 - 0.33 \times (\log W_{N,load}') - 0.60$</td>
<td>52</td>
</tr>
<tr>
<td>(5) NiRReLa (Harrison, Maranger et al. 2009)</td>
<td>$Re = \exp \frac{-v_s}{q_s}$</td>
<td>50</td>
</tr>
<tr>
<td>(6) FENL (this study)</td>
<td>$Re = \frac{q_s}{q_s + v_s}$ if $W_{N,load} \geq W_P r_f$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>= $\frac{q_s}{q_s + v_s} \frac{W_P}{W_{N,load}'} r_f$ if $W_{N,load} &lt; W_P r_f$</td>
<td></td>
</tr>
</tbody>
</table>

$E_{50}$ is the predicted reduction in N export for a reduction in N loading by 50%. The equations were algebraically modified and variable names changed to facilitate comparison. $Re$ is the fraction of N export to N loading, $q_s$ is the areal hydraulic loading ($q_s = \frac{H}{\tau_w} = \frac{Q}{A_s}$, m yr$^{-1}$), $v_s$ is the apparent settling velocity (m yr$^{-1}$), $W_{N,load}$, $W_P$ are N and P loading (kg yr$^{-1}$), $W_{N,load}' = \frac{W_{N,load}}{A_s}$ is the areal N loading (g N m$^{-2}$ d$^{-1}$). Equation (3) is derived from equations (3) and (4) in reference applied to long term (larger n). The $E_{50}$ is the average value calculated from the two reservoirs in the reference. In equation (4), $E_{50}$ is calculated from the average of data in Fig. 7 in the reference.
2.2.3 N fixation

If the fraction of N removed in lakes/reservoirs is constant, N export will be reduced proportionally with N loading (we use “loading” to mean all inputs except N fixation, which may include point sources, runoff, groundwater, atmospheric deposition and others). However, reducing N loading without also reducing P loading will lower the N/P ratio, which may favor cyanobacteria that can fix N from the atmosphere. N fixation can contribute significantly to the N budget in lakes. For example, Horne and Goldman (1972) estimated that the annual N fixation in Clear Lake was about 43% of the annual N input. The authors also point to the significance of this source of N to the watershed and downstream San Francisco Bay. From 1970 to 1992, N fixation contributes variably and up to 52% of N input to Lake 227 in the Experimental Lakes Area (ELA) (Findlay, Hecky et al. 1994).

The amount of N fixation is believed to be related to the N/P balance. Hellström (1996) analyzed data from 40 northern temperate lakes and found that for most lakes N fixation effectively balances N with P so that the N/P concentration ratio is about 10-15 (total N and P, by weight (i.e. mg / L) is used throughout this paper). Flett, Schindler et al. (1980) estimated that N fixation occurred in Shield lakes when the N/P loading ratio is less than about 10. Howarth, Marino et al. (1988a) summarized data for a number of lakes and concludes that N fixation occurs in lakes with N/P loading ratio less than approximately 8.1.

When N loading is reduced without also reducing P, cyanobacteria and N fixation may increase (Schindler 1977). For example, Lake 227 was fertilized with nutrients and monitored for 37 years. P input was held constant, but N fertilizer input was reduced 2
times during the experiment by 64% and 100% (no fertilizer N input). However, after 20 years without adding any N fertilizer (an 80% reduction in total N loading), the N concentration in the lake was only reduced by 30% (Schindler, Hecky et al. 2008). A mesocosm experiment conducted by Vrede et al. in Lake Limmaren (Vrede, Ballantyne et al. 2009) showed that reducing the N input (without P reduction) can increase N fixing cyanobacteria and N fixation, but not the N concentration. The authors argue that, because of this mechanism, reducing the N load without reducing P will not reduce N export to coastal waters.

2.2.4 Overview of research

Our aim here is to present a simple model that explicitly accounts for N fixation in lakes and reservoirs. The model, called Fixation and Export of Nitrogen from Lakes (FENL), is based on a steady-state mass balance of N in a lake, with loading (all inputs except fixation) and N fixation input, outflow and in-lake loss (e.g. denitrification, sediment bed retention). An important question is how much N will be fixed when N loading is reduced? One view is that lake primary production is ultimately limited by P, a common assumption for freshwater systems, and that sufficient N is fixed to balance the N pool (Schindler 2012). Another view is that production is not simply limited by P but also N and that N fixation may not balance the N pool (Paerl 2009; Scott and McCarthy 2010; Paerl, Xu et al. 2011b). This issue is the subject of considerable debate, which will undoubtedly continue for some time. Unfortunately, management decisions have to be made with imperfect knowledge and from that perspective, the assumption of P limitation can be considered a “worst case” scenario. The FENL model thus assumes that lake
primary production is ultimately limited by P and that sufficient N is fixed so that the ratio of total N input (loading + fixation) to total P input is at a threshold value.

The FENL model is parameterized and tested using microcosm laboratory experiments, lake field observations/budgets and lake ecosystem model applications. Nitrogen fixation in lakes has been the subject of a lot of research and a large database of observations (microcosm, mesocosm, whole lake) and models are available and have been analyzed extensively (some of this research is reviewed above). However, most of these studies have focused on general relationships across lake/reservoir systems and not on the effect of reducing N loading. Here we focus on the relationship between N input/output as N loading is reduced and many of the existing studies are therefore of limited use. For that purpose we perform new lab experiments and use a smaller, selected database of literature observations. The microcosm lab experiments were done with different types of water and phytoplankton assemblages. Reactors were started with different N/P ratios and monitored for up to three weeks. Lake field observations/budgets were based on published literature or provided by lake associations for lakes with different N loading. Lake ecosystem model applications were based on existing applications from the AQUATOX sample library (Park and Clough 2010), which were run with different N loading. Thus, our simple model is compared to results from a more complex ecosystem model, which explicitly resolves the processes underlying phytoplankton ecology and N fixation, and presumably adequately reflects how the system would change under reduced N loading. Our results suggest that N export will not be reduced proportionally with N loading. Accounting for N fixation will improve the accuracy of models and their utility in evaluating management options.
2.3 Approaches and Model Development

2.3.1 Microcosm lab experiments

**Strains and media.** *Anabaena flos-aquae* (UTEX B1444) and *Microcystis sp.* (UTEX B2668) cyanobacteria were purchased from UTEX. Natural phytoplankton assemblages were obtained from the Charles River in Boston, Massachusetts. Water was sampled from the Esplanade Dock and filtered through a 70 µm mesh net to remove zooplankton. Experiments were performed in three different media, including modified BG-11, and autoclaved and 0.45 µm membrane filtered Charles River water. Additional nutrients (nitrogen as NaNO₃ and phosphorus as K₂HPO₄) were added to create initial conditions with different N/P ratios and concentrations. Experiments are summarized in Table S1.

**Reactor set-up.** 200 ml of water was contained in 250 ml Pyrex flat bottom round flasks/Erlenmeyer flasks covered with cotton swabs to allow gas exchange. The reactors were kept under constant and continuous cool-white (2 of 34 W) and gro-lux fluorescent (2 of 40 W) at room temperature (20°C), and shaken at 200 rpm on an Excella E2 open air platform shaker. Cells were inoculated (10 µL of grow-up culture for *A. flos-aquae* and *Microcystis sp.*, 20 mL of filtered Charles River water for natural assemblage) and after 10 minutes of mixing the initial samples were taken and analyzed. Reactors were then sampled on a two-day or weekly basis for up to three weeks.
Reactor set-up

**Nutrient analyses.** Nutrient concentrations were measured following standard methods (1999). Persulfate digestion was used for both TN and TP (EWWSM, 1999). Stannous chloride color method was used to develop colors of P samples. Spectrophotometer (HACH DR 2700) and IC (DIONEX DC ICS 5000) attached to an automatic sampler were used to determine the concentration of P and N, respectively.

**Chlorophyll a measurement.** Phytoplankton biomass was quantified as chlorophyll a (chl. A). Samples were stored in 1.2 ml Costar 8 strip tubes in the dark and frozen after sampling and thawed right before analysis. For the extraction of chl. A, 200 µl of 90% ethanol was added to 50 µl of algal samples and chl. A standards, shaken in dark for 3 hours, then measured with a BioTex microplate reader (Synergy HT), with excitation at wavelength 410 nm and emission at wavelength 670 nm (Aruoja, Kurvet et al. 2004; Gregor and Maršálek 2004).
**Microscopic observations.** A 3.0 MP Tucsen camera installed on a microscope (Galen III) was used to determine phytoplankton species and the occurrence of heterocysts (N fixing cells). 1 ml of preserved sample (Lugol’s iodine solution) was placed on a Sedgewick-Rafter chamber with cover slide. After allowing the cells to settle for 15 minutes, species and heterocyst were identified visually under the microscope.

**Nitrogen fixation via acetylene reduction assay.** Nitrogenase activity was evaluated with acetylene reduction assay by measuring the amount of C₂H₄ yielded. The relationship of mole C₂H₄ yielded per mole N₂ fixed is 4:1. 5 ml of samples were taken and added to a 10-mL gastight serum bottles, immediately injected with 1 mL of acetylene (≥ 99.5% purity, Dirigo Tech., ME) addition to the headspace. Overpressurization was relieved by pricking the rubber septa with a needle to release the excess gas (Capone 1993). The final concentration of C₂H₂ was approximately 20% (v/ v). Samples were incubated and shaken at 20 °C under light for 4 h (Findlay, Hecky et al. 1994) and terminated by an addition of 1N NaOH. The concentration of ethylene (C₂H₄) was measured with SRI 8610C Gas Chromatograph (GC) equipped with flame ionization detection (FID) (Restek Corp). 1 ml of the gas in the head space was injected in to GC and the amount of C₂H₄ was measured. To calculate the N fixation, 4 moles of C₂H₂ reduced/C₂H₄ yielded is equivalent to 1mole of N₂ fixed.

2.3.2 Lake field observations/budgets

The FENL model is compared to lake field observations/budgets from the literature or provided by lake associations. Consistent with the purpose of the model (i.e. evaluate response as N loading is lowered), we thought out systems with historically substantially
variable N loading. Specifically, systems were selected based on two criteria. (1) The database needs to contain multiple years of data (N loading, output and P loading). (2) The difference between the highest and lowest N loading should be at least 20%. Based on these criteria, 5 lakes were selected (Table 2.2 and Table S2.2).

2.3.3 Lake ecosystem model applications

The FENL model is also compared to results from a lake ecosystem model. The assumption is that such a more complex (vs. FENL) ecosystem model, which explicitly resolves the underlying processes, can adequately predict how a lake/reservoir would respond when N loading is reduced. Numerous operational, peer-reviewed and widely-used lake models are available (e.g. WASP, CE-QUAL, AQUATOX). We selected the EPA AQUATOX (Park and Clough 2010) model, because it includes N fixation and a number of applications (i.e. model set up for specific lakes) are available in the sample database distributed with the model. AQUATOX is a surface water ecosystem model that simulates nutrients and phytoplankton, including cyanobacteria and their N fixation. The growth rate of cyanobacteria is not limited by the available fixed nitrogen. There are two conditions that determine if N fixation occurs. Fixation happens when the concentration of available dissolved nitrogen is less than 1/2 of the half-saturation constant for N (0.4 mg/L by default), which is a parameter in the model. Alternatively, fixation occurs when the ratio of N/P falls below a threshold (7 by default).

Specific systems were selected from the EPA AQUATOX (Park and Clough 2010) sample library, which includes eight lakes/reservoirs, all of which include nutrients and phytoplankton. Two systems were excluded because they were deemed unsuitable for our
study. Evers Reservoir was not included because the N loading is mostly in the form of detritus with a fixed N/P ratio, so the N loading cannot be adjusted independently from the P loading. Clear Lake was also excluded because the N budget was not realistic (R.A. Park, personal communication). Characteristics of the applications are listed in Table S2.3. AQUATOX was run with variable N loading (e.g. x0.5) by adjusting inorganic N loading and initial concentration of N (e.g. x0.5).

### 2.4 FENL Model

The FENL model is based on a mass balance of N on a lake, with inflow, outflow and retention/loss processes. In addition, and this is how the model differs from the existing ones (Table 2.1), we explicitly consider N fixation and assume that sufficient N is fixed so that the ratio of total N input (loading + fixation) to total P input is at a threshold value \( r_f \) (Figure 2.2a). When the N/P ratio of the input is greater than \( r_f \), there is no N fixation. When the N/P ratio of the input is less than \( r_f \), sufficient N is fixed to raise the N/P ratio of the input to \( r_f \).

The N mass balance is:

\[
V \frac{dC_N}{dt} = W_{N,\text{load}} + W_{N,\text{fix}} - QC_N - v_s A_s C_N
\]  
(1)

Where \( V \) (\( m^3 \)) is the volume, \( C_N \) (kg/m\(^3\)) is the in-lake N concentration, \( Q \) (\( m^3/yr \)) is the flow rate, \( v_s \) (m/yr) is the apparent settling velocity (accounts for sedimentation and denitrification) and \( A_s \) (\( m^2 \)) is the surface area.
Figure 2.1. Model of N input/export to/from lakes and reservoirs, including N fixation: (a) Model schematic showing N mass balance terms. (b) Model behavior under different N loadings. Effective N export fraction vs. normalized N loading.

The total N input consists of two parts, N loading ($W_{N,\text{load}}, kg/yr$) and N fixation ($W_{N,\text{fix}}, kg/yr$). N fixation is a function of the N/P ratio of the loading. When $W_{N,\text{load}} \geq W_{P}r_{f}$, there is no N fixation, thus $W_{N,\text{fix}} = 0$. When $W_{N,\text{load}} < W_{P}r_{f}$, it is the difference of total N input and N loading.
\[ W_{N,fx} = 0 \quad \text{if } W_{N,\text{load}} \geq W_P r_f \]  
\[ = W_P r_f - W_{N,\text{load}} \quad \text{if } W_{N,\text{load}} < W_P r_f \]  

The ratio of N export to N loading, which we refer to as effective export fraction, is:

\[ Re = \frac{QC_N}{W_{N,\text{load}}} \]  

Equations (1) – (3) can be combined, at steady state, with areal hydraulic loading,

\[ q_s = \frac{q}{A_s} \]  

and solved for \( Re \).

\[ Re = \frac{q_s}{q_s + v_s} \quad \text{if } W_{N,\text{load}} \geq W_P r_f \]  
\[ = \frac{q_s W_P}{q_s + v_s W_{N,\text{load}}} r_f \quad \text{if } W_{N,\text{load}} < W_P r_f \]  

For the case of no N fixation, the FENL model is equivalent to the SPARROW lake model (Schwarz, Hoos et al. 2006). In contrast to the existing simple models (Table 2.1), the FENL model predicts a non-linear relationship between the N loading and export, or a changing effective export fraction with N loading (Figure 2.2b). The effective N export fraction on the y-axis is the export divided by the loading. The N loading on the x-axis is normalized to the threshold input \( (W_P r_f) \). The vertical dashed line is when N/P ratio of the loading equals \( r_f \). When N/P loading ratio is greater than \( r_f \), there is no N fixation, total N input is only from the N loading, and the fraction of N exported is constant. When N/P loading ratio is less than \( r_f \), cyanobacteria fix N and the fixed N contributes to total N loading. Under this condition, the effective N export fraction is not constant and varies
as a fraction of N loading. Reducing N loading without also reducing P would move a system towards the left on this graph.

2.5 Results

2.5.1 Microcosm lab experiments

In the experiments with *Anabaena flos-aquae* or natural assemblages, at high initial N/P the N concentration remained relatively constant. At low initial N/P ratio, the N concentration increased. These experimental results are similar to those of Vrede et al. (Vrede, Ballantyne et al. 2009). For example, in the experiment with natural assemblage in autoclaved Charles River water (Figure 2.2a), only the reactors with the lower initial N/P ratio showed an increase of N concentration. A number of cyanobacteria species were found in the reactors after several days (i.e., *Aphanizomenon* and *Anabaena* with heterocysts, *Oscillatoria* and other non-N fixing species). In the experiments with *A. flos-aquae* in modified BG-11, the N fixation rate was measured with a maximum value of 0.48 mg/L/hr (Figure S2.1d), and abundant heterocysts were observed under the microscope. In the experiments with *Microcystis sp*, which does not fix N, there is no change in the N concentration. Full results are presented in Figures S2.1-S2.8.

2.5.2 Lake field observations/budgets

For most systems, for years with higher N loading, the effective N export fraction is relative constant, but for lower N loading, we observed that the effective N export fractions increased. For example, Figure 2.2b presents a time series of relevant
observations for Lake 227. This lake was fertilized variably with N and P and monitored
over 30 years. The P loading remained relative constant throughout the years. When the
N fertilizer loading was reduced in 1975, the N export was not reduced proportionally,
and the effective N export fraction increased slightly. In 1990, the N fertilizer input was
terminated. From 1990 to 1992, the N export was not reduced but increased, and the
effective N export fraction almost doubled during the three years. Similar results are
found for three out of five systems. However, for Gr. Mueggelsee and Harp Lake, for the
available data, the effective export fraction is relatively constant (which can be explained
by the relatively high N loading, see Section 5.1). Full results are presented in Figures
S2.9-S2.13.

2.5.3 Lake ecosystem model (AQUATOX) applications

Results for the lake ecosystem model (AQUATOX) applications show a similar
pattern. For example, Figure 2.2c shows the results of four simulations of Onondaga Lake
with different N loading. AQUATOX predicts that, as the N loading is reduced, the N
export reduces, but not proportionally. Consequently, the effective N export fraction
increases. This can be explained by a change in N fixation, which contributes 0% and 12%
of the total N input for loading ratios 2.0 and 0.1, respectively. Similar results were
observed in three out of six systems. For Lake George, the effective export fraction
increases at lower N loading, as expected from the FENL model. However, in this case
this is not the result of N fixation, but a change in phytoplankton species with different
properties (e.g. biomass N content). Full results are presented in Figures S2.14-S2.19.
Figure 2.2. Example results from the three approaches. (a) Microcosm lab experiment. Natural assemblage in autoclaved Charles River water. Time series of N concentration. Each line represents the average of two experiments. (b) Lake field observations/budgets. Lake 227, annual results. (c) Lake ecosystem model applications. Onondaga Lake application with variable N loading.
2.5.4 Estimation of $r_f$ parameter

The only new parameter introduced in the FENL model is the N/P threshold ($r_f$), which needs to be estimated in order to apply the model. We estimate $r_f$ based on the results of the three approaches (microcosm lab experiments, lake field observations/budgets and lake ecosystem model applications). Specifically, we use the FENL model to calculate the effective N export fraction ($Re$) and compare it to the observed $Re$. We calculate the root mean square error (RMSE), and optimize $r_f$ and $v_s$ for each system to minimize the RMSE using a numerical optimization routine (MS Excel Solver). The resulting values for the two parameters are listed in Table 2.2. The results suggest $r_f$ values ranging from 1.62 – 20.65 with a mean of 9.90. Five systems (see Table 2.2, Fig. S2.10, S2.13, S2.15, S2.16 and S2.18) did not show evidence for N fixation for the years included and they are omitted from these statistics. The average $r_f$ value is relatively close to the Redfield ratio (7.2) and N/P threshold ratios for N fixation found by others, including the loading ratios of Flett et al. (Flett, Schindler et al. 1980) (<10) and Howarth et al. (Howarth, Marino et al. 1988a) (8.1) and the in-lake concentration ratio of Hellström (1996) (10-15). The system-to-system variability in $r_f$ values is substantial. It is not uncommon to see differences in the relationship between N/P and N fixation. For example, Howarth et al. (Howarth, Marino et al. 1988a) reviewed a number of lakes. ELA Lake 261 did not have any N fixation at $r_f = 5.0$, whereas Lake Superior had N fixation at $r_f = 27$. This variability points to a need for better understanding of the factors controlling N fixation. From a management perspective, the error introduced by this variability should decrease as the number of systems increases (i.e. as the watershed size goes up), but it should be considered when applying the model.
Table 2.2. Model parameters, RMSEs for FENL (this study) and SPARROW

<table>
<thead>
<tr>
<th>System</th>
<th>FENL</th>
<th>SPARROW</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r_f$</td>
<td>$v_s$ (m/yr)</td>
<td>RMSE</td>
<td>$v_s$ (m/yr)</td>
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<td><strong>Microcosm lab experiments</strong></td>
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<td>Onondaga Lake</td>
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<td>Overall average</td>
<td>9.90</td>
<td>0.29</td>
<td>13.32</td>
<td>1.31</td>
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</table>

* Systems did not show evidence of N fixation for years included. Value not included in overall average.
2.6 Discussion

2.6.1 Comparison of FENL model to data and AQUATOX

The results of all three approaches (microcosm lab experiments, lake field observations/budgets and lake ecosystem model applications) are summarized along with the FENL model in Figure 2.3, which shows the normalized effective N export fraction vs. normalized N loading. The effective N export fraction is normalized by the mean fraction when $W_{N,\text{load}} \geq W_p r_f$ (or by the minimum fraction when there are no data with $W_{N,\text{load}} \geq W_p r_f$). This is done to eliminate differences between systems in effective N export fraction that are due to differences in loss processes (i.e. $q_s / q_s + v_s$ term in Eq. 4). The N loading is normalized to $W_p r_f$ to eliminate differences in absolute loading (i.e. system size). With these normalizations, the FENL model can be presented as a single line. Taken together, the results show that the effective N export fraction is not constant, but that it increases as N loading is reduced. Most systems showed this pattern. For the systems with relatively constant export fraction (e.g. Harp Lake, as discussed above), the FENL model reproduces this behavior because the N loading is greater than $W_p r_f$. Full results are presented in Figures S2.20-S2.36.
2.6.2 Comparison of FENL to SPARROW

We compare FENL model to the SPARROW lake model. For that, we optimized the SPARROW $v_s$ for each system to minimize the RMSE as we did for FENL (see Table 2.2). The overall RMSE is 0.29 for FENL, and 1.31 for SPARROW. The individual RMSE results showed that when there is no evidence of N fixation, the two
models performed equally well (e.g. Gr. Mueggelsee, Coralville Res.). However, when N fixation occurs, FENL shows a better agreement with the observations. Full results are presented in Figures S2.37-S2.39.

To understand the significance of this difference in a management context, we predict the reduction in N export achieved for a reduction in N loading using both models. For this analysis we use the lake observations/budgets and lake ecosystem model applications included in this study. We reduce the N loading for each system by 50% from the average loading. These results are only applicable to this set of systems and can not be assumed to apply to others. We first explored a 50% reduction of N loading. SPARROW predicts a 50% reduction in N export for all systems. FENL predicts a reduction of 32% (FENL results are presented as average across the 11 systems, see Table S2.4). We then explore how much reduction in loading is needed to achieve a 50% reduction in export. For some systems, a 50% reduction cannot be attained by reducing N loading. This is because once the N loading is below the threshold, the export is a function of P loading and independent of N loading. FENL predicts that the maximum N export reduction achievable by reducing N loading alone (i.e. 100% N loading reduction) is 45% (average across systems). We then explore a balanced nutrient loading reduction. FENL predicts that when both N and P loadings are reduced by any amount (e.g. 50%, see Table S2.4), the N export is reduced by the same amount. This can be attributed to reduced N loading for systems that are above the threshold and reduced P loading for systems that are below the threshold. Therefore, a dual nutrient management strategy may be needed to significantly reduce N export from watersheds.
As pointed out in the Introduction, the FENL model assumes P limitation and that sufficient N is fixed to balance the N pool, which is the subject to considerable debate in the literature (Paerl 2009; Scott and McCarthy 2010; Paerl, Xu et al. 2011b; Schindler 2012). From a management perspective, this assumption and FENL constitutes a “worst case” scenario. At the opposite end of the spectrum, assuming no increase of N-fixation as N loading is reduced, as is inherent in SPARROW and other existing models, is a “best case” scenario. We can expect the real response to be somewhere in between these extremes.

### 2.7 Summary and Outlook

We presented a simple model for N input/output to/from lakes and reservoirs, and parameterized it using three different approaches. Our results suggest that N export will not be reduced proportionally when reducing N loading. The next natural step is to explore the significance of this process in the context of the watershed N budget and export to downstream coastal systems. The FENL model is simple enough to be applied at the watershed scale, possibly by modifying the full SPARROW model (incl. other watershed components), to predict N export under N loading reduction management scenarios.
## 2.8 Supporting material

Table S 2.1. Microcosm lab experiments: Experimental set-up

<table>
<thead>
<tr>
<th>Reactor ID</th>
<th>Reactor Media</th>
<th>Strain</th>
<th>N/P Loading ratio $^e$</th>
<th>Sampling frequency</th>
<th>Number of reactors</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ana. Mod.</td>
<td>Modified BG-11 $^a$</td>
<td>$A. flos-aquae$</td>
<td>0, 1, 2, 3, 4, 5, 6, 7, 8, 9 &amp; 10</td>
<td>11 days</td>
<td>11×1</td>
<td>TN, TP, Chl a, N fixation</td>
</tr>
<tr>
<td>Ana. Mod.</td>
<td>Modified BG-11 $^a$</td>
<td>$A. flos-aquae$</td>
<td>3.6, 5.4, 7.2, 9, 10.8, 12.6</td>
<td>Weekly, for 2 weeks</td>
<td>6×2 $^b$</td>
<td>TN, TP, Chl a</td>
</tr>
<tr>
<td>Mic. Mod.</td>
<td>Modified BG-11</td>
<td>$Microcystis$</td>
<td>0, 3.6, 7.2, 14.4</td>
<td></td>
<td>4×2 $^b$</td>
<td></td>
</tr>
<tr>
<td>Ana. Auto.</td>
<td>Autoclaved Charles</td>
<td>$A. flos-aquae$</td>
<td>3.6, 5.4, 7.2, 9, 10.8, 12.6</td>
<td>Weekly, for 2 weeks</td>
<td>6×2</td>
<td>TN, TP, Chl a</td>
</tr>
<tr>
<td>Mic. Auto.</td>
<td>Autoclaved Charles</td>
<td>$Microcystis$</td>
<td>min. 3.6, 7.2, 14.4</td>
<td></td>
<td>4×2</td>
<td></td>
</tr>
<tr>
<td>Nat. Natural</td>
<td>Natural Charles $^c$</td>
<td>Natural</td>
<td>min. 3.6, 7.2, 10.8</td>
<td>Weekly, for 2 weeks</td>
<td>4×2</td>
<td>TN, TP, Chl a</td>
</tr>
<tr>
<td>Nat. Natural</td>
<td>Natural Charles $^c$</td>
<td>Natural</td>
<td>0, 3.6, 7.2, 10.8</td>
<td>Weekly, for 2 weeks</td>
<td>4×2</td>
<td>TN, TP, Chl a</td>
</tr>
</tbody>
</table>

Volume of each reactor is 200 ml, and TP concentration is 1 mg/L.

$a$ BG-11 media with modified N, P concentrations

$b$ Autoclaved Charles River water, initial TN = 1.56 mg/L

$c$ Natural Charles River water, initial TN = 1.21 mg/L

$d$ Charles River natural assemblage $e$ Different ratio of nutrients loading by variable N loading

$^e$ Number of reactors 11×1, 6×2 and 4×2 represent number of different N loading × replicates
Table S 2.2. Lake field observations/budgets: Site characteristics

<table>
<thead>
<tr>
<th>System</th>
<th>Years</th>
<th>Area (m²)</th>
<th>Total discharge (m³/yr)</th>
<th>Hydraulic load (m/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr. Mueggelsee</td>
<td>1978-84</td>
<td>7,200,000</td>
<td>265,533,120</td>
<td>36.88</td>
</tr>
<tr>
<td>Harp Lake</td>
<td>1978-2001</td>
<td>713,800</td>
<td>31,536</td>
<td>0.04</td>
</tr>
<tr>
<td>Lake 227</td>
<td>1970-92</td>
<td>50,000</td>
<td>1,261,440</td>
<td>25.23</td>
</tr>
<tr>
<td>Lake Kinneret</td>
<td>1992-2009</td>
<td>167,000,000</td>
<td>500,000,000</td>
<td>2.99</td>
</tr>
<tr>
<td>Impound. Rietvlei</td>
<td>1976-1977</td>
<td>1477500</td>
<td>270000000</td>
<td>18.45</td>
</tr>
</tbody>
</table>

Table S 2.3. AQUATOX applications: Site characteristics

<table>
<thead>
<tr>
<th>System</th>
<th>Years</th>
<th>Area (m²)</th>
<th>Total discharge (m³/yr)</th>
<th>Hydraulic load (m/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coralville Res</td>
<td>1969-1978</td>
<td>19,825,400</td>
<td>17,486,353,299</td>
<td>882.02</td>
</tr>
<tr>
<td>Cheney Res</td>
<td>1999-2000</td>
<td>40,000,000</td>
<td>93,839,208</td>
<td>2.35</td>
</tr>
<tr>
<td>Lake George</td>
<td>1971-1973</td>
<td>23,380,000</td>
<td>111,257,158</td>
<td>4.76</td>
</tr>
<tr>
<td>Lake Jesup</td>
<td>1996-2002</td>
<td>32,000,000</td>
<td>788,753,657</td>
<td>24.65</td>
</tr>
<tr>
<td>Lake Pyhjarvi</td>
<td>1992-1993</td>
<td>154,000,000</td>
<td>357,501,597</td>
<td>2.32</td>
</tr>
<tr>
<td>Onondaga lake</td>
<td>1989-1990</td>
<td>12,000,000</td>
<td>938,204,448</td>
<td>78.18</td>
</tr>
</tbody>
</table>
Table S 2.4. Reduction in N export by reducing N loading alone, and both N&P loading

<table>
<thead>
<tr>
<th>Lake/ Reservoir</th>
<th>N export reduction</th>
<th>50% reduction in N loading</th>
<th>100% reduction in N loading</th>
<th>50% reduction in N &amp; P loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impound. Rietvlei</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Gr. Mueggelsee</td>
<td>36</td>
<td>36</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Harp Lake</td>
<td>31</td>
<td>32</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Lake 227</td>
<td>3</td>
<td>3</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Lake Kinneret</td>
<td>41</td>
<td>49</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Coralville Res</td>
<td>50</td>
<td>74</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Cheney Res</td>
<td>36</td>
<td>36</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Lake George</td>
<td>50</td>
<td>81</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Lake Jesup</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Lake Pyhajarvi</td>
<td>50</td>
<td>98</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Onondaga lake</td>
<td>50</td>
<td>87</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>32</td>
<td>45</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
Figure S 2.1. Microcosm lab experiments. *A. flos-aquae* in modified BG-11 a
Figure S.2. Microcosm lab experiments. *A. flos-aquae* in modified BG-11 b
Figure S 2.3. Microcosm lab experiments. *A. flos-aquae* in autoclaved Charles River water.
Figure S 2.4. Microcosm lab experiments. Natural assemblage in natural Charles River water
Figure S 2.5. Microcosm lab experiments. Natural assemblage in autoclaved Charles River water.
Figure S 2.6. Microcosm lab experiments. Natural assemblage in modified BG-11
Figure S 2.7. Microcosm lab experiments. *Microcystis sp.* in modified BG-11
Figure S 2.8. Microcosm lab experiments. *Microcystis sp.* in autoclaved Charles River water
Figure S 2.9. Lake field observations/budgets. Impoundment Rietvlei
Figure S 2.10. Lake field observations/budgets. Gr. Mueggelsee
Figure S 2.11. Lake field observations/budgets. Lake 227
Figure S 2.12. Lake field observations/budgets. Lake Kinneret
Figure S 2.13. Lake field observations/budgets. Harp Lake
Figure S 2.14. AQUATOX applications. Cheney Res.
Figure S 2.15. AQUATOX applications. Coralville Res.
Figure S 2.16. AQUATOX applications. Lake George
Figure S 2.17. AQUATOX applications.Lake Jesup
Figure S 2.18. AQUATOX applications. Lake Pyhajarvi
Figure S 2.19. AQUATOX applications. Onondaga Lake

Onondaga Lake

P loading (10^6 kg/yr)

0
0.05
0.1
0.15
0.2

N loading (10^6 kg/yr)

0
0.05
0.1
0.15
0.2

N export (10^6 kg/yr)

0
0.05
0.1
0.15
0.2

Effective N export fraction

0
0.2
0.4
0.6
0.8

N loading ratio to baseline

2.0
1.5
1.0
0.5
0.0
Figure S 2.20. Comparison of FENL to microcosm lab experiments. *A.flos-aquae* in modified BG-11 a
Figure S 2.21. Comparison of FENL to microcosm lab experiments. *A.flos-aquae* in modified BG-11 b.
Figure S 2.22. Comparison of FENL to microcosm lab experiments. *A.flos-aquae* in autoclaved Charles River water
Figure S 2.23. Comparison of FENL to microcosm lab experiments. Natural assemblage in natural Charles River water
Figure S 2.24. Comparison of FENL to microcosm lab experiments. Natural assemblage in autoclaved Charles River water.
Figure S 2.25. Comparison of FENL to microcosm lab experiments. Natural assemblage in modified BG-11
Figure S 2.26. Comparison of FENL to lake field observations/budgets. Impoundment Rietvlei
Figure S 2.27. Comparison of FENL to lake field observations/budgets. Gr. Mueggelsee
Figure S 2.28. Comparison of FENL to lake field observations/budgets. Lake 227
Figure S 2.29. Comparison of FENL to lake field observations/budgets. Lake Kinneret
Figure S 2.30. Comparison of FENL to lake field observations/budgets. Harp Lake

NPt = 34.45
vs = 2.73

Effective N export fraction

Normalized N loading

Lake Harp obs.
FENL
SPARROW

External N input = NNPt

Effective N export fraction

Normalized N loading

Lake Harp obs.
FENL
SPARROW

Effective N export fraction

Normalized N loading

Lake Harp obs.
FENL
SPARROW

Effective N export fraction

Normalized N loading

Lake Harp obs.
FENL
SPARROW

Effective N export fraction

Normalized N loading

Lake Harp obs.
FENL
SPARROW

Effective N export fraction

Normalized N loading

Lake Harp obs.
FENL
SPARROW
Figure S 2.31. Comparison of FENL to AQUATOX applications. Cheney Res.
Figure S 2.32. Comparison of FENL to AQUATOX applications. Coralville Res.
Figure S 2.33. Comparison of FENL to AQUATOX applications. Lake George
Figure S 2.34. Comparison of FENL to AQUATOX applications. Lake Jesup

Lake Jesup model

External N input = NNPt

FENL

SPARROW

NPt = 7.242

vs = 6.376

Normalized effective N export fraction

Normalized N loading

Effective N export fraction

Effective N export fraction

Normalized N loading

Normalized effective N export fraction

Normalized N loading
Figure S 2.35. Comparison of FENL to AQUATOX applications. Lake Pyhajarvi
Figure S 2.36. Comparison of FENL to AQUATOX applications. Onondaga Lake
Figure S 2.37. FENL and SPARROW models comparison for microcosm lab experiments. Dashed lines are 1:1 indicating perfect agreement between model and data. $Re$ is effective N export fraction, calculated as final N concentration divided by initial N concentration. $C_N$ is N concentration at end of the experiments.
Figure S 2.38. FENL and SPARROW models comparison for lake field observations/budgets. Dashed lines are 1:1 indicating perfect agreement between model and data. $Re$ is effective N export fraction. $W_{N,exp}$ is N export.
Figure S 2.39. FENL and SPARROW models comparison for AQUATOX applications. Dashed lines are 1:1 indicating perfect agreement between model and data. Re is effective N export fraction. \( W_{N,exp} \) is N export.
2.9 References


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Chapter 3 Effect of Lake N Fixation on Watershed Export under N Loading Reduction Scenarios

3.1 Introduction

3.1.1 Coastal water eutrophication

Coastal water eutrophication is an important problem that can result in degradation of water quality, hypoxia, fish kills and harmful algal blooms (HABs). A recent global survey of coastal eutrophication identified more than 400 systems as experiencing hypoxia (Diaz and Rosenberg 2008; Rabalais, Diaz et al. 2010). Examples include Chesapeake Bay, where seasonal hypoxia has occurred for decades (Hagy, Boynton et al. 2004) and the continental shelf along the northern Gulf of Mexico (“The Dead Zone”), which has become the second largest coastal hypoxic area in the world (Rabalais, Turner et al. 2002b).

A primary cause of coastal water eutrophication is excessive nutrient input. Which nutrient is limiting productivity, and thus the culprit of the problem and target for management, is a more difficult question (Smith 1984; Paerl 2009). In addition, the limiting nutrient may change in time and space. For example, experimental nutrient enrichment studies for Chesapeake Bay showed that N was limiting in late summer and P was limiting in late winter (D'Elia 1987). Model analysis for Chesapeake Bay also suggests that P, N or Si can be limiting depending on the time, location or nutrient
loading scenario (Cerco 1995). A study on the Louisiana shelf found that P was limiting in May and July (of year 2001) and N was limiting in September (Sylvan, Dortch et al. 2006).

Although there is considerable uncertainty about the limiting nutrient, it is clear that N is an important factor, and its increased input is often considered to be the main cause of eutrophication. A 52-yr long-term nutrient loading record of Chesapeake Bay has shown that the hypoxia is positively correlated with N loading (Hagy, Boynton et al. 2004). Also, “The Dead Zone” is believed to be caused primarily by an increase of N loading from the Mississippi River (Alexander, Smith et al. 2000; Rabalais, Turner et al. 2002a; Scavia and Donnelly 2007). Thus, in order to reduce coastal eutrophication, management plans often focus on the reduction of watershed N loading (Heathwaite, Sharpley et al. 2000).

For management purpose, it is important to understand how watershed N export changes under different N loading reduction scenarios. Watersheds are complex systems including numerous sources and sinks of N. Lakes and reservoirs are an important component of the watershed N budget as shown in Figure 3.1. Sedimentation/burial, denitrification and fixation of atmospheric N in lakes may constitute a significant source and/or sink (Horne and Goldman 1972; Harrison, Maranger et al. 2009). For example, 16% of N load to Missouri River watershed is lost in lakes and reservoirs before reaching the Mississippi River (Brown, Sprague et al. 2011). N fixation in Clear Lake contributes about 43% of the annual N input to the lake, and this can be a significant source to the watershed and downstream San Francisco Bay (Horne and Goldman 1972). This source/sink needs to be considered when estimating/modelling N export from the
watershed to the coastal area. The focus of this paper is on modeling lake and reservoir loading and export in the context of watershed N budgets.

Figure 3.1. Watershed N budget. Watershed mass balance: Watershed loading + Lake fixation = Land & stream loss + Lake loss + Watershed export. Lakes mass balance: Lake loading + Lake fixation = Lake loss + Lake export. Arrow width is proportional to load^{0.5} for the FENL2, 60% N reduction scenario.

3.1.2 Existing models

The N cycle of watersheds is complex and the available data are limited. Therefore, simple models are needed that can be applied at the watershed scale to evaluate management strategies. A number of models have been developed and applied at the watershed scale to estimate watershed nutrient export. SPARROW (Spatially Referenced
Regression on Watershed Attributes) predicts nutrient point and nonpoint source loading to and transport and loss in the stream and lake/reservoir network (Smith, Schwarz et al. 1997). SPARROW has been applied at the national scale and a number of higher resolution regional models are also available (Ator, Brakebill et al.; Moore, Johnston et al. 2011; Wise and Johnson 2013). The Chesapeake Bay nitrogen SPARROW model (CBTN_v4) is used to understand N fate and transport within the watershed and export to the bay. For lakes and reservoirs, the model assumes N is removed in a first-order fashion using a net loss rate or apparent settling velocity, which accounts for loss by sedimentation and denitrification and gain by N fixation (Alexander, Elliott et al. 2002; Schwarz, Hoos et al. 2006; Alexander, Smith et al. 2007; Preston, Alexander et al. 2011). A similar empirical regression model (RivR-N) has been applied to watersheds in the northeastern U.S. (Seitzinger, Styles et al. 2002). That model also describes lake and reservoir loss using a first-order formulation. We previously summarized a number of existing lake/reservoir models (Ruan, Schellenger et al. 2014). Although the formulations differ, the existing models generally predict that N export is proportional to N loading, which means a certain reduction in loading will result in a proportional reduction in export.

### 3.1.3 FENL model

The problem with the existing models is that they do not explicitly account for N fixation, which may change under N loading reduction scenarios. Specifically, reducing N loading will reduce the N/P ratio and favor cyanobacteria that can fix N. For example, Lake 227 was undergone a whole-lake experiment, that it was fertilized with nutrients and monitored for 37 years. P input was held constant, but N input was reduced 2 times
by 64% and 100% (no N fertilizer input) during the experiment. However, the results showed that after reducing N fertilizer without reducing P, N fixation by cyanobacteria contributes significantly to N input to the lake and even after 20 years without N fertilizer, N concentration in the lake was only reduced by 30% (Findlay, Hecky et al. 1994; Schindler, Hecky et al. 2008). Another mesocosm experiment conducted in Lake Limmaren showed that reducing the N input only (without P reduction) can favor cyanobacteria which can fix N, and the fixed N may compensate the N concentration and N export to downstream. The authors argue that, because of this mechanism, N export to coastal waters may not be reduced by reducing N load only (Vrede, Ballantyne et al. 2009).

Previously, we presented a model of lake loading and export (Fixation and Export of Nitrogen from Lakes, FENL, in this paper, called FENL1 to distinguish it from the 2nd version) that explicitly accounts for N fixation. The model suggests that watershed N export will not be reduced proportionally due to N fixation in lakes (Ruan, Schellenger et al. 2014). We provided estimates of the expected reductions under N loading reduction scenarios, but those were of limited practical utility for two reasons. First, the model makes the conservative assumption that sufficient N will be fixed so that the input N to P ratio is at a threshold value (see next paragraph). Second, we predicted export for a select number of lakes and did not put the results in context of the whole watershed.

How lakes and reservoirs will respond when N loading is reduced is the subject of considerable debate (Paerl 2009; Paerl and Scott 2010; Scott and McCarthy 2010; Paerl, Xu et al. 2011; Schindler 2012). The assumption that N fixation balances the N pool is
conservative, but not very realistic. That is because N fixation is a metabolically expensive process and it may be limited by environmental factors, such as turbulence and vertical mixing or the availability of trace metals (e.g. molybdenum) (Howarth, Marino et al. 1988b; Paerl 1990; Paerl 2009; Paerl, Xu et al. 2011). Cyanobacteria consistently grow slower on N\(_2\) than on fixed N (NO\(_3\) or NH\(_4\)) in laboratory studies (Kratz and Myers 1955; Meeks, Wycoff et al. 1983; Rhee and Lederman 1983; Frias, Flores et al. 1997). Therefore, the amount of fixed N may not be enough to balance P in lakes or reservoirs. In order to provide a better estimate we modified the FENL1 model to limit the amount of N that can be fixed. This is controlled by a new parameter, which we estimate based on data in the literature (see Table 1) (Flett, Schindler et al. 1980; Ashton 1981; Levine and Lewis 1987; Findlay, Hecky et al. 1994).

Watersheds generally include a diverse set of lakes with different properties that affect N fixation (i.e., the turbulence in the water column, light intensity, temperature, trace metals etc.) (Howarth, Marino et al. 1988a). Previous models either assumed that N fixation does not change (SPARROW) or that it increases to make up the deficit up to an N/P threshold (FENL1). Although either of these scenarios may occur for a specific lake, we suppose that the average response of watershed lakes will be somewhere in between. The revised model presented here (FENL2) is an attempt to provide a realistic average response.
3.1.4 Overview of the research

This paper aims to quantify the effect of lake and reservoir N fixation on watershed N export under different N loading reduction scenarios, using Chesapeake Bay as a case study. Note that we consider lakes and reservoirs, but for simplicity we refer to them as “lakes” below. We first modify our precious model (FENL1) to include a limit on the amount of N deficit that can be made up by N fixation (the revised model is called FENL2). Then we parameterize and test the revised model by applying it to the calibration dataset consisting of laboratory experiments, lake field budgets and ecosystem models (Ruan, Schellenger et al. 2014). FENL1 and FENL2 are then coded into the Chesapeake Bay SPARROW model. After recalibrating the modified Chesapeake Bay SPARROW models, a series of N loading reduction scenarios are evaluated using SPARROW with the original lake model (referred to as SPARROW) and SPARROW with FENL1 and FENL2 lake models (referred to as FENL1 and FENL2) to predict watershed N export.

3.2 Chesapeake Bay

Chesapeake Bay is the largest estuary in the U.S. Like many coastal systems, the bay suffers from eutrophication. Seasonal hypoxia has occurred for decades (Hagy, Boynton et al. 2004) and is associated with numerous environmental and economic problems, like the death of oysters (D’Elia 1987). The increase of nutrient loading to the bay is considered the primary cause of the problem. There has been considerable debate over which nutrient limits production and should be controlled (Boesch, Brinsfield et al. 2001). D’Elia (D'Elia 1987) used nutrient enrichment studies to show that the pattern of N and P
limitation varies seasonally in the Patuxent estuary. Similar results were found by Cerco who used a time-variable simulation of load reduction, to show that P is limiting in spring and N for summer (Cerco 1995). Nutrient control in Chesapeake Bay originally focused on controlling P loading because it was believed to be more effective in limiting primary production (Committee 1986). EPA Chesapeake Bay program released a report implementing that both N and P are needed to be controlled in order to improve water quality (Committee 1986).

The Chesapeake Bay watershed covers the District of Columbia and parts of six states. Its area is 166,000 km² and includes more than 100,000 streams, creeks and tributaries. Due to the eutrophication in the bay, the watershed has received considerable attention over the past half century (Malone, Boynton et al. 1993). Agriculture (i.e. fertilizer application) and urban development contribute a large percentage of nutrient loading (Ator, Brakebill et al.).

A number of watershed models have been set up and applied to the Chesapeake Bay watershed. For example, (Linker, Stigall et al. 1993) used HSPF to estimate watershed nutrient (N and P) export under different management scenarios. More recently, Ator et al. (Ator, Brakebill et al.) used SPARROW to estimated N and P loadings to the bay. The Chesapeake Bay SPARROW model estimates the source, fate and transport of nutrients in the watershed. This model is implemented with higher resolution reach file NHDPlus (1:100,000-scale). It predicts that the bay receives 132 Gg of nitrogen per year from the watershed (Ator, Brakebill et al.).
Tremendous efforts have focused on controlling the eutrophication in the bay by reducing nutrient loads to the watershed (i.e. fertilizer application, new technology in WWTPs). And a series actions have been implemented to restore the watershed. Various nutrient reduction scenarios have been contemplated for the bay. In 1987, “Chesapeake Bay Agreement” was established to improve water quality, aiming for 40% reduction for both N and P controllable sources to the Bay by the year 2000 (Council 1987). Hagy et al. (Hagy, Boynton et al. 2004) suggest a 40% reduction in N. The Chesapeake Bay watershed model concludes that a 40% reduction in both N and P is needed to restore the water quality (Linker, Stigall et al. 1993). In 2010, the Chesapeake Bay TMDL was established to limit the nutrients inputs to the watershed. The most recent one in 2014, the revised “Chesapeake Bay Watershed Agreement” expects to achieve a goal to reduce nutrient and sediment pollution load by 60% by year 2017 compared to 2009 levels (Program 2014).

3.3 Lake model

3.3.1 Revised model of N input/output (FENL2)

The FENL2 model is based on a mass balance of N on a lake, with inflow, outflow, retention/loss and N fixation processes (Figure 3.2a). The N mass balance is:

\[ V \frac{dC_N}{dt} = W_{N,load} + W_{N,fix} - QC_N - v_s A_s C_N \]  

(1)

Where \( V \) (m³) is the volume, \( C_N \) (kg/m³) is the in-lake N concentration, \( Q \) (m³/yr) is the flow rate, \( v_s \) (m/yr) is the apparent settling velocity (accounts for sedimentation and denitrification) and \( A_s \) (m²) is the surface area.
Figure 3.2. Model of N input/export to/from lakes and reservoirs including N fixation: (a) Model schematic showing N mass balance terms. (b) Three lake models (SPARROW, FENL1 and FENL2) behavior under different N loadings. For FENL1, $r_f = 10.2$. For FENL2, $r_f = 10.2$, $f_m = 0.25$. The N loading is normalized by $W_p r_f$. The effective N export fraction is normalized by the mean fraction when $W_{N,\text{load}} \geq W_p r_f$, or by the minimum fraction when there is no data with $W_{N,\text{load}} \geq W_p r_f$ (Ruan, Schellenger et al. 2014).

The total N input consists of two parts, N loading ($W_{N,\text{load}}, kg/yr$) and N fixation ($W_{N,\text{fix}}, kg/yr$). N fixation is a function of the N/P ratio of the loading. When
$W_{N,\text{load}} \geq W_P r_f$, where $r_f$ is the threshold N/P ratio, there is no N fixation, thus

$W_{N,\text{fix}} = 0$. When $W_{N,\text{load}} < W_P r_f$, there is N fixation. Note that we use total N and P and N/P on a mass basis throughout this paper. In FENL1, we assumed sufficient N is fixed to bring the ratio of total N input to P input to the threshold value ($r_f$). However, N fixation may not balance the N pool (see 3.1.3 FENL model). Thus in FENL2, the N fixation is reduced to a fraction ($f_m$) of the deficit. The deficit is calculated as the N equivalent of the P input ($W_P r_f$) minus the N loading ($W_{N,\text{load}}$). The parameter $f_m$ controls the amount of N that is fixed.

\[
W_{N,\text{fix}} = 0 \quad \text{if} \quad W_{N,\text{load}} \geq W_P r_f 
\]

\[
= (W_P r_f - W_{N,\text{load}}) f_m \quad \text{if} \quad W_{N,\text{load}} < W_P r_f
\]

When $f_m = 1$, FENL2 is equivalent to FENL1. When $W_{N,\text{load}} > W_P r_f$ FENL1 and FENL2 are equivalent to SPARROW (Figure 3.2b). The ratio of N export to N loading, which we refer to as effective export fraction, is:

\[
Re = \frac{Q C_N}{W_{N,\text{load}}}
\]

Equations (1) – (3) can be combined, at steady state, with areal hydraulic loading,

$q_s = \frac{Q}{A_s}$, and solved for $Re$. 
\[ Re = \frac{q_s}{q_s + v_s} \quad \text{if } W_{N,\text{load}} \geq W_P r_f \]

\[ = \frac{q_s}{q_s + v_s} \left( 1 + f_m \left( \frac{W_P}{W_{N,\text{load}}} r_f - 1 \right) \right) \quad \text{if } W_{N,\text{load}} < W_P r_f \] (4)

Figure 3.2b illustrates how \( Re \) changes with the N loading for SPARROW, FENL1 and FENL2. Reducing N loading will move a lake to the left on this graph. By including a limit \( (f_m) \) on the amount of deficit that can be made up by N fixation, FENL2 predicts a lower effective N export fraction than FENL1.

### 3.3.2 Parameter estimate

To apply the model to the Chesapeake Bay watershed, the parameters \( (v_s, r_f, f_m) \) need to be specified. One method of estimating the parameters is to let the SPARROW model calibrate them against observations (Schwarz, Hoos et al. 2006). There are two problems with this approach for these parameters. First, the model is designed to predict changes of N export for a lake as N loading is reduced, not changes between lakes. The database of observed loadings in Chesapeake Bay is thus of limited utility. Second, the lake loss process is only a minor player at the watershed scale (0.7% of the watershed input is lost in lakes in the SPARROW baseline scenario) and the existing SPARROW model matches the observations relatively well. Including the FENL2 parameters in the calibration set can result in a slightly better match (lower RMSE), which is expected because of the added parameters. However, this is not always realized and we find that the calibrated parameter value, are affected by their initial value. This complicates the model optimization problem. Thus, we estimate the values for \( r_f \) and \( f_m \) apriori, from the literature. The \( v_s \) parameter is different in the SPARROW and FENL models. In
SPARROW, it includes N fixation, but in FENL that process is explicitly considered. We therefore recalibrated $v_s$ for FENL1 and FENL2.

The N/P loading threshold ($r_f$) is estimated from the literature. Hellström (Hellström 1996) analyzed data for a number of lakes and found that N fixation balances N with P so that N/P concentration ratio is about 10-15 for most of the lakes. Howarth et al. (Howarth, Marino et al. 1988a) summarized data from 11 lakes and concludes that when N/P loading ratio is less than approximately 8.1, N fixation occurs. An average value 10.2 based on these literature data is used in FENL1 and FENL2 (Table 3.2).

The maximum fixation factor ($f_m$) is also determined from the literature by calculating the percentage of N fixation that compensates N to P in lake observations (Table 3.1). Field budgets for several ELA lakes are based on (Flett, Schindler et al. 1980). Estimates for lakes 226 NE and 227 are presented in Table 2. Lake 302 is not included because it’s estimated N:P loading ratio was 20. Lake 261 had N/P loading ratio of 5, but estimates for N fixation are uncertain. The average value of the $f_m$ 0.25 is used in FENL2.
Table 3.1. Estimates for maximum fixation fraction ($f_m$).

<table>
<thead>
<tr>
<th>$f_m$</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8% (3.3%, 6.2%)</td>
<td>average (1976, 1977) for Rietvlei impound.</td>
<td>(Ashton 1981)</td>
</tr>
<tr>
<td>12%</td>
<td>Lake Valencia for 1981</td>
<td>(Levine and Lewis 1987)</td>
</tr>
<tr>
<td>52% (77%, 27.6%)</td>
<td>average (Lake226 NE for 1973-1975, Lake 227 for 1975)</td>
<td>(Flett, Schindler et al. 1980)</td>
</tr>
<tr>
<td>30% (7.6% – 93%)</td>
<td>average (range) for Lake 227 for 1975-1992</td>
<td>(Findlay, Hecky et al. 1994)</td>
</tr>
<tr>
<td>25%</td>
<td>average</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2. Estimates for N/P loading threshold ($r_f$).

<table>
<thead>
<tr>
<th>$r_f$</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5 (10-15)</td>
<td>N fixation effectively balances N with P so that the N/P concentration ratio is about 10-15</td>
<td>(Hellström 1996)</td>
</tr>
<tr>
<td>10</td>
<td>N fixation occurred when the N/P loading ratio was less than about 10</td>
<td>(Flett, Schindler et al. 1980)</td>
</tr>
<tr>
<td>8.1</td>
<td>N fixation occurs in lakes with N/P loading ratio less than approximately 8.1</td>
<td>(Howarth, Marino et al. 1988a)</td>
</tr>
<tr>
<td>10.2</td>
<td>average</td>
<td></td>
</tr>
</tbody>
</table>

3.3.3 Watershed N budget and loading reduction scenarios

The three watershed models are run in prediction mode. In a previous application of the Chesapeake Bay SPARROW model, where the objective was to produce estimates of actual nutrient loadings, the predicted loadings were adjusted based on observed loadings (Ator, Brakebill et al.). Here, we are evaluating scenarios with different nutrient inputs, so we do not perform this adjustment.
The watershed loading is calculated as the sum of the five sources: point source, manure, N fertilizer and fixation by crops, atmospheric deposition and urban activity sources (Ator, Brakebill et al.). The watershed export to the bay is the sum of the terminal reaches including all nontidal bay tributaries and tidal reaches. The land loss is determined by the factors including: plant-uptake, redox condition and hydrogeological conditions etc. The in-stream N loss for flowing streams is modeled as a first-order decay process, which is a function of estimated time of travel. Lake fixation is calculated based on equation (2), and lake loss in FENL models uses the modified formulation of equation (4). The lake loading is the sum of two parts of N: the N delivered to the reach from the upstream and the N sources from the incremental drainage area, and the lake export is the sum of the export from each lake (note that one lake’s export can be another lake’s loading). Detailed calculation method can be found in SI.

Three scenarios are simulated using the three models: baseline, 60% N loading reduction and 60% N+P loading reduction.

3.4 Results and discussion

3.4.1 Comparison of models to calibration dataset

As discussed above (and in Ruan, Schellenger et al. 2014)), the existing database of lake loading and export from the literature and for Chesapeake Bay is extensive but of limited utility, because it includes only limited observation for changes in N loading for lakes. For that reason, we preciously compiled a number of datasets from laboratory experiments, lake field budgets and ecosystem models, that characterize how systems may change as N loading is reduced. We previously compared FENL1 to this dataset. To
provide some estimate of the skill of FENL2, we also compare FENL2 to this dataset. We recalibrated/calibrated the FENL1 and FENL2 models against each system from the calibration dataset. This is different from the previous paper, because, as discussed above, the parameters controlling N fixation ($r_f$ in FENL1 and $r_f$ and $f_m$ in FENL2) are not calibrated, but based on literature. The only parameter calibrated in the two models is the settling velocity ($v_s$) with a range of 0-25 m yr$^{-1}$ (Alexander, Elliott et al. 2002), which had no constraints previously. The values of $v_s$ and the RMSEs are listed in the Table S 3.4. Parameters and RMSEs for FENL1 ($r_f = 10.2$), FENL2 ($r_f = 10.2$, $f_m = 0.25$) and SPARROW. The results of all the three approaches and recalibrated models are summarized in Figure 3.3 (detailed method can be found in (Ruan, Schellenger et al. 2014)).
Figure 3.3. Comparison of SPARROW, FENL1 and FENL2 models to calibration dataset. For FENL1, $r_f = 10.2$. For FENL2, $r_f = 10.2$, $f_m = 0.25$. Summary of observations from microcosm lab experiments, lake field observations/budgets, and lake ecosystem model applications. See Figure 3.2b. legend for normalization.

3.4.2 Chesapeake Bay application

The results for the three models for the three scenarios are summarized in Table 3. The table shows results for the watershed (left columns) and for the lakes (right columns). The watershed loading varies slightly because each model was calibrated independently, including the loading parameters. We therefore focus our comparison on how each of the models changes under different scenarios, rather than the absolute difference between
them. As an example of an individual lake, we include results for Lake Jackson. We will look at the results for each loading scenario below.

a. **Baseline scenario**

For the baseline scenario, each model was calibrated to observed loadings. Thirteen parameters are estimated for each model and two parameters are fixed for FENL1 and FENL2 (see section 3.2). The estimated results of the parameters and the RMSEs for the three calibrated models are listed in Table S2. Both FENL1 and FENL2 have lower RMSE compared to SPARROW, but the difference is small.

For the baseline scenario, the watershed effective export fraction ($R_e$) for all models is less than 0.2. The loss can be attributed to land & stream loss and lake loss. At the watershed scale, lake loss is not a major factor in any of the models. For example, in FENL2 lake loss constitutes 0.9% of the total watershed loss and eliminating it would only increase the watershed export by 3.1%. The amount of N fixation predicted by the FENL models is also small compared to the watershed loading (Table 3.3). This suggests lake processes are not important at the watershed scale (for the baseline scenario).

We also calculated the overall lake effective export fraction (the fraction of total N export to total N loading for all lakes), which is 0.98-0.99 for all models, meaning only about 0.01-0.02 of the N load is lost. However, this number is not representative of the typical lake in the Chesapeake Bay watershed, because it is dominated by a few large lakes (the lakes/reservoirs connected to the Susquehanna River) with high N export fraction (0.99), which dominate 80% of the total N export from all lakes. The average and
median of the individual lake export fractions for FENL1 are 0.76 and 0.77, which is much lower than the overall export fraction (0.99).

The FENL1 and FENL2 models consider the relationship between the N/P ratio and the threshold for N-fixation ($r_f$). Figure 4 presents the distribution of N/P loading ratio for the 4325 lakes in Chesapeake Bay watershed. The lakes cover a large range of N/P ratios with a median of about 17.7 (Figure 3.4). For FENL1 and FENL2, lakes below the threshold ($r_f$) are predicted to have N fixation, which constitutes about 0.2 of the lakes.

We illustrate the behavior of a single lake using Lake Jackson as an example. The N/P ratio for the baseline scenario is about 13.0, which is greater than the threshold value ($r_f = 10.2$), the lake falls on the right side of the threshold and no N fixation occurs (Figure 5).
Table 3.3. N loading reduction scenarios for the whole watershed and for lakes (Gg)

<table>
<thead>
<tr>
<th>Scenario/Model</th>
<th>Watershed loading</th>
<th>Watershed export</th>
<th>Land &amp; stream loss</th>
<th>Lake loading</th>
<th>Lake export</th>
<th>Lake loss</th>
<th>Lake fixation</th>
<th>Watershed Re</th>
<th>Lake Re</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Baseline</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPARROW</td>
<td>686</td>
<td>124</td>
<td>557</td>
<td>286</td>
<td>281</td>
<td>4.8</td>
<td>-</td>
<td>0.18</td>
<td>0.98</td>
</tr>
<tr>
<td>FENL1</td>
<td>685</td>
<td>125</td>
<td>557</td>
<td>291</td>
<td>288</td>
<td>5.5</td>
<td>2.5</td>
<td>0.19</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL2</td>
<td>685</td>
<td>124</td>
<td>557</td>
<td>288</td>
<td>284</td>
<td>4.8</td>
<td>0.8</td>
<td>0.18</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>60% N reduction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPARROW</td>
<td>274</td>
<td>49 (60%)**</td>
<td>223</td>
<td>114</td>
<td>112</td>
<td>1.9</td>
<td>-</td>
<td>0.18</td>
<td>0.98</td>
</tr>
<tr>
<td>FENL1</td>
<td>274</td>
<td>71 (43%)</td>
<td>224</td>
<td>168</td>
<td>189</td>
<td>3.6</td>
<td>24.6</td>
<td>0.26</td>
<td>1.13</td>
</tr>
<tr>
<td>FENL2</td>
<td>274</td>
<td>62 (50%)</td>
<td>223</td>
<td>136</td>
<td>147</td>
<td>2.4</td>
<td>13.4</td>
<td>0.23</td>
<td>1.08</td>
</tr>
<tr>
<td><strong>60% N+P reduction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPARROW</td>
<td>274</td>
<td>49 (60%)</td>
<td>223</td>
<td>114</td>
<td>112</td>
<td>1.9</td>
<td>-</td>
<td>0.18</td>
<td>0.98</td>
</tr>
<tr>
<td>FENL1</td>
<td>274</td>
<td>50 (60%)</td>
<td>223</td>
<td>116</td>
<td>115</td>
<td>2.0</td>
<td>1.0</td>
<td>0.18</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL2</td>
<td>274</td>
<td>50 (60%)</td>
<td>222</td>
<td>115</td>
<td>113</td>
<td>2.3</td>
<td>0.3</td>
<td>0.18</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*Overall effective export fraction. Re = export/load.
** Realized reduction.

b. 60% N reduction

We then use the three models to evaluate how watershed N export is affected by a 60% N loading reduction scenario. At the watershed scale, SPARROW predicts a proportional (60%) reduction. FENL1 and FENL2 predict that the reduction is not proportional (43% and 50%, respectively). This is also reflected in the watershed effective export fraction, which remains the same for SPARROW (0.18), but increases for FENL1 (0.26) and FENL2 (0.23). The difference between these models at the watershed scale is due to difference in the lakes. In SPARROW, the lake export fraction remains at 0.98. in FENL1
and FENL2 it increases to 1.13 and 1.08, respectively. Under the N loading reduction scenario, the lakes turn into a source, and the magnitude is significant in the watershed budget. Specifically, in FENL2, lake fixation contributes 4.7% to the total watershed input (watershed loading + lake fixation). The effect is larger for FENL1, because it assumes that N-fixation balances the N pool.

Under the 60% N reduction scenario, the N/P ratio of lakes decreases for all models (Figure 3.4). The fraction of lakes below the threshold increases from 0.2 to about 0.6 (Figure 3.4 B and C). In SPARROW, the N/P ratio does not affect the export, so the watershed N export decreases proportionally. For the FENL models, the 60% N reduction scenario pushes the majority of lakes into the N-fixation regime. The added N input by these lakes counteracts the N loading reduction and the N watershed export does not decrease proportionally (Table 3.3).
Figure 3.4. Distribution of Chesapeake Bay Watershed lakes and reservoirs N/P loading ratio for different models and scenarios. Note that the “baseline” and “60% N+P reduction” scenarios are the same for all models.

For Lake Jackson, the three models are applied to a series N loading reductions (10-70%), and the effective N export fraction is calculated (Figure 3.5). SPARROW predicts that the fraction is constant, and the N export will be reduced proportionally when reducing the N loading. FENL1 and FENL2 predict that the effective N export fraction
remains constant for both model up to 20% N loading reduction. A 30% reduction moves the lake below the N/P threshold ($r_f$) and N fixation begins to add N into the lake. Consequently, the effective export fraction increases. For the result of the 60% N reduction scenario with FENL2, the export fraction from Lake Jackson increased by 0.22, and N export was only reduced by 51% (Table 3.4).

Table 3.4. Lake Jackson N loading reduction scenarios (Gg)

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>N Load</th>
<th>N Export</th>
<th>N/P</th>
<th>N fixation</th>
<th>$R_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Baseline</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPARROW</td>
<td>0.34</td>
<td>0.34</td>
<td>13.1</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL1</td>
<td>0.34</td>
<td>0.34</td>
<td>12.9</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL2</td>
<td>0.34</td>
<td>0.34</td>
<td>13.1</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td><strong>60% N reduction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPARROW</td>
<td>0.14</td>
<td>0.14</td>
<td>5.2</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL1</td>
<td>0.16</td>
<td>0.27</td>
<td>5.9</td>
<td>0.11</td>
<td>1.70</td>
</tr>
<tr>
<td>FENL2</td>
<td>0.14</td>
<td>0.17</td>
<td>5.4</td>
<td>0.03</td>
<td>1.21</td>
</tr>
<tr>
<td><strong>60% N+P reduction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPARROW</td>
<td>0.14</td>
<td>0.14</td>
<td>13.1</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL1</td>
<td>0.14</td>
<td>0.13</td>
<td>12.9</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>FENL2</td>
<td>0.14</td>
<td>0.13</td>
<td>13.1</td>
<td>0</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Figure 3.5. Lake Jackson SPARROW, FENL1 and FENL2. Under N loading reduction scenarios: (a) N export, (b) N fixation, and (c) effective N export fraction.
c. 60% N+P reduction

The results from the N only reduction scenario suggest that N export will not be reduced proportionally when reducing N loading alone. We therefore evaluate a N+P reduction scenario in all three models. With a 60% N+P reduction plan (both N and P loading are reduced by 60%), all three models predict that N export will be reduced by 60%, and the effective N export fraction drops back to the baseline.

Under the N+P reduction, the N/P ratio of the lakes returns back to the baseline for all models (Figure 4). For FENL1 and FENL2, a proportional decrease in lake export is predicted regardless of the N/P ratio. Lakes that have N/P loading ratios above the threshold reduce the export as a consequence of N loading reduction, as in SPARROW. Lakes that have N/P loading ratios below the threshold reduce export as a consequence of P loading reduction. Both FENL models predict that any amount (in percentage) of N+P loading reduction will result in the same amount (in percentage) of N export reduction. Therefore, at the watershed scale, in order to achieve a proportional amount of N export from the watershed, P loading needs to be reduced as well.
Figure 3.6. Lakes and reservoirs in Chesapeake Bay watershed, green = N fixing. A is under baseline scenario and B is under 60% N loading reduction scenario.
3.5 Summary and outlook

In this study we estimated the role of lake and reservoir N fixation under N loading reduction scenarios at the watershed scale using Chesapeake Bay as a case study. Three scenarios and corresponding models were presented, including no change in N fixation (SPARROW), N fixation at a level that balances the N deficit (FENL1), and N fixation at a reduced level (FENL2). From a management perspective, these scenarios can be considered “best case”, “worst case” and “best estimate”. For a 60% N loading reduction, the majority of lakes (fraction increase from 0.2 to 0.6) are pushed into the N-fixation regime, the added N by fixation in lakes counteracts the N loading reduction, and the lake N export becomes a more significant part of the overall N budget, thus, the watershed N export does not decrease proportionally. The magnitude of this effect of lake N fixation is substantial at the watershed scale. Under this scenario, the realized export reduction is 60% for the best case, 43% for the worst case, and 50% for the best estimate. For a 60% N+P reduction, all three cases result in 60% reduction.

These results are specified to Chesapeake Bay watershed and may be different from watersheds with more or less lakes, or different N/P loading ratios, or other factors that may affect N fixation. However, we expect the main conclusion, that watershed N export will not be reduced proportionally under a N only reduction scenario, but will be reduced proportionally under a balanced N+P reduction scenario, to apply to other watersheds as well. Application of the modified SPARROW model to other watersheds would be useful.
Our results support a dual nutrient management strategy. In addition to resulting in the desired N export reduction, a balanced reduction will also benefit P-limited lakes in the watershed and cases where the coastal system may be P-limited as well.

From a management perspective, pushing lakes into the N-fixing regime should be avoided. The N/P ratio of the lakes is heterogeneous (Fig. 6) and even for the 60% N reduction, about 40% of the lakes remain above rf. So it can be argued that some lakes are more vulnerable than others. A cost effective strategy for lake management might be to focus additional P controls on a limited number of lakes. On a lake-by-lake (or regional) basis, this vulnerability should be considered and may be exploited in management. A map of lakes colored based on their predicted N-fixing status (Figure 3.6. green = N fixing) shows an interesting spatial pattern. Specifically, the response to the 60% N reduction is not uniform. For example, for lakes in MD, the fraction of N-fixing lakes increases from 38 to 71%, whereas it increases from 24 to 87% in VA. This would suggest VA is more vulnerable as a region than MD.

In this research we applied a steady-state model to estimate watershed nutrient export. A natural next step is to consider the time-variable aspects of this problem. Many watersheds are presently experiencing a change in nutrient input due to changes in agriculture, urbanization, wastewater treatment or climate, and often considerable observations are available covering a long time span. Application of the model to these observations would allow for a more direct test of the model’s ability to predict watershed behavior and nutrient loading reduction scenarios. It may prompt future refinement, such as including storage in the sediment bed.
3.6 Supporting material

3.6.1 SPARROW Model

SPARROW mass balance (Schwarz, Hoos et al. 2006):

\[
F_i^* = \left( \sum_{j \in J_i} F_j' \right) \delta_i A(Z_i^S, Z_i^R; \theta_S, \theta_R) + \left( \sum_{n=1}^{N_i} S_{ni} \alpha_n D_n(Z_i^D; \theta_D) \right) A'(Z_i^S, Z_i^R; \theta_S, \theta_R)
\]

Load leaving the reach
Load generated within upstream reaches and transported to the reach via the stream network
Load originating within the reach’s incremental watershed and delivered to the reach segment

SPARROW original lake model nutrient decay process (N export fraction) equation:

\[
A(Z_i^S, Z_i^R; \theta_S, \theta_R) = Re = \frac{1}{1 + \theta_R(q_i^R)^{-1}} = \frac{q_S}{q_S + v_S}
\]

/* Specify the SAS IML reservoir decay function code. */
%let reservoir_decay_specification = 1 / ( 1 + data[,jresvar]*
beta[,jbrresvar]` ) ;

Box 1. Code for calculating N decay in the lake/reservoir for SPARROW.

FENL2 effective N export fraction equation:

\[
Re = \frac{q_S}{q_S + v_S} \quad \text{if } W_{N,\text{load}} \geq W_P r_f
\]

\[
= \frac{q_S}{q_S + v_S} \left( 1 + f_m \left( \frac{W_P}{W_{N,\text{load}}} r_f - 1 \right) \right) \quad \text{if } W_{N,\text{load}} < W_P r_f
\]

Where \( f_m = 0.25 \), and \( r_f = 10.2 \).
do i = 1 to nreach ;

/*XDR: Determine the total amount of load loading into the reach before decay;*/
rchldT[i] = incddsdc[i,1] + data[i,jfrac] # node[data[i,jfnode]] ;

if data[i,jfenltype]=2 then
  if rchldT[i,1]< data[i,jfenlvar]*10.2/1.0487708 then
    resdcayf [i,] = 1/(1+data[i,jresvar]*beta[jbresvar]*)#(1 + 0.25 *
      (data[i,jfenlvar] * 10.2 / 1.0487708 /rchldT[i,1]-1));
  else resdcayf [i,] = 1/(1+data[i,jresvar] * beta[jbresvar]*)
  else resdcayf = j(nreach,1,1);

if resdcayf [i,] = 0 then resdcayf = j(nreach,1,1);

end;

Box 2. Code for calculating N decay in the lake/reservoir for FENL2.

3.6.2 Calculating the phosphorus loading to each lake/reservoir

To calculate the N export for lakes and reservoirs (reachtype = 2) in FENL, the phosphorus loading for each lake/reservoir needs to be added to the model input data file (see section 3.3.1, eq.4). The steps are as follow:

1. Run the Chesapeake Bay SPARROW phosphorus model (CBTP_v4), export the “predict” data file in the “results” folder which contains the estimated export of phosphorus from each reach, given by the variable PLOAD_TOTAL ($TP_{OUT,TOTAL}$) into an excel spreadsheet, and then calculate the phosphorus loading ($TP_{IN,TOTAL}$) based on
equations related to the reservoir decay process and the estimated parameter.

(Note: $TP_{IN,TOTAL}$ and $TP_{OUT,TOTAL}$ is before and after the lake loss).

$$TP_{OUT,TOTAL} = TP_{IN,TOTAL} \times \frac{1}{1 + \frac{v_s}{q_s}} \quad (S1)$$

Thus, $$TP_{IN,TOTAL} = \frac{TP_{OUT,TOTAL}}{1 + \frac{v_s}{q_s}} \quad (S2)$$

The SPARROW model settling velocity for phosphorus ($v_{s,P}$) is 54.3 m yr$^{-1}$.

In equation S1 and S2, $q_s$ (m yr$^{-1}$) is the hydraulic loading, given the variable $reshload$ and is calculated based on the equation (Box 3) in the data modification file “tp02v7_f_2013.sas”. This step is also calculated in excel, values of the needed variables are obtained from the input data file “data1”.

```
reshload=(reachtype=2)*((maflowu*86400*365.25)/(areasqkm*35316389));
```

Box 3. Code for calculating the hydraulic loading

where $maflowu$ (cfs) is the mean annual flow at the bottom of reach, $areasqkm$ (km$^2$) is the feature area.

2. Create an excel spreadsheet named “fenl” which contains the phosphorus loading data ($TP_{IN,TOTAL}$). Then the data are sorted in the same way as the SPARROW “data1” by $COMID$ (common identifier of an NHD flowline).

3. Create a new data table by using the “merge function” of SAS to combine the data files “data1” and “fenl” to one data file “data2”. The input data file “data2” contains the phosphorus loading to each lake and reservoir.
3.6.3 Calculating N loading and export to/from the watershed, and the lakes

The model reach file (NHDPlus) contains 81908 reaches, and 4325 (5%) of which are identified as lakes or reservoirs outlets in the watershed (Ator, Brakebill et al.).

1. Calculate N loading to the watershed:

The N loading to the watershed includes five sources: point source, manure, N fertilizer and fixation by crops, atmospheric deposition and urban. The total N loading is calculated by summing up the five sources. The first four were obtained from the new input data file “data2”. For the urban source, it is calculated by multiplying the urban area by the calibrated corresponding coefficient “Urban (km$^2$)” in Table S1. The area is calculated according to the equation (Box 4) in the data modification file “tp02v7_f_2013.sas”, which is the sum of the area of the four land uses.

\[
\text{urban_km2} = \frac{(nlcd01_21 + nlcd01_22 + nlcd01_23 + nlcd01_24)}{1000000};
\]

Box 4. Code for calculating the total urban area.

The “Urban (km$^2$)” listed in Table S1 are slightly different for the three models (i.e., for SPARROW, the value is 1094 kg km$^{-2}$ yr$^{-1}$, and for FENL1, it is 1039 kg km$^{-2}$ yr$^{-1}$). Then the N loading from all sources to the Chesapeake Bay watershed for three models are calculated and listed in Table 3 (in section 3.4.2).

2. Calculate the N export from the watershed to the bay:

The total N export from the watershed to the bay is the sum of the N export (PLOAD TOTAL in the predict data file “predict”) of the 259 terminal reaches (where TERMINALFL=1). The results are listed in Table 3 (in section 3.4.2).
3. Calculate the N loading and export to/from all the lakes:

The calculation of N loading to all the lakes (reachtype = 2) is different from the N loading to the watershed. The N loading to each lake includes the N delivered to the reach from the upstream and the N sources from the incremental drainage area for that reach.

The N loading to the lake, given the variable “rchldT” is a new variable defined and calculated (Box 5) for this research, detailed code information (in “sparrow_calibrate” and “sparrow_predict” files) is described in the later section.

\[ rchldT[i,1] = incddsnc[i,1] + data[i,jfrac]#node[data[i,jfnode],1] \]

Box 5. Code for calculating N loading to the lakes.

The first part of the equation is the incremental sources that delivered to this reach, and the second part is the N from the upstream reach.

The N loading to all lakes is the sum of the “rchldT” of all the lakes in the data file “predict”. The N export to all lakes is the sum of the “PLOAD_TOTAL” lakes in the data file “predict”. (Note: the N export from one lake can be the loading to the downstream lake, as a result, the loading and export do not represent the net loading and export to/from all lakes.)

3.6.4 Lake Jackson example

Lake Jackson is located in suburban Prince William Country, Virginia. Lake Jackson is a reservoir created by the Lake Jackson Dam on the Occoquan River. The lake is used as an example for the comparison between model predicts and calculation by hand, as well as the evaluation of the nutrient loading reduction scenarios.
Table S 3.1. FENL2 Lake Jackson and Occoquan River: a reach across the threshold

<table>
<thead>
<tr>
<th>Reach Number&lt;sup&gt;a&lt;/sup&gt;</th>
<th>From Node&lt;sup&gt;b&lt;/sup&gt;</th>
<th>To Node&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Reach- Type</th>
<th>P load (kg/yr)</th>
<th>N load (kg/yr)</th>
<th>N Export (kg/yr)</th>
<th>N load (kg/yr)</th>
<th>N Export (kg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40835</td>
<td>108</td>
<td>519</td>
<td>1</td>
<td></td>
<td>1055</td>
<td>1055</td>
<td>422</td>
<td>422</td>
</tr>
<tr>
<td>40877</td>
<td>583</td>
<td>519</td>
<td>1</td>
<td></td>
<td>343446</td>
<td>343446</td>
<td>142902</td>
<td>142902</td>
</tr>
<tr>
<td>40833</td>
<td>519</td>
<td>502</td>
<td>2</td>
<td>26330</td>
<td>344530</td>
<td>340888</td>
<td>143336</td>
<td>172757</td>
</tr>
<tr>
<td>39527</td>
<td>502</td>
<td>105</td>
<td>0</td>
<td></td>
<td>340901</td>
<td>340564</td>
<td>172763</td>
<td>172592</td>
</tr>
</tbody>
</table>

The reach-type, 0 - stream reach, 1 - impoundment reach and 2 - outlet reach for impoundment. Also reach-type 2, the outlet reach of an impoundment is coded separately from other interior impoundment reaches to facilitate the pollutant attenuation calculations. a The reach number all had same first three number 223, i.e., for reach 40833, the original number was 22340833. b and c all had prefix number 9458701. For this example, to allow for direct comparison of the original SPARROW lake model and FENL, the upstream input is based on the original SPARROW model. When SPARROW is then using the FENL model, this value is different. d Phosphorus loading is not needed.
Figure S 3.1. Lake Jackson and Occoquan River
Table S 3.2. Lake Jackson and Occoquan River (A) SPARROW, (B) FENL2 baseline, and (C) FENL2 under 60% N loading reduction

<table>
<thead>
<tr>
<th>Reach number</th>
<th>Predicted P input (kg/yr)</th>
<th>Predicted N export</th>
<th>Predicted incremental (kg/yr)</th>
<th>Predicted N input(kg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40835</td>
<td>-</td>
<td>1066</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>40877</td>
<td>-</td>
<td>344195</td>
<td>901</td>
<td>-</td>
</tr>
<tr>
<td><strong>40833</strong></td>
<td><strong>26330</strong></td>
<td><strong>341627</strong></td>
<td><strong>29</strong></td>
<td><strong>345290</strong></td>
</tr>
<tr>
<td>39527</td>
<td>-</td>
<td>341307</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40835</td>
<td>-</td>
<td>1055</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>40877</td>
<td>-</td>
<td>343446</td>
<td>888</td>
<td>-</td>
</tr>
<tr>
<td><strong>40833</strong></td>
<td><strong>26330</strong></td>
<td><strong>340888</strong></td>
<td><strong>28.7</strong></td>
<td><strong>344530</strong></td>
</tr>
<tr>
<td>39527</td>
<td>-</td>
<td>340564</td>
<td>13.1</td>
<td>-</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40835</td>
<td>-</td>
<td>422</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>40877</td>
<td>-</td>
<td>142902</td>
<td>355</td>
<td>-</td>
</tr>
<tr>
<td><strong>40833</strong></td>
<td><strong>26330</strong></td>
<td><strong>172757</strong></td>
<td><strong>11.5</strong></td>
<td><strong>143336</strong></td>
</tr>
<tr>
<td>39527</td>
<td>-</td>
<td>172592</td>
<td>5.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Table S4 shows the predict results from the SPARROW baseline, FENL2 baseline and FENL2 under 60% N loading reduction. Below is the calculation by hand, which is compared to the model predicts. The comparisons are summarized in Table S5.
Table S 3.3. Comparison of Lake Jackson N export between the model predict and the calculation by hand

<table>
<thead>
<tr>
<th></th>
<th>N export (kg/yr)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>model predict</td>
<td>by hand</td>
</tr>
<tr>
<td>SPARROW baseline</td>
<td>341627</td>
<td>341937</td>
</tr>
<tr>
<td>FENL2 baseline</td>
<td>340888</td>
<td>341084</td>
</tr>
<tr>
<td>FENL2 under 60% N loading reduction</td>
<td>172757</td>
<td>172897</td>
</tr>
</tbody>
</table>

For reach 40833, the calculation is below, N total input is:

\[ W_{N,\text{load}} = W_{N,\text{load,up}} + W_{N,\text{load,inc}} \]

\[ W_{N,\text{load,up}} = W_{N,\text{exp,40835}} + W_{N,\text{exp,40877}} \]

\[ q_s = 552.7 \, m/yr, v_{s,\text{SPARROW}} = 5.93 \, m/yr, v_{s,\text{FENL2}} = 5.91 \, m/yr \]

Table S 3.3A, SPARROW by hand:

\[ Re = \frac{q_s}{q_s + v_s} = \frac{552.7}{552.7 + 5.91} = 0.99 \]

\[ W_{N,\text{load,up}} = 1066 + 344195 = 345261 \, kg/yr \]

\[ W_{N,\text{load,inc}} = 29 \, kg/yr \]

\[ W_{N,\text{exp}} = W_{N,\text{load}} \times Re = (345261 + 29) \times 0.99 = 341937 \, kg/yr \]

Compare to SPARROW predicted (in Table S5 A):

\[ W_{N,\text{exp}} = 341627 \, kg/yr \]

Table S 3.3 B, FENL2 baseline by hand:

\[ W_{N,\text{load}} = 344530 \, kg/yr, W_{P,\text{load}} = 26330 \, kg/yr, N/P = 13.0 \]
\[ Re = \frac{q_s}{q_s + v_s} \quad \text{if } W_{N,\text{load}} \geq W_P r_f \]

\[ = \frac{q_s}{q_s + v_s} \left(1 + f_m \left(\frac{W_P}{W_{N,\text{load}}} r_f - 1\right)\right) \quad \text{if } W_{N,\text{load}} < W_P r_f \]

\[ W_P r_f = 26330 \times 10.2 = 268566 \text{ kg/yr} < W_{N,\text{load}} \]

\[ Re = \frac{552.7}{552.7 + 5.91} = 0.99 \]

\[ W_{N,\text{exp}} = 344530 \times 0.99 = 341084 \text{ kg/yr} \]

Compare to FENL2 predicted (in Table S5 B):

\[ W_{N,\text{exp}} = 340888 \text{ kg/yr} \]

---

**Table S 3.3C, FENL2 under 60\% N loading reduction by hand:**

\[ W_{N,\text{load}} = 143336, \quad W_{P,\text{load}} = 26330, \quad N/P = 5.4 \]

\[ Re = \frac{q_s}{q_s + v_s} \quad \text{if } W_{N,\text{load}} \geq W_P r_f \]

\[ = \frac{q_s}{q_s + v_s} \left(1 + f_m \left(\frac{W_P}{W_{N,\text{load}}} r_f - 1\right)\right) \quad \text{if } W_{N,\text{load}} < W_P r_f \]

\[ W_P r_f = 26330 \times 10.2 = 268566 > W_{N,\text{load}}, \]

\[ Re = \frac{552.7}{552.7 + 5.91} \left(1 + 0.25 \left(\frac{26330}{143336} 10.2 - 1\right)\right) = 1.21 \]

\[ W_{N,\text{exp}} = 143336 \times 1.21 = 172897 \text{ kg/yr} \]

Compare to FENL2 predicted (in Table S5 C):

\[ W_{N,\text{exp}} = 172757 \text{ kg/yr} \]
3.6.5 Code modification

```sas
/* Program: sparrow.sas
   Written by: Greg Schwarz
   Modified by: Xiaodan Ruan */

1. In the control file “tn02v7_f_2013.sas”, define two new variables:

```sas
/*phosphorus load variable*/
%let fenlvar = fenl;
/*reach type variable*/
%let fenltype = reachtype;
```

2. In the file “sparrow_makemacros.sas”, add the variables to
   1) the model_summary, give display names to the variables,

```sas
put "FENLVAR: &fenlvar" ;
put "FENLTYPE: &fenltype";
```

2) the list of indata variables “variable_list”,

```sas
/* Make list of indata variables */

   %let variable_list = &waterid &arcid &optional_reach_information
   &fnode &tnode &hydseq &inc_area &tot_area &mean_flow &frac &iftran
   &target &ls_weight &staid &optional_station_information &lat &lon
   &depvar &srcvar &dlvvar &decvar &resvar &othvar &fenlvar &fenltype ;
```

3) the “addlist” to be read

```sas
/* Make list of variables to be read from the SAS indata data set and
   loaded into a matrix. */

   %let addlist = &depvar &srcvar &dlvvar &decvar &resvar &othvar
```
4) the list of vectors to be declared as global “globvar” in the feval module in the file “sparrow_predict.sas”,

```sas
/* Make a list of vectors to be declared as global in the feval module */
%let globvar =
data,node,obsloc,nreach,nnode,nobs,ndef,est,if_final_pass,weights,
jncnstrn,jfnode,jtnode,jfrac,jtarget,jiftran,jdepvar,jdlvvar, jdecvar, jresvar, jsrvcvar, jbdlvvar,jbdecvar,jbresvar,jbsrcvar,jwaterid,jstaid,jtota
rea,dlvdsgn,jfenlvar, jbfenlvar, jbfenlvar2, jfenltype ;
```

5) the column reference vectors “makecol”,

```sas
/* Assign a list of column reference vectors (used in proc iml) */
%let makecol =
...
%let jfenlvar = %col(datalst,&fenlvar) %str(;
%let jfenltype = %col(datalst,&fenltype) %str(;
...
```

3. Modify the lake/reservoir lake loss formula in the file “sparrow_calibration.sas”,

```sas
Purpose: Macro calibrates a sparrow model.
/* Macro calibrates the model */
%macro calibrate ;
  %let flag_zero_load = 0 ;
  %let n_npos_load = 0 ;
  proc iml ;
  /* Specify the SPARROW evaluation function that climbs down the...*/
```
reach network, accumulating loads, making comparisons to actual loads at monitored reaches and returning a vector of weighted errors. If the variable if_final_pass is set to one prior to running feval then the function returns a matrix consisting of actual load, predicted load, LN actual load, LN predicted load, error, and weighted error. If the macro variable if_test_calibrate is set to yes the function returns an additional column representing the number of reaches in each monitoring station sub-basin. */

start feval(beta) global(&globvar,error_report,n_npos_flux) ;

if ncol(beta) < ncol(est) then do;
est[jncnstrn] = beta;
beta = est;
end;

/*================================================================***/
if %length(%bquote(&reach_decay_specification)) > 0 %then
rchdcayf = &reach_decay_specification ;
%else rchdcayf = j(nreach,1,1) ;;

/*================================================================***/
if %length(%bquote(&reservoir_decay_specification)) > 0 %then
resdcayf = &reservoir_decay_specification ;
%else resdcayf = j(nreach,1,1) ;;

carryf = data[,jfrac] # rchdcayf # resdcayf ;

/*================================================================***/
if jsrcvar > 0 then do;
%if %length(%bquote(&incr_delivery_specification)) > 0 %then
incddsrc = ((&incr_delivery_specification # data[,jsrcvar]) *
beta[,jbsrcvar]`) ;
%else incddsrc = (data[,jsrcvar] * beta[,jbsrcvar]`) ;;
end;
else incddsrc = j(nreach,1,0) ;

if %upcase(if_test_calibrate) = YES %then %do;
run test_neg(rchdcayf,"Reach Delivery Factor") ;
run test_neg(resdcayf,"Reservoir Delivery Factor") ;
run test_neg(incddsrc,"Incremental Source Delivery") ;
%end ;

e = j(nobs,1,0) ;
e_flag = 0 ;
n_npos_flux = 0 ;
if all(beta[,jbsrcvar] <= 0) then e_flag = 1 ;
	node = j(nnode,1,0) ;
rchld = j(nreach,1,0) ;
rchldT = j(nreach,1,0) ;

carryf = data[,jfrac] # rchdcayf # resdcayf ;
inc_decay = rchdcayf ## .5 ;
/* Climb down the reach network, compute and accumulate incremental rchld */

%if %upcase(&if_accumulate_with_dll) = YES and %upcase(&if_test_calibrate) ^= YES %then %do ;
call modulei('tnode a',ndef,data[,jfnode || jtnode],data[,jiftran],incdds,carryf,data[,jdepvar],e) ;
%end ;
%else %do ;
node = j(nnnode,1,0) ;
i_obs = 1 ;
%if %upcase(&if_test_calibrate) = YES %then n_rch = e ;
do i = 1 to nreach ;
%if %upcase(&if_test_calibrate) = YES %then if i_obs <= nob then n_rch[i_obs,] = n_rch[i_obs,] + 1 ;

/*XDR: Determine the total amount of load loading into the reach before decay;*/
rchldT[i] = incdds[i,1] + data[i,jfrac] * node[data[i,jfnode]] ;

if data[i,jfenltype]=2 then
if rchldT[i,1]< data[i,jfenlvar]*10.2/1.0487708 then
resdcayf[i,] = 1/(1+data[i,jresvar]*beta[jbresvar])#(1 + 0.25 *(data[i,jfenlvar] * 10.2 / 1.0487708 /rchldT[i,1]-1))
else resdcayf[i,] = 1/(1+data[i,jresvar] * beta[jbresvar]`) ;
else resdcayf[i,] = j(nreach,1,1) ;

/* XDR: Expand carryf to include decay factor for all columns */
carryf[i] = carryf[i] # resdcayf[i] ;
inc_decay[i] = inc_decay[i] # resdcayf[i] ;

/* Determine the amount of load leaving the reach */
/* XDR: note: incdds, carryf, data[jtnode] need to be updated as they will be called later*/
incdds [i]= inc_decay[i] # incdds[i] ;

/* Determine the amount of load leaving the reach */
rchld = (incdds[i,] + carryf[i,] * node[data[i,jfnode]]) ;
rchld[i] = incdds[i] + carryf[i]* node[data[i,jfnode]] ;

if data[i,jdepvar] ^= . then do ;
/* Determine the residual for the observation */
%if %upcase(&if_test_calibrate) = YES %then %do ;
if rchld[i,1] <= 0 then do ;
e[i_obs,] = 0 ;
print "Non-positive rchld (" (trim(left(char(rchld))))
") for obs:" (trim(left(char(i_obs)))) " station:" (trim(left(char(data[i,jstaid])))) " at reach ID:" (trim(left(char(data[i,jwaterid])))) ;
print "Ifran:" (trim(left(char(data[i,jiftran]))))
"carryf:" (trim(left(char(carryf[i,])))"Flux upnode:" (trim(left(char(node[data[i,jfnode]],))))) ;
end ;
else e[i_obs,] = log(data[i,jdepvar] / rchld[i,1]) ;
%end ;
%else %do ;
if rchld[i,1] <= 0 then do ;
n_npos_flux = n_npos_flux + 1 ;
if e_flag <= 1 then do ;
x_rprt = &iter || &jter || if_final_pass || data[i,jstaid || jwaterid] || rchld || data[i,jsrcvar] || node[data[i,jfnode],] || incddsrc[i,] || rchdcayf[i,] || resdcayf[i,] || beta ;
if type(error_report) = {u} then error_report = x_rprt ;
else error_report = error_report // x_rprt ;
print "Error Report (Iteration &iter, Seed &jter)" ;
print "A negative value for predicted flux has been detected at a monitored reach." ;
error_report_header = {iter jter if_final_pass &staid &waterid "Predicted flux" &srcvar "Upnode flux" "Incremental delivered flux" "Instream attenuation factor" "Reservoir attenuation factor" &betalst} ;
print (error_report_header`) (x_rprt`) ;
end ;
rchld [i,1] = . ;
end ;
e[i_obs,] = log(data[i,jdepvar] / rchld[i,1]) ;
%end ;
/* Set the reach load to the observed value for further accumulation downstream */
rchld [i,1] = data[i,jdepvar] ;
i_obs = i_obs + 1 ;
end ;
node[data[i,jtnode]] = node[data[i,jtnode]] + data[i,jiftran] * rchld[i,1] ; /* Accumulate load to nodes */
end ;
%end ;
f = sqrt(weights) # e ;

if if_final_pass = 1 then do ;
lactual = log(data[obsloc,jdepvar]) ;
lpredict = lactual - e ;
lpredyld = lpredict - log(data[obsloc,jtotarea]) ;
f = data[obsloc,jdepvar] || exp(lpredict) || lactual || lpredict || lpredyld || e || f ;
end ;
%if %upcase(&if_test_calibrate) = YES %then f = f || n_rch ; ;
4. Modify the lake/reservoir decay formula in “sparrow_predict” file

Purpose: Macro predicts loads for all reaches in a sparrow model.

%macro predict ;
  %if &sysver >= 9.0 %then %do ;
    %if %symexist(if_exclude_inc_decay) = 0 %then %let if_exclude_inc_decay = no ;
    %end ;
  %else %let if_exclude_inc_decay = no ;
  proc iml ;
    /* Specify the evaluation function */
    start feval_predict(beta) global(&globvar,mean_exp_weighted_error) ;
    /* Compute the reach decay factors */
    %if %length(%bquote(&reach_decay_specification)) > 0 %then
      rrchdcayf = &reach_decay_specification ;
    %else
      rrchdcayf  = j(nreach,1,1) ;;
    /* Compute the reservoir decay factors */
    %if %length(%bquote(&reservoir_decay_specification)) > 0 %then
      resdcayf = &reservoir_decay_specification ;
    %else
      resdcayf = j(nreach,1,1) ;;
    /* Compute the incremental delivered and decayed sources */
    if jsrcvar > 0 then do ;
      %if %length(%bquote(&incr_delivery_specification)) > 0 %then
        incddsdc = &incr_delivery_specification # data[,jsrcvar] # beta[,jbsrcvar] ;
      %else
        incddsdc = data[,jsrcvar] # beta[,jbsrcvar] ;;
    end ;
    else incddsdc = j(nreach,1,0) ;;
    /* Build incremental delivered loads, total and by source */
    incdds = incddsdc[,] || incddsdc ;
    n_src = ncol(incdds) ;
    n_vars = 2*ncol(incdds)+1;
/* Compute incremental decay - the decay applied to incremental load to get incremental load leaving the reach */
/* inc_decay = rchdcayf ** .5 # resdcayf ;*/

/* XDR: Compute incremental decay for streams*/
inc_decay = rchdcayf ** .5;

/* Pre-concatenate incremental delivered loads (delivered to the reach outlet) to incremental delivered loads (to the reach - without instream decay), and append a vector of zeros for the total load decayed in reservoirs */
/* incddsrc = inc_decay # incddsrc || incddsrc ||
j(nreach,1,0) ;*/
/* n_vars = ncol(incddsrc) ;*/
incddsrc = incddsrc || incddsrc || j(nreach,1,0) ;

/* Initialize variables */
node = j(nnode,n_vars,0) ;
rchld = j(nreach,n_vars,0) ;
rchldT = j(nreach,1,0) ;
Nfix = j(nreach,1,0) ;

/* Initialize adjustment of load placed in downstream node for if_adjust = yes case */
adjust_load = j(1,n_src,1/mean_exp_weighted_error) || j(1,n_vars - n_src,1) ;

/* Expand carryf and iftran to cover all columns */
/* carryf = repeat(data[,jfrac] # rchdcayf # resdcayf,1,n_src) ||
repeat(data[,jfrac],1,n_src + 1) ;*/
carryf = repeat(data[,jfrac],1,n_src) || repeat(data[,jfrac],1,n_src + 1) ;
iftran = repeat(data[,jiftran],1,n_src) || j(nreach,n_src + 1,1) ;

/* Climb down the reach network, compute and accumulate incremental rchld. Note, the concept of transfer of load downstream for reaches with no flow is that load is delivered to the stream but that there is no flow at the stream outlet. Therefore, the stream has load, but none of this load is transferred to the downstream node. For delivery (see below), we retain the interpretation that flow is zero at the downstream node so the reach does not deliver any load to a downstream estuary. */

do i = 1 to nreach ;

/*XDR: Determine the amount of load loading into the reach */
rchldT[i,1] = incddsrc[i,1] + data[i,jfrac] # node[data[i,jfnode],1] ;
/* data[i,jfenlvar] = data[i,jfenlvar] * 0.4 ;*/
if data[i, jfenltype] = 2 then 
if rchldT[i, 1] < data[i, jfenlvar] * 10.2 / 1.0487708 then 
  /* if data[i, jfenlvar] > 0 then */ 
  resdcayf[i,] = 1 / (1 + data[i, jresvar] * beta[jresvar]) * (data[i, jfenlvar] * 10.2 / 1.0487708 / rchldT[i, 1] - 1)); 
else resdcayf[i,] = 1 / (1 + data[i, jresvar] * beta[jresvar])); 
else resdcayf = j(nreach, 1, 1); 

if resdcayf[i,] = 0 then resdcayf = j(nreach, 1, 1); 

/* XDR: Expand carryf to include decay factor for all columns */
/* note: there is no non-decay in carryf */
carryf[i,] = carryf[i,] # rchdcayf[i,] # resdcayf[i,];
inc_decay[i,] = inc_decay[i,] # resdcayf[i,];

/* Determine the amount of load leaving the reach */
node[data[i, jfnode],]; */
rchld[i,] = inc_decay[i,] # incddsrc[i,] + carryf[i,] # node[data[i, jfnode],]; 

Nfix[i, 1] = 0.25 * (data[i, jfenlvar] * 10.2 / 1.0487708 - rchldT[i, 1]); 
if Nfix[i, 1] < 0 then Nfix[i, 1] = 0; 

/* If test mode is on for prediction, output intermediate results */
%if %upcase(&if_test_predict) = YES %then %do ;
  if any(i = &test_obs) then do ;
    test = data[i,] || rchdcayf[i,] || resdcayf[i,] || incddsrc[i,] || node[data[i, jfnode],]; 
    if type(test_out) = {u} then test_out = test ;
    else test_out = test_out // test ;
  end ;
%end ;

/* Determine load lost in reservoirs (column nvars). Note, this estimate does not accumulate downstream. Load lost in reservoir - Load entering reservoir - Load leaving reservoir = Load lost in reservoir * resdecayf Therefore, Load lost in reservoir = Load entering reservoir * (1 - resdecayf) = (Load leaving reservoir / resdecayf) * (1 - resdecayf) */
rchld[i, n_vars] = ((1 / resdcayf[i,]) - 1) # rchld[i, 1];
%if %upcase(&if_adjust) = YES %then %do ;
  if data[i, jdepvar] ^= . then do ;
    rchld[i, 1:n_src] = (data[i, jdepvar] / rchld[i, 1]) * rchld[i, 1:n_src];
    node[data[i, jtnode],] = node[data[i, jtnode],] + iftran[i,]
# adjust_load # rchld[i,]; /* Accumulate load to nodes */
  end ;
else node[data[i,jtnode],] = node[data[i,jtnode],] + 
iftran[i,] # rchld[i,]; /* Accumulate load to nodes */
%end;
%else %do;
node[data[i,jtnode],] = node[data[i,jtnode],] + iftran[i,] # rchld[i,]; /* Accumulate load to nodes */
%end;
end;

if type(test_out) ^= {u} then do;
testnames = {&datalst rchdcayf resdcayf} ||
({incddsresc_} + {total &srcvar}) ||
({ndincddsresc_} + {total &srcvar}) ||
{incddsres_loss} ||
({node_} + {total &srcvar}) ||
({nd_node_} + {total &srcvar}) || {node_res_loss};
create test_data from test_out [colname = testnames];
append from test_out;
close test_data;
end;

/* Determine the delivery factor and delivered incremental amounts. To do this, we set delivery factors for target reaches (reaches we wish to compute delivery to) to one and then carry the multiplicative decay factors to the upstream node. NOTE, the delivery fraction includes decay within the reach. Thus, incremental load delivered to a target is the incremental load times the delivery fraction. Note that the algorithm must check for a target twice, the first time to set delfrac without the incremental decay. This value of delfrac is used in determining the delivery fraction to be transferred upstream (after multiplication by the full decay in the reach segment). The second time is to adjust the delivery fraction for the incremental decay. */

node = j(nnode,1,0);
delfrac = j(nreach,1,0);

if jtarget > 0 then do;
do i = nreach to 1 by -1;
   if data[i,jtarget] then delfrac[i,] = 1;
   else delfrac[i,] = data[i,jiftran] # node[data[i,jtnode],] ;
   node[data[i,jfnode],] = node[data[i,jfnode],] + delfrac[i,] # carryf[i,1];
%if %upcase(&if_exclude_inc_decay) = YES %then delfrac[i,] = delfrac[i,] # inc_decay[i,] ;;
end;
end;
else delfrac = j(nreach,1,.) ;

/* Concatenate the delivery fraction and incremental loads (total and by source - no stream decay) to reach predictions. */

/* Offset the columns used in the incddssrc if want incremental loads that do not reflect incremental reach decay */
%if %upcase(&if_exclude_inc_decay) = YES %then %let strtindx = n_src +;
%else %let strtindx = ;


rchld = rchld[,1:(n_vars - 1)] || incddsinc[,&strtnde(1:n_src)] || rchld[,n_vars] || delfrac || rchldT ||Nfix ;

return(rchld) ;
finish ;

/* Module determines the column locations within a master list for each element of a row vector search list. If the search element is not in the master list, the column location is given as zero. */

start locin(search_list,master_list) ;
if type(master_list) ^= {u} & type(search_list) ^= {u} then do ;
do i = 1 to ncol(search_list) ;
  if i = 1 then loc_list = loc(master_list = search_list[,i]) ;
  else loc_list = loc_list || loc(master_list = search_list[,i]) ;
end ;
end ;
else loc_list = 0 ;
return(loc_list) ;
finish ;

/* Determine the columns of various variables */
&makecol ;

/* Create the delivery design matrix */
dlvdsign = {&dlvdsign} ;

/* Load the initial parameter estimates */
use boot_betaest ;
read next var {&betalst} into beta ;
read var {mean_exp_weighted_error} into mean_exp_weighted_error ;
close boot_betaest ;

/* Load the data */
use indata ;
read all var {&datalst} into data ;
close indata ;

/* Specify the number of reaches, nodes and observations */
Nreach = nrow(data) ;
Nnode = max(data[,,(jfnode || jtnode)]) ;
OBSloc = loc(data[,jdepvar] ^= .) ;
NObs = ncol(OBSloc) ;

/* Create variable names for labeling output and assign to a macro variable for use elsewhere */
varnames = {total & srcvar} ;
predlst = compress(({pload_} + varnames) || ({pload_nd_} + varnames) || ({pload_inc_} + varnames) || {res_decay} || {delfrac} || {rchldT} || {Nfix}) ;
varnames = compress({&waterid & staid & depvar} || predlst) ;
call symput("predlist",compbl(rowcat(predlst + " ")));  
%if %length(&retrans_exclude_list) = 0 %then %do;  
   exclude_list = 0 ;  
%end ;  
%else %do;  
   exclude_list = locin({&retrans_exclude_list},predlst) ;  
%end ;  
exclude_list = locin({&retrans_exclude_list},predlst) ;  
/* Compute the results. Note that all results except the delivery  
fraction get  
inflated by the retransformation bias factor. */  
retransform_factor = j(1,ncol(predlst),mean_exp_weighted_error) ;  
if any(exclude_list) then retransform_factor[,exclude_list] = 1 ;  
/*  predict = retransform_factor # feval_predict(beta) ;*/  
%if %upcase(&if_adjust) = YES %then %do;  
   j_src = 1:(ncol(jsrcvar) + 1) ;  
   predict[obsloc,j_src] = predict[obsloc,j_src] # (1 /  
retransform_factor[,j_src]) ;  
%end ;  
predict = data[(jwaterid || jstaid || jdepvar)] || predict ;  
/* Output predictions */  
create predict from predict [colname = varnames] ;  
append from predict ;  
close predict ;  
/* Module computes the upstream monitored loads, by source */  
start feval_predict_upmonload(beta) global(&globvar,predict) ;  
/* Compute the reach decay factors */  
%if %length(&bquote(&reach_decay_specification)) > 0 %then  
rchdcayf = &reach_decay_specification ;  
%else rchdcayf = j(nreach,1,1) ;;  
/* Compute the reservoir decay factors */  
%if %length(&bquote(&reservoir_decay_specification)) > 0 %then  
resdcayf = &reservoir_decay_specification ;  
%else resdcayf = j(nreach,1,1) ;;  
n_src = ncol(jsrcvar) + 1 ;  
upload = j(nreach,n_src,0) ;  
nodes = j(nnode,n_src,0) ;  
carryf = data[,jfrac] # rchdcayf # resdcayf ;  
do i = 1 to nreach ;  
   if predict[i,3] = . then do ;  
      upload[i,] = carryf[i] * nodes[data[i,jfnode],] ;  
      nodes[data[i,jtnode],] = nodes[data[i,jtnode],] +  
data[i,jiftran] * upload[i,] ;  
   end ;
else nodes[data[i,jtnode],] = nodes[data[i,jtnode],] + 
data[i,jiftran] * predict[i,4:(n_src + 3)] ;
end ;
return(upload) ;

finish ;

/* Output the upstream monitored loads */

%if %upcase(&if_adjust) = YES %then %do ;
upmonload = data[,jwaterid] || feval_predict_upmonload(beta) ;
varnames = {&waterid} || compress({umpload_} + {total &srcvar}) ;
create upmonload from upmonload [colname = varnames] ;
append from upmonload ;
close upmonload ;
%end ;
quit ;
%mend predict ;
Table S 3.4. Parameters and RMSEs for FENL1($r_f = 10.2$), FENL2 ($r_f = 10.2, f_m = 0.25$) and SPARROW.

<table>
<thead>
<tr>
<th></th>
<th>FENL1</th>
<th></th>
<th>FENL2</th>
<th></th>
<th>SPARROW</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vs</td>
<td>RMSE</td>
<td>vs</td>
<td>RMSE</td>
<td>vs</td>
<td>RMSE</td>
</tr>
<tr>
<td>Impoundment Rietvlei</td>
<td>25.00</td>
<td>4.130</td>
<td>25.00</td>
<td>0.272</td>
<td>0</td>
<td>0.465</td>
</tr>
<tr>
<td>Gr. Mueggelsee</td>
<td>7.53</td>
<td>0.065</td>
<td>7.51</td>
<td>0.065</td>
<td>7.5</td>
<td>0.065</td>
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<tr>
<td>Harp Lake</td>
<td>2.70</td>
<td>0.115</td>
<td>2.70</td>
<td>0.115</td>
<td>2.7</td>
<td>0.115</td>
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<tr>
<td>Lake 227</td>
<td>25.00</td>
<td>0.629</td>
<td>25.00</td>
<td>0.313</td>
<td>25.00</td>
<td>0.313</td>
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<tr>
<td>Lake Kinneret</td>
<td>18.68</td>
<td>0.046</td>
<td>17.29</td>
<td>0.049</td>
<td>17.13</td>
<td>0.054</td>
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<tr>
<td>Ana. Mod. BG-11 a</td>
<td>-</td>
<td>0.954</td>
<td>-</td>
<td>3.734</td>
<td>-</td>
<td>4.771</td>
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<tr>
<td>Ana. Mod. BG-11 b</td>
<td>-</td>
<td>0.725</td>
<td>-</td>
<td>1.092</td>
<td>-</td>
<td>1.241</td>
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<tr>
<td>Ana. Auto. Charles</td>
<td>-</td>
<td>1.414</td>
<td>-</td>
<td>1.813</td>
<td>-</td>
<td>1.950</td>
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<tr>
<td>Nat. Natural Charles</td>
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<td>1.745</td>
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<td>Nat. Mod. BG-11</td>
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<td>0.991</td>
<td>-</td>
<td>2.212</td>
<td>-</td>
<td>2.634</td>
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<tr>
<td>Coralville Res</td>
<td>25.00</td>
<td>1.798</td>
<td>25.00</td>
<td>0.450</td>
<td>25.00</td>
<td>0.001</td>
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<tr>
<td>Cheney Res</td>
<td>9.88</td>
<td>0.018</td>
<td>7.22</td>
<td>0.045</td>
<td>6.62</td>
<td>0.071</td>
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<tr>
<td>Lake George</td>
<td>9.45</td>
<td>0.091</td>
<td>9.43</td>
<td>0.092</td>
<td>9.42</td>
<td>0.093</td>
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<tr>
<td>Lake Jesup</td>
<td>18.96</td>
<td>0.120</td>
<td>0.00</td>
<td>1.746</td>
<td>0</td>
<td>3.319</td>
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<tr>
<td>Lake Pyhajarvi</td>
<td>25.00</td>
<td>0.213</td>
<td>11.71</td>
<td>0.103</td>
<td>6.37</td>
<td>0.013</td>
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<tr>
<td>Onondaga lake</td>
<td>25.00</td>
<td>2.134</td>
<td>25.00</td>
<td>0.520</td>
<td>25.00</td>
<td>0.065</td>
</tr>
<tr>
<td>Overall</td>
<td>17.47</td>
<td>0.98</td>
<td>14.17</td>
<td>1.07</td>
<td>13.32</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Table S 3.5. Parameter estimates for SPARROW, FENL1 and FENL2

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>SPARROW</th>
<th>FENL1</th>
<th>FENL2</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sources</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Point sources (kg yr(^{-1}))</td>
<td>0.774</td>
<td>0.758</td>
<td>0.765</td>
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<tr>
<td>Cropfertilizer and fixation (kg yr(^{-1}))</td>
<td>0.237</td>
<td>0.239</td>
<td>0.238</td>
<td></td>
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<tr>
<td>Manure (kg yr(^{-1}))</td>
<td>0.0582</td>
<td>0.056</td>
<td>0.058</td>
<td></td>
</tr>
<tr>
<td>Atmospheric deposition (kg yr(^{-1}))</td>
<td>0.267</td>
<td>0.251</td>
<td>0.261</td>
<td></td>
</tr>
<tr>
<td>Urban (km(^2))</td>
<td>1.094</td>
<td>1039</td>
<td>1090</td>
<td>kg km(^2) yr(^{-1})</td>
</tr>
<tr>
<td>Land-to-water delivery</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ln[Mean EVI for WY02 dimensionless]</td>
<td>-1.70</td>
<td>-1.70</td>
<td>-1.69</td>
<td></td>
</tr>
<tr>
<td>ln[Groundwater recharge (mm)]</td>
<td>0.707</td>
<td>0.731</td>
<td>0.712</td>
<td>mm</td>
</tr>
<tr>
<td>ln[Mean soil AWC (fraction)]</td>
<td>-0.829</td>
<td>-0.907</td>
<td>-0.854</td>
<td></td>
</tr>
<tr>
<td>ln[Piedmont carbonate (percent of area)]</td>
<td>0.158</td>
<td>0.159</td>
<td>0.159</td>
<td></td>
</tr>
<tr>
<td>Aquatic decay</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impoundments, inverse hydraulic load (yr m(^{-1}))</td>
<td>5.93</td>
<td>6.28</td>
<td>5.91</td>
<td>m yr(^{-1})</td>
</tr>
<tr>
<td>(r_f)</td>
<td>-</td>
<td>10.2*</td>
<td>10.2*</td>
<td></td>
</tr>
<tr>
<td>(f_m)</td>
<td>-</td>
<td>-</td>
<td>0.25*</td>
<td></td>
</tr>
<tr>
<td>Streams, time of travel (d) in:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small (MAQ ≤ 3.45 m(^3) s(^{-1}))</td>
<td>0.339</td>
<td>0.306</td>
<td>0.330</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Large (MAQ &gt; 3.45 m(^3) s(^{-1}), T30 &gt; 18.5°C)</td>
<td>0.153</td>
<td>0.158</td>
<td>0.156</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>Large (MAQ &gt; 3.45 m(^3) s(^{-1}), T30 ≤ 15°C)</td>
<td>0.0131</td>
<td>0.008</td>
<td>0.011</td>
<td>d(^{-1})</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.2892</td>
<td>0.2879</td>
<td>0.2886</td>
<td></td>
</tr>
</tbody>
</table>

* Not optimized.
Figure S 3.2. Comparison of SPARROW, FENL1 and FENL2 to microcosm lab experiments. *A. flos-aquae* in modified BG-11 a
Figure S 3.3, Comparison of SPARROW, FENL1 and FENL2 to microcosm lab experiments. *A. flos-aquae* in modified BG-11 b
Figure S 3.4. Comparison of SPARROW, FENL1 and FENL2 to microcosm lab experiments. *A.flos-aquae* in autoclaved Charles River water
Figure S 3.5. Comparison of SPARROW, FENL1 and FENL2 to microcosm lab experiments. Natural assemblage in natural Charles River water
Figure S 3.6. Comparison of SPARROW, FENL1 and FENL2 to microcosm lab experiments. Natural assemblage in autoclaved Charles River water.
Figure S 3.7. Comparison of SPARROW, FENL1 and FENL2 to microcosm lab experiments. Natural assemblage in modified BG-11
Figure S 3.8. Comparison of SPARROW, FENL1 and FENL2 to lake field observations/budgets. Impoundment Rietvlei
Figure S 3.9. Comparison of SPARROW, FENL1 and FENL2 to lake field observations/budgets. Gr. Mueggelsee
Figure S 3.10. Comparison of SPARROW, FENL1 and FENL2 to lake field observations/budgets. Harp Lake
Figure S 3.11. Comparison of SPARROW, FENL1 and FENL2 to lake field observations/budgets. Lake 227
Figure S 3.12. Comparison of SPARROW, FENL1 and FENL2 to lake field observations/budgets. Lake Kinneret
Figure S 3.13. Comparison of SPARROW, FENL1 and FENL2 to AQUATOX applications. Cheney Res.
Figure S 3.14. Comparison of SPARROW, FENL1 and FENL2 to AQUATOX applications. Coralville Res.
Figure S 3.15. Comparison of SPARROW, FENL1 and FENL2 to AQUATOX applications. Lake George
Figure S 3.16. Comparison of SPARROW, FENL1 and FENL2 to AQUATOX applications. Lake Jesup
Figure S 3.17. Comparison of SPARROW, FENL1 and FENL2 to AQUATOX applications. Lake Pyhajarvi
Figure S 3.18. Comparison of SPARROW, FENL1 and FENL2 to AQUATOX applications. Onondaga Lake
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4.1 Summary and conclusions

This research quantifies the effect of lake and reservoir N fixation on watershed N export under N loading reduction scenarios. The hypothesis is that lake and watershed N export is not reduced proportionally when N loading is reduced. The hypothesis was tested by analysis of data from three approaches: microcosm lab experiments, lake field observations/budgets and lake ecosystem model applications. Then a model with two versions, Fixation and Export of Nitrogen from Lakes (FENL1 and FENL2) was developed and parameterized against the dataset from the three approaches. The models were then incorporated into a full watershed model, Chesapeake Bay SPARROW and applied to the Chesapeake Bay watershed. Three models: SPARROW (no change in N fixation), FENL1 (N fixation at a level that balances the N deficit) and FENL2 (N fixation at a reduced level) are calibrated against the dataset of Chesapeake Bay watershed observations. From management perspective, the three models can also be consider as “best case”, “worst case” and “best estimate” accordingly. SPARROW, FENL1 and FENL2 are then used to evaluate three scenarios: baseline, 60% N loading reduction and 60% N+P loading reduction. The main conclusions of this study are:

(1) The relationship between N loading and export to/from lakes is not linear, as assumed in existing models. When N loading is reduced, N fixation will counteract the reduction and N export will not be reduced proportionally.
(2) At the watershed scale the effect of lake and reservoir N fixation under N loading reduction scenarios is significant. Specifically, the results of the Chesapeake Bay watershed application show that from the management perspective, for a 60% N loading reduction, the realized export reduction is 60% for the best case (SPARROW), 43% for the worst case (FENL1) and 50% for the best estimate (FENL2). Obtaining these quantitative estimates was the main objective of the research (Figure 1.1). The magnitude of this effect of lake N fixation is substantial at the watershed scale, especially when only N loading is reduced. This result is specified to Chesapeake Bay watershed and may be different from watersheds with more or less lakes, or different N/P loading ratios, or other factors that may affect N fixation.

(3) The general conclusion is that, at the watershed scale, N export will not be reduced proportionally under an N only reduction scenario. In order to achieve a proportional amount of N export from the watershed, P loading needs to be reduced as well. Both FENL models predict that any amount (in percentage) of N+P loading reduction will result in the same amount (in percentage) of N export reduction.

4.2 Contribution

This work has significant implications for watershed management. Coastal eutrophication is an important environmental and economic problem and the cost of management actions is projected to be substantial. It is important to develop effective management plans. Ineffective or inaccurate management decision can waste money and/or may fail to achieve the desired improvement to the coastal water quality.
Watershed models are important tools to relate management actions to watershed export. A number of watershed models have been developed, but they do not explicitly account for lake and reservoir N fixation, which may increase and counteract management actions. This research quantified this effect by analyzing data from microcosm lab experiments, lake field observations/budgets, and lake ecosystem model applications. A model (FENL2) was developed, implemented into SPARROW, calibrated, and then applied to the Chesapeake Bay watershed to evaluate the management strategies. To my knowledge, this is the first model that estimates the effect of lake N fixation at the watershed scale under N loading reduction scenarios. The results suggest that watershed N export will not be reduced proportionally under a N only reduction scenario due to the effect of lake N fixation, but will be reduced proportionally under a balanced N+P reduction scenario. The results of this research are a significant contribution to the coastal water eutrophication management decision making process.

### 4.3 Future work

The model was applied to Chesapeake Bay and the quantitative estimates are specific to this watershed. Applications of the modified SPARROW model to other watersheds would be useful.

Our analysis is based on steady-state conditions and a natural next step is to consider the time-variable aspects of this problem. Many watersheds are presently experiencing a change in nutrient input due to changes in agriculture, urbanization, wastewater treatment or climate, and often considerable observations are available covering a long time span. Application of the model to these observations would allow for a more direct test of the...
model’s ability to predict watershed behavior under nutrient loading reduction scenarios. It may prompt future refinement, such as including storage in the sediment bed.