Predicting Nitrogen and Phosphorus Concentrations using Chlorophyll-a Fluorescence and Turbidity

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Agricultural practices and land modification introduce excess nutrient and sediment loads into inland watersheds. Modification of tributary streams and rivers within these watersheds decreases the ability of floodplains to respond to increased loads. Therefore, large amounts of nutrients and sediments are transferred to coastal aquatic systems. Aquatic systems are facing increased nuisance algal growth and premature senescence leading to hypoxic conditions, threatening recreational and commercial fish yields. Furthermore, sedimentation and turbidity create intolerant conditions for aquatic organisms, and can trap phosphorus in these systems. To address these issues, states are developing nutrient criteria for inland waters. As inland water bodies are numerous, the usefulness of such criteria is dependent on efficient monitoring. We investigated the potential use of a handheld chlorophyll-a (chl-a) fluorometer as an estimator of total phosphorus (TP) and total nitrogen (TN) in oxbow lakes of the Mississippi Alluvial Valley. Several adjustments were explored to improve the ability of the fluorometer to accurately represent chl-a. Past studies in Mississippi lakes have shown a poor relationship between TP and chl-a (r^2 = 0.18), but a moderate relationship between TN and chl-a (r^2 = 0.53). The poor TP-chl-a relationship is partially attributable to naturally high levels of phosphorus and turbidity in the region. We found the relationships between chl-a and nutrient concentrations were improved in oxbow lakes; adding covariates such as turbidity and suspended solids further improved predictability. Estimating TP and TN with in-situ handheld-meter measurements of chl-a supplemented with measures of suspended solids may, in many cases, be adequate for temporal or spatial monitoring of nutrients in oxbow lakes.

Introduction

High sedimentation and nutrient loading is a major issue leading to undesirable water quality conditions, especially in extensive agricultural systems (Turner and Rabalais 2003). Eutrophication in both inland and coastal systems has shown to be deleterious to aquatic ecosystem functioning (Dodds and Whiles 2010). Controlling excess nutrients such as phosphorus and nitrogen can slow eutrophication, but is difficult due to their ubiquitous presence in the landscape. With the development of regional and state specific nutrient criteria to meet EPA regulations and promote well-functioning ecosystems and maintain waters for designated uses, monitoring efforts will be an essential need for water quality programs and will aid in better understandings of nutrient movement across the landscape over time. In the Mississippi Alluvial Valley (MAV), high ranges in observed nutrient conditions can be even more challenging to understand as they may often produce desirable ecological communities (FTN Associates 2007). There are hundreds of small water bodies scattered across the MAV, and, because of this abundance, monitoring each individual body can be expensive and impractical. Predicting nutrient concentrations through monitoring of alternate parameters may provide a way to reduce such costs.

Measuring a response variable such as phytoplankton biomass, which could represent an elevated nutrient concentration, can make monitoring more efficient. Phytoplankton-nutrient relationships for both phosphorus and nitrogen are well established (Dillon and Rigler 1974; Jones and Bachmann 1976; Watson et al. 1992; Brown et al. 2000; Jones and Knowlton 2005; Phillips et al. 2008). In Mississippi, however, these relationships across all types of lentic systems are poor (FTN Associates 2007). Turbidity is a major factor that may contribute to these poor relationships, especially in small and shallow oxbow lakes. Regional soil minerology and composition not only contributes to the naturally high phosphorus levels in the region, but also limits phytoplankton growth due to reduced light conditions (McDowell et al. 1989; Knowlton and Jones 1996; Sobolev et al. 2009). Estimates of both phytoplankton and suspended solids can be obtained instantaneously with handheld meters. Simultaneously collected parameters, including those that affect phytoplankton growth or nutrient cycling, may be used as covariates in predicting nutrient concentrations. The combination of a few select covariates can provide predictive models for nutrient concentrations that optimize lentic monitoring efforts.

To reduce costs associated with monitoring of numerous oxbow lakes in the MAV, we set out to achieve three objectives:

1. Assess the relationship between field estimates and lab measurements of suspended solids and primary productivity (via chlorophyll-a).
2. Assess the relationship between nutrients and easily obtained field measurements of chlorophyll-a fluorescence, turbidity, Secchi depth, water temperature, maximum depth, dissolved oxygen, pH, and alkalinity.
3. Determine if surrogate measures of chlorophyll-a and suspended solids are appropriate for predicting phosphorus and nitrogen concentrations in oxbow lakes.

Methods

Thirty oxbow lakes were sampled during June and July of 2011. Ten 1-L surface (< 0.5 m) subsamples were collected from open-water areas in each lake and combined for a composite sample. Secchi depth was measured with a standard 0.2-m Secchi disk. Standard measurements of surface temperature, dissolved oxygen (DO), and pH were also measured using a YSI 556 multiprobe (YSI Inc., Yellow Springs, OH). Overall maximum depth of each lake was recorded.

Immediately upon return to shore, the turbidity (NTU) and relative fluorescence (RFU) of the composite sample were measured using portable handheld meters (2100p, HACH and Aquafluor 8000, respectively). Signal averaging mode was used on the turbidimeter; the first reading of the sample was used for the fluorometer. Alkalinity was estimated using LaMotte test kit number 9844-01 (LaMotte, Chestertown, MD). Approximately 150 ml of the sample was filtered through a 0.45-μm glass-fiber filter. The residual filter was folded and placed in aluminum foil within a sealed plastic bag. The bag and 4-L of sample was stored on ice for transport Mississippi State University. Upon arrival, 1-L of the sample was used for suspended solid analysis, using standard methods for total suspended solids (TSS) (APHA 1998). The remaining 3-L of the composite water sample and the residual filter for chlorophyll-a analysis was frozen at -20oC for future analyses. Chlorophyll-a was analyzed, after overnight extraction in 90% buffered acetone, using standard methods (Tri-colorometric; APHA 1998) with a HACH DR5000 spectrophotometer. Frozen composite water samples were transported on ice to USDA-ARS National Sedimentation Laboratory in Oxford, Mississippi for total phosphorus (TP) and total kjehldahl nitrogen (TKN) analysis.

Simple linear regression was used to compare NTU and RFU to their analytical equivalent, TSS and chlorophyll-a. Once linear relationships were confirmed, meter estimates were used, along with a suite of other limnological variables (maximum depth, alkalinity, surface and mid epilimnetic temperature, DO and pH) to determine the best correlations with TKN and TP. The highest correlated variables were used in a multiple regression model to predict TKN and TP. Variables were transformed with natural logarithms when necessary to straighten curvilinear relationships.

Results

The relationship between NTU and TSS was linear and had a coefficient of determination (R^2) of 0.77 (Table 1). The relationship between RFU and chlorophyll-a was log-linear and had a R^2 of 0.81 (Table 1), after removal of one outlier lake that had a noticeable cyanobacteria algal bloom at the time of sampling. Therefore, NTU and RFU were used in place of TSS and chlorophyll-a concentration in further model development.

Correlations between TP, TKN, and various field limnological measurements ranged from 0.01 to 0.87 (Table 2). An outlier at an extremely clear, yet highly enriched, lake was removed from analysis. The highest correlations were found between nutrients, chlorophyll-a fluorescence, and turbidity; therefore, these variables were used to create predictive models for TP and TKN using multiple regression. A multiple regression model was established to predict TP from NTU and RFU measurements. We chose not to include Secchi depth as a predictor variable due to its subjectivity and user bias when an alternate measure of water clarity and suspended solids was available. As correlations between field measurements and TKN were lower than between field measurements and TP, we used our model for TP to further predict TKN, which indirectly incorporates NTU and RFU. The final models for TP and TKN are shown in Table 1.

Discussion

The handheld meters used in this study provided estimates of surface suspended solids and chlorophyll-a that were satisfactory ($p<0.05$; $r>0.85$) for use. Correlations between nutrient concentrations and both NTU and RFU were higher than any other standard field measurements tested. High correlation ($r=0.85$) between chlorophyll-a (as estimated through RFU) and TP was contrasted from a previously low correlation ($r=0.42$) found in lakes and reservoirs in Mississippi (FTN Associates 2007). The chlorophyll-a and TKN relationship was not improved ($r=0.68$ in our study; $r=0.73$ previously). Based on these results, we suggest that nutrient concentrations may be monitored in oxbow lakes through the use of both a turbidity and chlorophyll-a estimation made with field meters. While RFU is partially dependent on NTU, we included both to improve the predictability of TP across multiple combinations of these parameters represented in MAV lakes. Nitrogen concentrations are not as tightly correlated with these estimations, and therefore further work may be necessary to incorporate additional covariates. However, TKN was closely correlated with TP ($r=0.83$), which has been found to be true in other systems (Bachmann 1980; Jones and Knowlton 2005). We used this relationship to provide a limited prediction model for TKN.

Oxbow lakes in the MAV have become highly eutrophic, and as such, diminishing clarity and high algal content often leads to lower perceived value in the resource (Cooper et al. 2003). Ecological changes such as eutrophication warrant the need for more frequent monitoring, especially in systems where there are nutrient criteria to be met. Using biotic and abiotic parameters that can be quickly and inexpensively obtained can save expenses traditionally used for sparse nutrient concentration analysis. While use of these parameters directly in regulations would be ideal, our models may help predict whether nutrient levels are within compliance. Furthermore, these estimations of nutrients can help redirect efforts towards monitoring and understanding how a response variable changes as a result of other factors. However, these models should only be used in shallow oxbow lakes of the MAV, and should be used with caution especially with lakes known to contain unusual trophic characteristics. Sampling events should make note of extreme algal blooms, and estimations of chlorophyll-a may need to be confirmed with laboratory analysis or additional sampling.

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Table 1: Regression models for handheld meters and laboratory analysis and for nutrient concentration prediction in oxbow lakes of the Mississippi Alluvial Valley. All models significant ($p \leq 0.05$).Total phosphorus* = predicted mg/L from TP model.

Regression models	R^2
Total suspended solids (mg/L) = 8.31 + 0.68 × Turbidity (NTU)	0.77
Chlorophyll-a (µg/L) = e-2.31 × Fluorescence (RFU)$^{1.17}$	0.81
Total phosphorus (µg/L) = 87.7 + 1.69 × Turbidity (NTU) + 0.22	0.89
Total kjehldahl nitrogen (mg/L) = 3.97 + 1.41 × log (Total phosphorus*)	0.59

Table 2: Correlation coefficients (r) for nutrients and common limnological measurements in 29 oxbow lakes of the Mississippi Alluvial Valley. S=surface measurements; m=mid epilimneon measurements. * Denotes significance ($p \leq 0.05$). + Denotes relationship with loge(TP).

Parameter	TKN	TP
Log_e(Total phosphorus)	0.83*	-
Turbidity (NTU)	0.71*	0.87*
Log(Secchi depth)	-0.76*	-0.83*
Fluorescence (RFU)	0.68*	0.85*+
Alkalinity	-0.57*	-0.35
Log_e(Maximum depth)	-0.53*	-0.63*+
Log_e(s Dissolved oxygen)	-0.11	-0.29
s pH	0.01	-0.18
s Temperature	-0.13	-0.25
Log_e(m Dissolved oxygen)	-0.2	-0.2
m pH	0.11	0.07
m Temperature	-0.22	-0.21