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Effects of internal phosphorus loading on nutrient limitation in a eutrophic reservoir

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ABSTRACT

While lake and reservoir management has historically focused on controlling external nutrient loads to improve water quality, internal mechanisms can also contribute to the processes of eutrophication. We assessed how the release of phosphorus (P) from anoxic sediments in the hypolimnion of a eutrophic reservoir affected epilimnetic nutrient concentrations and ratios. We also conducted nutrient bioassay experiments to determine if water column total nitrogen:total P (TN:TP) ratios could be used to predict nutrient limitation in the reservoir. We estimated that anoxic sediments from the lacustrine zone of the reservoir released 7.1 mg P/m^2/day into the reservoir during stratification. This internal load was an important source of P to the epilimnion of the reservoir that helped to lower TN:TP ratios and create N limiting conditions following thermocline erosion. With respect to the enrichment bioassays, we found that nutrient limitation varied both spatially and temporally in the reservoir with observed periods of no nutrient limitation, N limitation, P limitation, and N and P co-limitation. However, corresponding water column TN:TP ratios correctly identified the limiting nutrient in less than 50% of the nutrient bioassays. As such, total nutrient ratios should be used with caution when trying to predict nutrient limitation in individual systems.

Introduction

Cultural eutrophication is the process by which nutrients from anthropogenic origins (mainly nitrogen [N] and phosphorus [P]) enter the environment and stimulate primary production (Smith and Schindler, 2009). In freshwater systems, symptoms of eutrophication include changes in algal community structure (Smith, 1983), food web shifts (Elser et al., 2000), harmful algal blooms (Paerl et al., 2011), and reductions in oxygen as a result of aerobic decomposition (Antoniades et al., 2011). Manifestations of these symptoms not only degrade water quality for biota, but also result in economic losses to property values and recreational revenues (Dodds et al., 2009).

Eutrophication management has historically focused on reducing external nutrient loads (Sas, 1989). However, as nutrients are introduced into a lake or reservoir through erosion and runoff, they build up in the sediment creating the potential for an internal load that can be released back into the water column under differing environmental conditions (Carpenter et al., 1998). The internal release of nutrients from sediments is often associated with anoxia (see Hupfer and Lewandowski, 2008) where P release occurs through the redox-mediated reduction of iron in phosphate binding iron hydroxides. Previous work has shown that sedimentary P release can range from 1 to 50 mg P/m^2/day in eutrophic and hypereutrophic lakes and reservoirs (Nürnberg, 1988; Carter and Dzialowski, 2012). Anoxia can also influence N concentrations in lakes and reservoirs. Nitrate reduction is a bacterially mediated, anoxic process that occurs in sediments where nitrate is reduced to ammonium. This process is of ecological importance because it provides N in a dissolved form that is available for biological uptake (Tomaszek and Gruca-Rokosz, 2007). Denitrification is also a bacterially mediated, anoxic process but it acts as an N sink because it reduces nitrate to nitrogen gas. For example, David et al. (2006) showed that 58% of annual nitrate inputs into Lake Shelbyville, Illinois were removed by denitrification (David et al., 2006).

The release of nutrients from sediments under anoxic conditions has the potential to alter water column nutrient concentrations and ratios (e.g. total N:total P [TN:TP]) if they reach the epilimnion through diffusion and/or water column mixing (Nürnberg, 1985). Changes in N and/or P availability and, hence the nutrient status of the phytoplankton, can be indicated by changes in

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the TN:TP ratios that can in turn help to determine which nutrient is limiting in a system at a given time. For example, if excess P is released from the sediment relative to N, the system may become N-limited and this may be indicated by a decreased TN:TP ratio. Under these conditions, there is not enough N relative to P to meet the metabolic requirements of phytoplankton production. Furthermore, cyanobacteria can dominate when TN:TP ratios are low because they are able to fix atmospheric N and outcompete other taxa when N is relatively low (Smith, 1983; Havens et al., 2003).

Previous studies have attempted to use water column TN:TP ratios as indicators of nutrient limitation. This approach is appealing because it allows for the rapid estimation of the limiting nutrient without labor intensive bioassay experiments. While some studies have used the Redfield ratio (C:N:P, 41:7:1; all ratios reported as mass) to predict nutrient limitation (Wang and Wang, 2009), others have modified these ratios (e.g., Sakamoto, 1966; Downing and McCauley, 1992). For example, Guildford and Hecky (2000) suggested that TN:TP > 22 indicated P limitation, TN:TP < 9 indicated N limitation, and TN:TP between 9 and 22 indicated N and P co-limitation. The lack of a concise range of ratios to predict nutrient limitation across systems is not surprising considering the variance in TN:TP ratios between algal species (Klausmeler et al., 2004). This uncertainty has been demonstrated when water column TN:TP ratios were compared to corresponding nutrient enrichment bioassays and failed to consistently predict the correct limiting nutrient (Maberly et al., 2002; Wang et al., 2008; Lv et al., 2011). Kobayashi and Church (2003) found that TN:TP ratios correctly identified the limiting nutrient in only 33% of their bioassay studies in Austrian reservoirs. In contrast, however, Dzialowski et al. (2005) found that TN:TP ratios presented by Guildford and Hecky (2000) correctly predicted 88% of nutrient bioassays in Central Plains reservoirs, USA. The varying success of these studies highlights the importance of testing ranges of TN:TP ratios with corresponding nutrient bioassays before they are used to predict nutrient limitation in individual lakes or reservoirs.

We assessed internal nutrient loading, nutrient limitation, and the relationships between nutrient loading, nutrient limitation, and TN:TP ratios in a large multi-use reservoir, Grand Lake O' the Cherokee (Grand Lake), Oklahoma, USA. We monitored epilimnetic and hypolimnetic nutrient concentrations in the lacustrine zone of the reservoir and used in situ hypolimnetic P increases and hydrographic data to estimate the internal P load. We predicted that as the thermocline eroded and the lake mixed in the late summer, epilimnetic TN:TP ratios would decrease and the reservoir would experience N-limitation due to P inputs from the sediment. We also conducted monthly nutrient bioassay experiments to examine the spatial and temporal variation in nutrient limitation and determine if the ranges of TN:TP ratios proposed by Guildford and Hecky (2000) correctly predicted nutrient limitation.

Methods

Study reservoir

Grand Lake is located in northeast Oklahoma and has a surface area of 188 km^2, a mean depth of 11 m, and a maximum depth of 41 m near the dam (OWRB, 2009). Grand Lake's watershed is dominated by agriculture and includes crop (wheat, corn, hay), livestock (cattle and swine), and poultry production (OWRB, 2007). Grand Lake has been designated as eutrophic with dissolved oxygen and turbidity concentrations not supporting of fish and wildlife propagation standards (OWRB, 2010).

Sampling and nutrient analyses

We sampled the reservoir biweekly from June to October 2011. Samples were collected from five locations that were spaced roughly two miles apart in the thalweg of the lacustrine zone (Fig. 1). Depth profiles of temperature and dissolved oxygen (D.O.) were collected at each site using a YSI© multiparameter probe (Model: 6600 V2®). The epilimnion and hypolimnion were defined on each sampling date as continuous water layers where temperature change was $\leq 1\,^{\circ}$C/m. The depth of the thermocline was defined as the rate of maximum temperature change within the metalimnion. We collected three individual water samples using a Wildco® Van Dorn bottle from both the epilimnion (1 m below the surface, 1 m above the bottom of the epilimnion, and midpoint) and the hypolimnion (1 m below the top of the hypolimnion, 1 m off the reservoir bottom, and midpoint). Samples were immediately placed on ice and returned to the laboratory for analyses as described below.

We analyzed nutrients at the Grand River Dam Authority (GRDA) Water Quality Research Laboratory within 48 h of collection. Total P (TP), ammonia (NH_3–N), and nitrate (NO_3–N) were analyzed in each water sample colorimetricaly using Hach® methods 8190, 8038, 8192, respectively, with a Hach® DR2800™ spectrophotometer. TN was analyzed using a Shizmazdu© TNCP-4110C® autoalayzer.

We averaged the triplicate samples from the epilimnion and hypolimnion to determine single epilimnetic and hypolimnetic means for each sample site and date. We used two way repeated measures Analysis of Variance (RM-ANOVA) with sample date and water layer (epilimnion or hypolimnion) as the dependent variables and sample site as the repeated measure. We used these RM-ANOVAs to determine if there were differences ($p < 0.05$) over time in TP, TN, TN:TP, ammonia (NH_3–N), and nitrate (NO_3–N) between sample sites and water layers. Holm-Sidak post hoc tests were used to determine pair wise differences ($p < 0.05$) when RM-ANOVA indicated significant treatment effects. Data were log transformed in order to achieve the assumption of equal variance. While normality could not always be achieved through transformation, previous work has shown that ANOVA's are robust and perform well even if all assumptions are not met (Glass et al., 1972).

We also determined the "anoxic depth" for each sample date, which we defined as the depth in the water column from the surface down where D.O. < 2 mg/L; lower anoxic depths indicate more anoxia in the water column. For example, an anoxic depth of 1 m indicates that the entire water column from 1 m below the surface to the bottom of the reservoir is anoxic; an anoxic depth of 30 m indicates that the water column is anoxic below 30 m to the bottom of the reservoir. We then used linear regression to examine relationships between the anoxic depth and epilimnetic TP, TN, and TN:TP ratio. Data were analyzed both over the entire sample period and after stratification weakened in the late summer and the reservoir began to mix (i.e. mixing period; see results below). Data for linear regressions were log transformed as necessary to meet the assumptions of normality and homoscedasticity. All statistical analyses were performed in Sigmaplot10.

Internal phosphorus load estimates

An in situ estimate of the sediment P load was determined according to Nürnberg (2009) for a stratified lake:

$$L_{\text{int}} = \frac{((\text{TP}_{t2} \times V_{t2}) - (\text{TP}_{t1} \times V_{t1}))}{(A)}$$

where TP was the hypolimnetic water column average of total phosphorus, V was the volume of the hypolimnion, and A was the surface area of the reservoir. L_{int} is a measure of the P accumulation rate in the hypolimnion and is represented as the difference