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Environmental significance

Understanding the drivers of lake eutrophication and loss of water quality is important for sustainability of aquatic ecosystems. This work identifies and quantifies the effect of such drivers on the epilimnetic phosphorus concentration in 132 Maine, USA, lakes. The results show that lake physicochemical, climate, and watershed land-use attributes control lake phosphorus concentration. The models developed here can serve as management decision tools for public agencies and other stakeholders to assess lake vulnerability to eutrophication.

Controls on the epilimnetic phosphorus concentration in small temperate lakes

Aria Amirbahman,[a*] Kaci N. Fitzgibbon,[b] Stephen A. Norton,[b] Linda C. Bacon[c], and Sean D. Birkel,[b,d]

[a] Department of Civil and Environmental Engineering, University of Maine, Orono, Maine 04469 USA
[b] School of Earth and Climate Sciences, University of Maine, Orono, Maine 04469 USA
[c] The Maine Department of Environmental Protection, Augusta, Maine 04333 USA
[d] Climate Change Institute, University of Maine, Orono, Maine 04469 USA

* Corresponding author at aamirbahman@scu.edu
Present address: Department of Civil, Environmental and Sustainable Engineering,
Santa Clara University, Santa Clara, CA 95053 USA

Abstract

Phosphorus (P) is one of the key limiting nutrients for algal growth in most fresh surface waters. Understanding the determinants of P accumulation in the water column of lakes of interest, and the prediction of its concentration is important to water quality managers and other stakeholders. We hypothesized that lake physicochemical, climate, and watershed land-use attributes control lake P concentration. We collected relevant data from 126 lakes in Maine, USA, to determine the major drivers for summer total epilimnetic P concentrations. Predictive regression-based models featured lake external and internal drivers. The most important land-use driver was the extent of agriculture in the watershed. Lake average depth was the most important physical driver, with shallow lakes being most susceptible to high P concentrations; shallow lakes often stratify weakly and are most subject to internal mixing. The sediment NaOH-extracted aluminum (Al) to bicarbonate/dithionite-extracted P molar ratio was the most important sediment chemical driver; lakes with a high hypolimnetic P release have low ratios. The dissolved organic carbon (DOC) concentration was an important water column chemical driver; lakes having a high DOC concentration generally had higher epilimnetic P concentrations. Precipitation and temperature, two important climate/weather variables, were not significant drivers of epilimnetic P in the predictive models. Because lake depth and sediment quality are fixed in the short-term, the modeling framework serves as a quantitative lake management tool for stakeholders to assess the vulnerability of individual lakes to watershed development, particularly agriculture. The model also enables decisions for sustainable development in the watershed and lake remediation if sediment quality is conducive to internal P release. The findings of this study may be applied to bloom metrics more directly to support lake and watershed management actions.

1. Introduction

Temperate regions of North America and Europe have abundant lakes, the majority of which are smaller than 2.5 km^2.[1] These lakes perform important ecosystem functions: they are home to a diversity of flora and fauna, provide various ecosystem services, and have a great impact on local and state economies. For example, Boyle et al.[2] reported that lakes in Maine, USA, contributed approximately $5 billion to the state economy; this value has nearly doubled by 2021. These lakes are also less resilient to external stimuli and can undergo loss of water quality faster than larger lakes. Most of these lakes have excess phosphorus (P) availability as the leading cause of eutrophication and loss of water quality.[3] P flux into a lake is seasonally variable and can be external from the watershed, and/or internal, when externally added P is recycled from the sediment within the lake. Effective management of lake water quality requires a fundamental understanding of physical and chemical factors that lead to cultural eutrophication. Quantification of such underlying factors also allows the successful development of models to predict lake vulnerability to eutrophication. Aquatic nutrient cycling research and modeling is especially timely given the growing threat of harmful algal blooms (HABs).[4] HABs are not restricted to eutrophic lakes, but can also occur in low-nutrient lakes, including those in temperate regions.[5-8]

The classic 'input-output' models for P, introduced by Vollenweider,[9] rely on estimates of watershed point and non-point source export to assess lake P loading. Anthropogenic activity, particularly agricultural development in the watershed, increases the sediment and nutrient loads to a lake through application of fertilizers and increased soil erosion, making watershed land-use and hydrology important variables. Phosphorus can also originate from the dissolution of apatite ($Ca_5(PO_4)_3(OH)$), the most abundant P-containing primary mineral in boreal ecosystems, and via transport of DOC, and particulate $Al(OH)_3$ and $Fe(OH)_3$ with adsorbed P.[10]

Although important, knowledge of external P inputs to a lake is insufficient to evaluate vulnerability to eutrophication and should be augmented with data from in-lake and climate/weather-related factors. Lakes that develop summer hypolimnetic anoxia may be subject to internal P loading via sediment P release that has also been reported due to anoxic condition even in shallow areas.[11] The classic model of sediment P release involves the microbially-catalyzed reductive dissolution of sediment $Fe(OH)_3$ as the predominant mechanism.[12-16] In oxic sediments, $Fe(OH)_3$ binds orthophosphate strongly, but upon its dissolution, the adsorbed P is released and becomes bioavailable to algae as it reaches the photic zone. However, excess sediment $Al(OH)_3$ can effectively sequester P and inhibit its release to the overlying water despite anoxia.[17-20] P sequestration by $Al(OH)_3$ occurs in low pH, low P lakes.[21] $Al(OH)_3$, in contrast to $Fe(OH)_3$, is not redox-sensitive, and therefore, P adsorption to $Al(OH)_3$ is unaffected under anoxic condition. Thermodynamically, P adsorption onto $Fe(OH)_3$ surface is favored over that of $Al(OH)_3$. Equilibrium adsorption, however, is not only controlled by thermodynamics, but also by the concentration of surface adsorption sites. Therefore, excess $Al(OH)_3$ can provide sufficient surface sites to effectively compete with the $Fe(OH)_3$ surface for adsorption. Indeed, soluble Al salts, such as alum, have commonly been added as a lake management strategy to prevent internal P release.[22]

The sequential chemical extraction procedure developed by Psenner *et al.*[23] allows the fractionation of sediment P, Fe, and Al into exchangeable (NH_4Cl), reducible (Na bicarbonate-dithionite; BD), and NaOH- and HCl-extractable fractions. Laboratory experiments and field observations showed that lakes with sediment molar ratios of $Al_{BD+NaOH}:Fe_{BD}$ (henceforth Al:Fe) > 3 and $Al_{BD+NaOH}:P_{BD}$ (henceforth Al:P) > 25 release a negligible amount of hypolimnetic P during summer anoxia, indicating that an increase in sediment extractable Al concentration leads to sequestration of sediment P.[17,24]

Characteristics other than land use and geochemistry influence the effect of external loading on the lake P budget. The watershed area to lake area ratio (WA:LA) has been used as a metric to characterize watershed contribution with respect to nutrient loading in a lake.[25,26] The studies reported a positive correlation between lake P and WA:LA. Further, Huser et al.[22] found that WA:LA correlated negatively and significantly with hydraulic residence time (HRT), a variable that has been used as a metric to characterize the role of hydrology in lake water quality modeling.[9] Specifically, HRT correlates negatively with the external P flux into the lake.[27]

Lake water quality is also influenced by lake morphometry, including depth and surface area that, along with water temperature, affect lake thermal structure and strength of stratification.[28,29] In strongly stratified lakes, characterized by relatively large decreases in temperature and increasing density with depth, mass transfer between hypolimnetic and epilimnetic waters is slow; consequently, seasonal increases in high hypolimnetic P in these stable lakes may not result in simultaneous increases in the epilimnetic P.[30] However, lakes with negligible thermal stability, especially shallow lakes that experience ephemeral anoxia in their metalimnia, are more susceptible to mixing by wind. In shallow lakes, entrainment of the bottom water may happen frequently,[31] potentially leading to higher epilimnetic P concentrations.[32]

Lake thermal stability has been implicated as a factor influencing the occurrence of HABs.[33] Increased thermal stability in the water column, brought about by increased air temperature, decreased wind speed, and decreased cloudiness can reduce the vertical turbulent mixing, favoring the buoyant cyanobacteria over other species of phytoplankton.[34]

We hypothesize that (a) lake physiochemical characteristics, (b) climate/weather characteristics, and (c) watershed/land use characteristics strongly influence lake epilimnetic P concentration. We have used relevant data from 126 lakes in Maine, USA (Tables S1 and S2),[35] to test our hypotheses and develop models that predict lake P concentrations based on the above drivers of lake water quality. We developed regression-based models based on 98 of these lakes for which complete data existed that incorporate various components of watershed, lake (including the direct role of sediment chemistry with respect to P mobilization), and climate/weather characteristics to estimate lake summer total epilimnetic P. In particular, incorporating variables that represent sediment chemistry along with other established measures, such as lake depth and extent of agriculture, into predictive models for lake water quality is unique to our knowledge. These models are especially appropriate for studies that inform stakeholders, guide regional efforts to maintain lake water quality by managing land use, and aim to remediate high internal P loading.

2. Methodology

2.1. Field sites

The lakes in this study were sampled in 2010–2012 (90 by the Maine Department of Environmental Protection; DEP), 2013 (12 by the Lakes Environmental Association), and 2015 (24 by Fitzgibbon[27]), using the same techniques everywhere. All lakes are predominantly located in the southern and central regions of Maine (Fig. S2), and were sampled in the months of July, August, or early September in a few cases. These are the period of maximum stratification in Maine. All data are in Tables S1, S2 and Fitzgibbon.[35]

2.2. Sampling and analysis

Water and sediment samples were obtained from the deepest point in each lake. Dissolved oxygen (DO) and temperature were measured in 1–2 m increments from the surface to 1 m from the sediment surface. Integrated epilimnetic core water samples were collected using a flexible PPE sampling tube from the lake surface to 1 m below the bottom of the epilimnion. Water samples from the hypolimnion were collected with a Kemmerer grab sampler from 1 m above the sediment-water interface. Samples were collected for closed-cell pH and total P in all lakes. Samples for anions (SO_4^{2-}, NO_3^-, Cl^-), unfiltered total cations (Ca, Mg, Na, K, Al, and Fe), and dissolved organic carbon (DOC) were collected for a subset of lakes. Closed-cell pH was measured with a TitraLab TIM860 Titration Manager. Total (unfiltered) P (henceforth P) was measured with a Varian Cary 50 spectrophotometer using a molybdate blue coloring reagent following ammonium peroxydisulfate digestion (250 °C, 0.5 h). Ion chromatography (Dionex DX-500) was used to analyze the anions. Cation samples were acidified with 50% HNO_3 to a pH < 2 in the field. A high resolution ICP-MS (Thermo Element 2) was used to measure cation concentrations. For quality control, blank, replicate, and analyte-spiked samples were run every 10 water samples; the error was within 5% for all samples and analytes.

Sediment samples were obtained using a Hongve-style gravity corer.[36] Sediment samples from the top 2 cm were composited from three cores collected within a 3 m radius and kept frozen in the dark until analysis. Diagenetic processes in the sediment alter the speciation and concentrations of P, Al, and Fe.[14] Thus, we have limited our focus to the top 2 cm of sediment with an age of probably < 10 years. It is largely this interval of sediment that interacts most with hypolimnetic water (or epilimnetic water in shallow lakes) during anoxia.

The sediment sequential extraction procedure was a modified version of Psenner *et al.*[23] The first (ion-exchangeable fraction) was omitted because several studies on Maine lake sediments indicated that the typical extractable Al, Fe, and P concentrations in the first extraction step were <1% of those of the second and third extraction steps (e.g., Lake *et al.*[24]). The third extraction step was modified from Psenner *et al.* [23] by using 0.1 M NaOH, rather than 1 M NaOH.[18] We also eliminated the fifth extraction step (total residual extractable fraction) because this high temperature extraction (85 ^{o}C) with 1 M NaOH removes only very insoluble material that is not biologically available.

Two grams of wet sediment were sequentially extracted with 25 ml of solution of (a) 0.11 M Na bicarbonate ($NaHCO_3$) and 0.11 M Na dithionite (NaS_2O_4) at 40 °C for 30 min to extract reducible Fe (Fe_{BD}) and the associated P (P_{BD}) via the reductive dissolution of $Fe(OH)_3$; (b) 0.1 M NaOH at 25 °C for 16 hr to extract Al (Al_{NaOH}) via the dissolution of $Al(OH)_3$, and P (P_{NaOH}) that is largely associated with $Al(OH)_3$ and organic matter; and (c) 0.5 M HCl at 25 °C for 16 hr to extract P associated with any calcite ($CaCO_3$) or apatite present,[17] as well as the less soluble $Al(OH)_3$ and $Fe(OH)_3$ phases that did not dissolve in the previous two extraction steps. Calcite was not observed in the sediment of any of these soft water and generally low-P lakes, based on the relatively low extracted Ca^{2+} concentrations in the HCl sediment extracts and lack of proportionality of Ca^{2+} and P.[35] Lakes in Maine, as a group, are comparatively low in Ca^{2+} and Mg^{2+} because of low amounts of limestone ($CaCO_3$) and/or rapidly weathering lithologies in the bedrock and glacial materials. In Maine, apatite occurs commonly in post-glacial marine and lake sediment below an elevation of 75 m ASL near the coast, rising to 128 m inland.[37]

Acidic deposition, starting in earnest after WWII, peaking in the early 1970s and then declining, has had long-term effects on water and sediment chemistry of Maine lakes. However, this study was not designed to specifically address lake responses to recovery from acid rain in Maine (ubiquitous but originally of declining strength from southwest to northeast), or other spatially discontinuous influences that typically have shorter recoveries than from acid rain, including fire, cycles of drought followed by acidic pulses of runoff, pest invasion with defoliation, altered land use, forestry harvesting practices, changing DOC, and climate changes. The latter, also ubiquitous, include higher temperatures and more intense rainfall events with higher annual totals, all well documented.[38] Of course, it is possible that short-lived events disproportionately impacted surface sediment chemistry of a lake, but most lake catchments were chosen based on relatively little or no recent land-based disturbance. The spatial breadth (nearly state-wide), short sampling period (2010-2015), and large number of lakes in this study provides a snapshot of recent water and sediment chemistry.

Concentrations of P, Al, Fe, and Ca in the sediment extracts were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES; Thermo Element 2). For quality control, blank and replicate samples were run for every 10 field samples, with typical variability of < 5%.

2.3. Calculated variables and watershed information

Several variables that reflect lake physical characteristics were calculated. Lake area-averaged depth (Z_{avg}) considers the lake morphometry as,

$$Z_{avg} = \frac{1}{A_S}\int_{0}^{Z_{max}} A(z)dz \qquad \text{Eq. 1}$$

where, Z_{avg} is the lake area-averaged depth, A_s is the lake surface area, $A(z)$ is the lake area at depth z, and Z_{max} is the maximum depth. The relationship between lake depth and surface area can be characterized using the Osgood Index (OI),[39]

$$\mathrm{OI} = \frac{Z_{avg}}{A_S^{1/2}} = \frac{1}{A_S^{3/2}} \int_0^{Z_{max}} A(z)dz \qquad \text{Eq.2}$$

A measure of a lake's thermal stability, the Schmidt stability, *Sch* (J m^{-2}), is the energy required to mix a unit area of a lake to a uniform water density,[40]

$$Sch = \frac{g}{A_0} \int_0^{Z_{max}} (z - z_v)\rho(z)A(z)dz \qquad \text{Eq. 3}$$

where, g is the acceleration of gravity, A_0 is the lake surface area, $\rho(z)$ is the density of water at depth z, and z_v is the depth to the center of volume of the lake,

$$\mathrm{z}_v = \frac{\int_0^{Z_{max}} zA(z)dz}{\int_0^{Z_{max}} A(z)dz} \qquad \text{Eq. 4}$$

Lakes with a high *Sch* are less susceptible to physical mixing than those with a low *Sch*. In thermally stable lakes (i.e., a high *Sch* value), the density difference between the epilimnion and hypolimnion is sufficient to counteract the shear forces created by wind. *Sch* does not explicitly account for wind velocity, even though the destabilizing effect of wind is implicitly included in the homogenization of the density gradient.[41] We used the rLakeAnalyzer package v. 3.3 to calculate *Sch* (Global Lake Ecological Observatory Network; http://www.gleon.org/).

Stream Stats (https://water.usgs.gov/osw/streamstats/) from the United States Geological Survey (USGS) was used to access lake watershed information that included the percentage of storage for the water bodies and associated wetlands (from the National Wetlands Inventory), and the mean basin slope, which was computed from the 10-m digital elevation model (DEM) from Stream Stats (https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/). Lake area included contiguous wetlands. Maine Office of GIS's (MEGIS; http://www.maine.gov/megis/) GeoLibrary was accessed to acquire the land cover spatial data in each watershed[35] from the Maine Land Cover Dataset (MELCD; http://www.maine.gov/megis/catalog/metadata/melcd.html#ID0EUEA), a land cover map derived from Landsat Thematic Mapper 5 and 7 from the years 1999-2000. Spatial data were collected with a resolution of 30 m. We used SPOT 5 panchromatic imagery from 2004 to refine this map. The SPOT 5 imagery was collected with a spatial resolution of 5 m.

The effect of agriculture on lake epilimnetic P was assessed by determining the hay/pasture plus cultivated crop land area in watersheds and dividing by the watershed or lake area to obtain agricultural land:watershed area ratio (Ag:WA) and agricultural land:lake area ratio (Ag:LA), respectively. We also considered the contribution of the agricultural land contiguous with the lake to obtain the adjacent agricultural land:watershed area ratio (AdjAg:WA).

Daily precipitation (maximum, average, and sum) and temperature (degree-day) data from January 1st and May 1st to the sampling date in the same year were collected to assess their influence on epilimnetic P. The data at each lake latitude/longitude center point were obtained from the Parameter-Elevation Regressions on Independent Slopes Model (PRISM).[42,43] PRISM is a statistical mapping system that uses *in situ* point measurements to generate high-resolution spatial climate solutions using a digital elevation model and a weighted regression scheme. Gridded data products, such as PRISM, offer an ideal means to obtain climate estimates over areas where local observations are not available. In this study, we used the 4 km × 4 km PRISM solutions downloaded from the PRISM Climate Group.[44]

2.4. Statistical analysis

Multiple linear regression (MLR) models were developed and ranked to provide a predictive tool for the epilimnetic P concentrations, given a set of predictor variables. Variables whose variances did not meet the assumptions of normality and homogeneity were log transformed. The level of multicollinearity among the predictor variables was determined by calculating the variance inflation factor (VIF); a cutoff value of 2 was used above which predictor variables were not included. The corrected Akaike information criterion (AIC_C) was used as a means for model selection. The AIC_C estimates the relative quality of the models for a data set by accounting for a limited sample size, with the lowest AIC_C indicating the highest quality. The models are ranked based on the maximum likelihood and minimum number of predictor variables. The ΔAIC_C of a model is the difference between AIC_C of that model and the model with the lowest AIC_C. Models are considered of equal quality when $\Delta AIC_C < 2$, while $\Delta AIC_C > 10$ denotes models that are significantly different.[45] An estimate of the predictor variables for the MLR models was provided by performing a regression tree analysis (see the SI section). The MLR analysis was performed using the R package Hmisc.

Quantile regression (QR) models were developed to explore the response of epilimnetic P concentration to agricultural development for a top multiple regression model across different quantiles. QR models are generally utilized to provide a more comprehensive description of the relationship among variables by estimating the conditional quantiles of the response variable distribution.[46] This technique estimates the conditional quantiles of the response variable as a function of the predictor variable; the 50th quantile ($\tau = 0.50$) corresponds to the conditional median, where 50% of the lakes have equal or less than a specified epilimnetic P concentration. Compared to linear least squares models, QR models have the advantage of reducing the influence of uncharacterized predictor variables on the response variable by estimating functional relations across the entire range of the probability distribution. This is especially important when the slope of the regression line differs for different quantiles.[47]

Quantile regression was further used in conjunction with percentile selection, as defined by Xu *et al.*,[48] to develop specific P management strategies for agricultural development. Specifically, they used this approach to analyze the response of lake chlorophyll to N and P concentrations, and set management targets for these nutrients. Different percentiles of concentrations of one nutrient were chosen and QR analysis was performed for each set of percentiles to fit the relationship between chlorophyll and other nutrients by the 99th quantile model. The QR models for each set of nutrient percentiles were used to predict the concentration of other nutrient that would reach the threshold chlorophyll target of 15 $\mu g\ L^{-1}$. We used this approach, in particular, to estimate the extent of agricultural development in a watershed in response to a threshold epilimnetic P concentration under ranked sediment Al:P ratios and Z_{avg}, two of the specific lake characteristics that control epilimnetic P concentrations. QR analysis was performed using the R package quantreg (2016), v. 5.26.

3. Results and Discussion

Based on our hypothesis that determinants of lake water quality include in-lake physiochemical characteristics, climate/weather factors, and watershed/land use characteristics, we chose several measured and calculated variables, including those related to lake morphometry, and sediment and water chemistry to represent these categories.

3.1. Physicochemical controls

3.1.1. Morphometry and thermal stability

We considered Z_{avg} (Eq. 1), OI (Eq. 2), *Sch* (Eq. 3), the hypolimnetic temperature (T_{hyp}; temperature at 1 m above the sediment-water interface at the deepest point), and the epilimnetic temperature (T_{epi}; temperature at a depth of 1 m of the water column) as potential determinants of epilimnetic P. Our results show a significant negative correlation between Z_{avg} and lake epilimnetic P (Table 1). Deeper lakes have low epilimnetic P, whereas shallow lakes have the highest epilimnetic P (Fig. 1a). Several studies have demonstrated depth as a significant predictor for lake TP.[49-51] Taranu and Gregory-Eaves[50] performed a meta-analysis of 358 lakes worldwide and showed that shallower lakes are more susceptible to P accumulation in the water column than deeper lakes. Deeds *et al.*[37] performed linear mixed effect modeling to classify lakes in different ecoregions of Maine with respect to epilimnetic P and found depth as the most significant predictor. Water residence time is also a function of Z_{avg}, with deeper lakes, in general, having a longer HRT. D'Arcy and Carignan[52] showed an inverse relationship between lake P and HRT in 30 Canadian Shield lakes, suggesting that shallower lakes are more susceptible to P enrichment. Deeper lakes with a higher HRT are not only thermally more stable (Table 1), they also increase the settling rate retention of P, leading to a lower epilimnetic P concentration.[9]

Osgood Index, a measure of lake morphometry, has been related to lake thermal stability. Osgood[39] suggested that lakes with OI > 6 develop a stable thermal stratification, whereas lakes with OI < 6 are susceptible to summer mixing during which the epilimnetic water quality is strongly influenced by the metalimnion or hypolimnion. Our results indicate that OI is significantly negatively correlated to lake epilimnetic P (Table 1), and lakes with a high OI (> 12) have low epilimnetic P concentrations (< 10 μg L^{-1} with average = 5.7 μg L^{-1}), whereas lakes with high epilimnetic P concentrations (> 15 μg L^{-1}) have a low OI (< 7; Fig. 1b). Lakes with OI < 7 have an average P concentration = 8.9 μg L^{-1}. However, several lakes with very low OI also have very low epilimnetic P concentrations. Our observations are similar to those by Mataraza and Cooke[32] who evaluated the OI for 114 temperate lakes and concluded that OI cannot be used as the only predictor for lake epilimnetic P concentrations.

Welch and Cooke[30] presented cases where an increase in the summer hypolimnetic P concentration in lakes with OI > 7 did not result in a similar increase in the summer epilimnetic P. Huser *et al.*[22] observed that alum treatment longevity in temperate lakes increased significantly at OI > 5.7. Clearly, shallow lakes with a low OI are more susceptible to wind-driven mixing, which allows internally released sediment P to reach the epilimnion at a faster rate. In deeper lakes with a high OI, internally released P may not reach the epilimnion rapidly, or until spring or fall overturn.

Our results show that lakes with *Sch* > 500 J/m^2 at the time of sampling have epilimnetic P concentrations < 6 $\mu g\ L^{-1}$ (Fig. 1c), suggesting that P-rich bottom waters migrate upward at a slower rate in thermally stratified lakes to the top in thermally stable lakes. However, in our study a large number of lakes with *Sch* < 600 J/m^2 had low epilimnetic P concentrations, indicating that similar to OI, *Sch* cannot be used as the only predictor of lake water quality. The yearly sum of *Sch*, derived from a lake physical model, may be a better indicator for the seasonal lake thermal stability and, potentially, epilimnetic P concentration.[53] Lake thermal stability, as characterized by *Sch*, is subject to change throughout the season depending on climate and weather factors, such as rainfall intensity, persistent wind, and air and water temperature. In lakes that undergo mixing in fall and spring, such as most of those studied here, *Sch* reaches its maximum value prior to the fall turnover, and zero immediately after the fall and spring turnovers.

The negative correlation between *Sch* and epilimnetic P (Table 1) is due to the enhancement of mass transfer between hypolimnia and epilimnia in lakes with a low *Sch*, causing erosion of the thermocline, more frequent oxygenation of the hypolimnion, and introduction of nutrients into the epilimnion.[54] Lathrop *et al.*[29] observed a positive relationship between summer Secchi depth and *Sch* in a temperate lake. In a survey of 231 lakes in northeastern North America during 1975–2012, Richardson *et al.*[55] showed that the strength of thermal stratification increases with increasing warming of surface temperatures, particularly for lakes at higher latitudes (above ~44°), which includes most of Maine.

Similar to OI and Z_{avg}, WA:LA may be used as an indirect measure of the hydrological landscape.[22,26] A low WA:LA suggests a potentially higher percentage of internally-loaded P. Conversely, lakes with higher WA:LA ratios are likely more influenced by external P sources.[25,52,56] However, in this study WA:LA was not significantly correlated to epilimnetic P and was not a determinant of epilimnetic P in the statistical analysis (Table 1).

Temperature degree-days did not correlate with the epilimnetic P in our study (Table S3). However, epilimnetic P was positively correlated with T_{hyp} (Table 1; Fig. 1d) and T_{epi} (Table S3). Higher temperatures, especially closer to the sediment, enhance microbial activity that leads to depletion of DO and release of P due to reductive dissolution of $Fe(OH)_3$ at the sediment-water interface.[57,58] The released P may be translocated to the epilimnion depending on the lake thermal stability. A warmer hypolimnion also reduces lake thermal stability, as manifested in the strong but inverse relationship between T_{hyp} and *Sch* ($r = -0.86$; Table 1). Even though a significant correlation was not observed between T_{epi} and *Sch*, the difference between T_{epi} and T_{hyp} was strongly and positively correlated to *Sch* ($r = 0.82$), indicating that lakes with a small temperature gradient are more susceptible to mixing.

3.1.2. Sediment geochemistry

Lake epilimnetic P was negatively correlated to sediment Al:P, positively correlated to sediment P_{BD}, and uncorrelated with sediment Al:Fe (Table 1). Our results show that lakes with relatively high sediment Al:P ratios have lower epilimnetic P concentrations, and lakes with high epilimnetic P concentrations have relatively small ratios (Fig. 2). The insignificant internal P release in lakes with threshold sediment molar ratios of Al:Fe > 3 and Al:P > 25,[17] however, is most clearly observed when assessed against the hypolimnetic P concentration (Fig. S3) or its sediment hypolimnetic flux.[24]

Equilibrium adsorption depends not only on surface reaction energetics, but also by the concentration of surface adsorption sites. The sediment Al:Fe = 3 and Al:P = 25 ratios, initially established via laboratory experiments, represent threshold relative sediment Al concentrations above which P is effectively bound to the $Al(OH)_3$ surface. At higher ratios, the $Al(OH)_3$ surface effectively competes with the $Fe(OH)_3$ surface for P adsorption in eroded soil,[10] water column,[59] and lake sediment.[17] Under anoxic conditions, sediment P associated with the reducible $Fe(OH)_3$ (i.e., P_{BD}) is susceptible to mobilization. $Al(OH)_3$ remains insoluble under anoxia provided that hypolimnetic pH remains between 5.5 and 8.5, and if present at sufficiently high concentrations, it can effectively prevent hypolimnetic sediment P release.[17,20] In lakes with a high sediment Al content, P is permanently buried. In these lakes, the sediment total P concentration does not decrease with sediment depth, as it typically does in eutrophic lake sediments. Instead, the mineralization of organic P takes place without its significant upward diffusion into the bottom waters; i.e. P remains conservative during sediment diagenesis.[14,19] Al addition to lake sediment is an established method for remediation of lakes that are subject to significant internal P cycling.[22,60] The threshold sediment ratios should be considered by lake managers and other stakeholders when adding Al to remediate lake eutrophication due to excess P concentrations.

As hypothesized, the determinants of lake epilimnetic P concentrations are not limited to the sediment geochemical factors. Whereas sediment Al:Fe and Al:P ratios below the threshold values are required for sediment P release (Fig. S3), meeting the thresholds does not result in a significant P release in some lakes. Further, even though P release may not be significant in some lakes, the ratios indicate lake vulnerability to internal P release. But, these ratios, by themselves, cannot be used for estimation of the lake internal P release, and the epilimnetic P concentration.

3.1.3. Water chemistry

Lake pH and DOC concentration are very important variables that control nutrient availability. In our study, epilimnetic P concentration positively correlated with pH (Table 1) in agreement with the observations of Chen *et al.* [61] in 72 Irish lakes, where all lakes with pH < 6 were in the mesotrophic/oligotrophic range. Sediment P_{BD} showed a significant positive correlation with pH (Table 1), corresponding to the observation that orthophosphate adsorption to surfaces of eroded soil decreases with increasing pH leading to P mobilization from the watershed.[62-64] pH is also significantly negatively correlated to sediment Al:P and Al:Fe ratios, suggesting enhanced mobilization of Al from the watershed with decreasing pH.[65] Other processes, however, may lead to enhanced P mobilization at a lower pH. Apatite, as a source of P from many Maine watersheds and lake sediments, is more soluble at a lower pH and lower Ca^{2+} concentrations; however, apatite is commonly depleted in mineral soils in a few thousand years.[66] Many lakes in Maine have easily and recently eroded post-glacial unweathered marine sediments containing apatite in their watersheds at elevations below 75 m ASL near the coast increasing to 128 m ASL inland.[37,67] In a survey of 257 lakes in Maine with little or no agricultural development in their watersheds, 16 lakes whose watersheds were dominated by marine clay had an excess of approximately 5 $\mu g\ L^{-1}$ epilimnetic P.[68]

The DOC concentration in our study lakes ranged from 1.7 to 8.1 mg L^{-1} (Table S1). There is a weak but significant positive relationship between lake DOC and epilimnetic P (Table 1), similar to that observed for other boreal lakes.[49,69,70] In our study, DOC concentrations are positively correlated with the percentage of agricultural land (Ag:LA; Table 1), and the wetland area-to-watershed area ratio.[35] However, WA:LA, previously correlated to lake DOC concentration by Rasmussen *et al.*,[71] is not significantly correlated with DOC in our study (Table 1). The magnitude of lake DOC concentration is determined by watershed land cover type, hydrological connectivity patterns, and lake HRT.[72-74]

In recent decades, DOC concentrations have been increasing in surface waters of Europe and North America,[75] and may be rebounding to values typical of pre-acid rain times.[76] DOC can transport nutrients, including P, to lakes.[20] DOC may also transport Al and Fe to lakes where photo-oxidation of these complexes yields precipitated $Al(OH)_3$ and $Fe(OH)_3$.[59] These amorphous phases may then adsorb P from the water column and become sediment. Increased DOC increases light attenuation that may result in enhanced lake stratification because of warming of shallower water, thereby decreasing the epilimnetic depth.[77,78] A higher thermal stability can, in turn, diminish the translocation of hypolimnetic P to the epilimnion.[31] The influence of DOC on lake nutrient cycling is complex and not fully understood,[77] confusing the interpretation of its statistical relationship with epilimnetic P.

3.2. External loading: watershed characteristics and precipitation

Our results show weak but significant relationships between epilimnetic P concentrations and Ag:WA, Ag:LA, and AdjAg:LA ratios (Table 1). Other land use and landscape features, such as areal road coverage (Road:WA, Table 1), urban development, and wetlands were considered, but did not contribute significantly to lake water quality.[35]

Several studies have observed a positive significant relationship between percent agricultural land use and lake nutrient concentrations, especially for lakes with no known point-source of pollution in their watersheds.[50,69,79-81] Among different land-use and landscape features, % pasture has shown the strongest correlation with lake P.[82,83]

In temperate lakes, precipitation has been reported to negatively affect water quality due to the enhanced transport of sediment and nutrients into the lake.[84,85] However, our data show a weak but significant negative relationship between maximum and average rainfall from May 1st to the time of sampling and lake epilimnetic P concentration (Table S3). Other precipitation measures were not significantly related to epilimnetic P (Table S3). The anomalous relationship between precipitation and the epilimnetic P concentration may be due lake-specific features. In particular, precipitation is positively correlated with the sediment Al:P ratio, and negatively correlated with agricultural development (Table S3), two of the most important drivers of epilimnetic P (Table 1). Indeed, where present in the watershed, agriculture has been found as the most important driver of lake water clarity between dry (increased clarity) and wet years (reduced clarity).[84] We also observe a relatively small range of precipitation across our study sites; the maximum and average precipitation values from May1st to the sampling date are 38.8±12.8 and 3.3±0.8 mm, respectively. The role of precipitation as a climate factor on lake water quality may best be explored by following the epilimnetic P concentration over long time periods.[86] This would also circumvent the complicating role of lake-specific effects.

3.3. Predictive tools for the epilimnetic P

We used the variables in Table 1 to build predictive linear models for summer epilimnetic P concentrations. We performed multiple regression analyses on 98 lakes, for which a complete dataset existed, to gain insights into relationship nuances. Linear models have been previously used to relate different lake water quality response variables to chemical, physical, watershed, and food web predictors.[22,29,49,87]

3.3.1. Linear regression models for the epilimnetic P

Multiple linear regression modeling results can be used as a predictive tool to evaluate lake vulnerability to eutrophication and loss of water quality. Table 2 shows the top 10 MLR models based on the ΔAIC_C values. The coefficients and intercept for each model are reported in Table S4. There are two models with $\Delta AIC_C < 2$ that account for 93% of the Akaike weight, resulting in a relatively low uncertainty for model selection. The models in Table 2 represent combinations of physiochemical variables (Al:P, P_{BD}, pH, DOC, and Z_{avg}), and watershed characteristics (Ag:WA, AdjAg:LA, and Ag:LA). Further, shallow lakes are more susceptible to changes in climate and weather factors including temperature variations and storm intensity. Hence, Z_{avg} can enhance the effects of climate change on a lake, such as the susceptibility of shallow lakes to mixing. The model coefficients consistently show that lower Al:P ratios and Z_{avg}, and higher P_{BD}, DOC, and agricultural development result in higher epilimnetic P concentrations (Table S4).

The top two models with $\Delta AIC_C < 2$ feature Z_{avg}, Al:P ratio, DOC concentration, and Ag:WA or AdjAg:LA. The VIF for all predictor variables was < 2. Predictor variables that represent climate/weather effects on lake water quality, including *Sch,* T_{hyp}, T_{epi}, and the maximum and average precipitation from May 1st, did not rank sufficiently high with respect to predicting the summer epilimnetic P. However, T_{hyp} and *Sch* correlate strongly with Z_{avg} (Table 1), a prominent predictor for the epilimnetic P in all of the MLR models; the variables affected by climate conditions (T_{hyp} and *Sch*) and the tendency to mixing are affected by Z_{avg}.

459 Previous studies that used MLR modeling have shown a linear dependence of lake P on depth and land-use variables, such as the watershed size, and agricultural area.[49-51,88] We have shown that the incorporation of sediment geochemical variables into MLR models improves model prediction of lake epilimnetic P (Table 2).

463 **3.3.2. Quantile regression modeling to set thresholds for agricultural development**

464 We used QR modeling with percentile selection[48] to analyze the extent of Ag:WA in response to a threshold epilimnetic P under ranked sediment Al:P ratio and Z_{avg}. Use of these three variables are based on results of a top MLR model with these three predictor variables (Table 2). We targeted lakes that may be more susceptible to the release of sediment reducible P, by using the lowest ranked sediment Al:P ratios. Ranked Al:P ratios ranged from 1.6 to 199 for the 75th percentile (n = 74), and 1.6 to 67 for the 50th percentile (n = 49). By ranking Z_{avg} we targeted the shallower lakes that may be more susceptible to effects of internal P release. Ranked Z_{avg} values ranged from 1.1 to 11.9 m for the 75th percentile, and 1.1 to 8.3 m for the 50th percentile. We did not report the 25th percentile because of the small number of data points.

473 We used a threshold of 15 μg L^{-1} (log P =1.18) for the summer epilimnetic P as transition from mesotrophic to lower eutrophic,[89] and the 90th quantile model to assess lake vulnerability with respect to agricultural development in the watershed. The 90th quantile epilimnetic P is the value where 90% of the lakes have concentrations less than or equal to the threshold of epilimnetic P = 15 μg L^{-1}. The crossing of the 90th quantile model and the threshold P concentration denotes the predicted Ag:WA that should not be exceeded to limit the maximum epilimnetic P concentration to 15 μg L^{-1}. The threshold value for the Ag:WA for lakes in the 75th percentile of sediment Al:P is 4.8%, and in the 50th percentile of sediment Al:P is 3.9% (Figs. 3a, b). The Ag:WA thresholds for lakes in the 75th and 50th percentiles of Z_{avg} are 5.4% and 4.1%,

respectively (Figs. 4a, b). Exceeding these threshold Ag:WA predicts >15 ppb epilimnetic P concentrations in most study lakes.

QR models relationships between predictor variables and conditional quartiles of the response variable, whereas MLR models relationships between predictor variables and conditional mean of the response variable. Significant differences between the slopes of QR and MLR models are indicative of different effects along the distribution of the response variable. In this study, however, the regression slopes at different quantiles were not significantly different than that of the MLR model (Figs. S4 and S5). This suggests a homogeneous variance and justifies the use of the MLR model in this study.[46] Our use of coupled QR and percentile selection is intended to define potential regulatory thresholds with respect to the extent of agricultural development in lake watersheds.

4. Conclusions

We have shown that lake vulnerability to eutrophication may be characterized by considering the combined effects of physiochemical, climate/weather, and watershed factors. This study identifies the determinants for epilimnetic P accumulation, and hence, variation of water quality in small temperate lakes. They are Z_{avg}, sediment Al:P ratio, DOC concentration, and the extent of agricultural development (i.e., Ag:WA, and AdjAg:LA). Lakes with unfavorable sediment geochemistry (i.e., low molar Al:P ratios or high P_{BD} concentrations) are more susceptible to sediment P release. Such lakes are especially vulnerable if they do not stratify stably during the summer. Shallow lakes often stratify weakly and are at a greater risk to internal mixing. Lake watershed land-use patterns determine the extent of external P contribution. Watersheds with greater areas of adjacent agriculture enhance dissolved and particulate P in surface runoff. Whereas individual factors studied here cannot be used for estimation of the epilimnetic P concentration, combined, they account for the external and internal sources of P to lakes.

The quantile regression, with percentile selection framework proposed here, sets thresholds for agricultural development that are modulated by Z_{avg} and lake sediment Al:P ratio; exceeding the thresholds predicts epilimnetic P concentrations > 15 ppb, the transition to eutrophic water quality. Such framework, by identifying determinants of epilimnetic P, informs lake managers, municipalities, and lake protection associations in how their management practices impact lake water quality.

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Table 1. Pearson rank correlations for the lake data.[a] Correlations with $p < 0.01$ are denoted by *.

	log EpiP	log HypoP	log Al:P	log P_{BD}	log Al:Fe	Ag:WA	AdjAg:LA	WA:LA	Ag:LA	Road:WA	Z_{avg}	T_{hyp}	log *Sch*	OI	pH	DOC
log EpiP	1															
log HypoP	0.700*	1														
log Al:P	-0.461*	-0.432*	1													
log P_{BD}	0.436*	0.437*	-0.971*	1												
log Al:Fe	-0.015	-0.163	0.551*	-0.488*	1											
Ag:WA	0.540*	0.522*	-0.515*	0.510*	-0.269*	1										
AdjAg:LA	0.428*	0.379*	-0.261*	0.289*	-0.032	0.614*	1									
WA:LA	0.087	0.183	-0.041	0.007	0.010	-0.006	0.066	1								
Ag:LA	0.466*	0.253	-0.298*	0.295*	-0.138	0.667*	0.449*	0.238*	1							
Road:WA	-0.038	0.096	-0.023	0.022	0.018	0.017	0.039	-0.056	-0.028	1						
Z_{avg}	-0.555*	-0.358*	-0.071	0.098	-0.504*	-0.163	-0.145	-0.108	-0.204	0.013	1					
T_{hyp}	0.456*	0.128	-0.009	-0.070	0.088	0.174	0.021	-0.078	-0.206	-0.126	-0.636*	1				
log *Sch*	-0.376*	-0.248	-0.144	0.215	-0.289*	-0.001	-0.090	-0190	-0.098	0.062	0.691*	-0.860*	1			
OI	-0.308*	-0.146	0.338*	-0.288*	0.219	-0.230	-0.080	-0.091	-0.153	0.044	0.055	-0.383*	0.234*	1		
pH	0.497*	0.507*	-0.596*	0.557*	-0.402*	0.521*	0.200	0.044	0.418*	0.016	-0.061	0.119	0.045	-0.225	1	
DOC	0.371*	0.216	0.042	-0.077	0.158	0.066	0.036	0.225	0.289*	-0.110	-0.348*	0.372*	-0.457*	-0.187	-0.060	1

[a] EpiP ($\mu g\ L^{-1}$): epilimnetic P; hypoP: hypolimnetic P; Al:P: sediment $Al_{BD+NaOH}$:P_{BD} molar ratio; P_{BD} ($\mu mol\ g^{-1}$): sediment P extracted in bicarbonate-dithionite extraction; Al:Fe: sediment $Al_{BD+NaOH}$:Fe_{BD} molar ratio; Ag:WA: %agricultural area:watershed area; AdjAg:LA: %lake adjacent agricultural area:lake surface area; WA:LA: watershed area:lake surface area ratio; Ag:LA: agricultural area:lake surface area ratio; Road:WA: road surface area:watershed area ratio; Z_{avg} (m): area-averaged lake depth; T_{hyp} (^{o}C): hypolimnetic temperature 1 m above lake bed; *Sch* ($J\ m^{-2}$): Schmidt Stability; OI: Osgood Index; DOC ($mg\ L^{-1}$): dissolved organic carbon. Watershed area does not include lake area.

Table 2. Results of the multiple linear regression analysis to predict lake epilimnetic P. The models are ranked based on the lowest ΔAIC_C. The top 10 models are shown. Models with predictor variables Z_{avg}, %Ag:WA, and DOC are also shown for comparison.

	Models	***n***	**K[a]**	**AIC_C**	**ΔAIC_C**	**-2*LnL**	**$exp(-\Delta AIC_C/2)$**	**w_i[b]**	**r^2**
1	log Al:P + Z_{avg} + %AdjAg:LA + DOC	98	6	-103.65	0.00	-112.29	1.00	0.65	0.721
2	log Al:P + Z_{avg} + %Ag:WA + DOC	98	6	-101.95	1.70	-110.60	0.43	0.28	0.712
3	log P_{BD} + Z_{avg} + %AdjAg:LA + DOC	98	6	-99.02	4.63	-107.67	0.10	0.06	0.708
4	log Al:P + Z_{avg} + Ag:LA + DOC	98	6	-94.77	8.87	-103.42	0.01	0.01	0.695
5	log Al:P + Z_{avg} + %Ag:WA + pH	98	6	-91.50	12.14	-100.15	0.00	0.001	0.684
6	log Al:P + Z_{avg} + %AdjAg:LA	98	5	-91.11	12.54	-98.26	0.00	0.001	0.676
7	log P_{BD} + Z_{avg} + %Ag:WA + pH	98	6	-89.76	13.89	-98.41	0.00	0.001	0.678
8	log Al:P + Z_{avg} + %Ag:WA	98	5	-89.30	14.34	-96.46	0.00	0.000	0.670
9	log Al:P + Z_{avg} + Ag:LA	98	5	-88.92	14.73	-96.07	0.00	0.000	0.669
10	log P_{BD} + Z_{avg} + %Ag:WA	98	5	-86.19	17.45	-93.35	0.00	0.000	0.659
	Z_{avg} + %Ag:WA + DOC	98	5	-71.49	32.16	-78.64	0.00	0.00	0.604
	Z_{avg} + %Ag:WA	98	4	-64.36	39.29	-70.07	0.00	0.00	0.565

[a] Number of model-estimated variables plus the intercept and variance. [b] Likelihood of the specific model relative to other models.

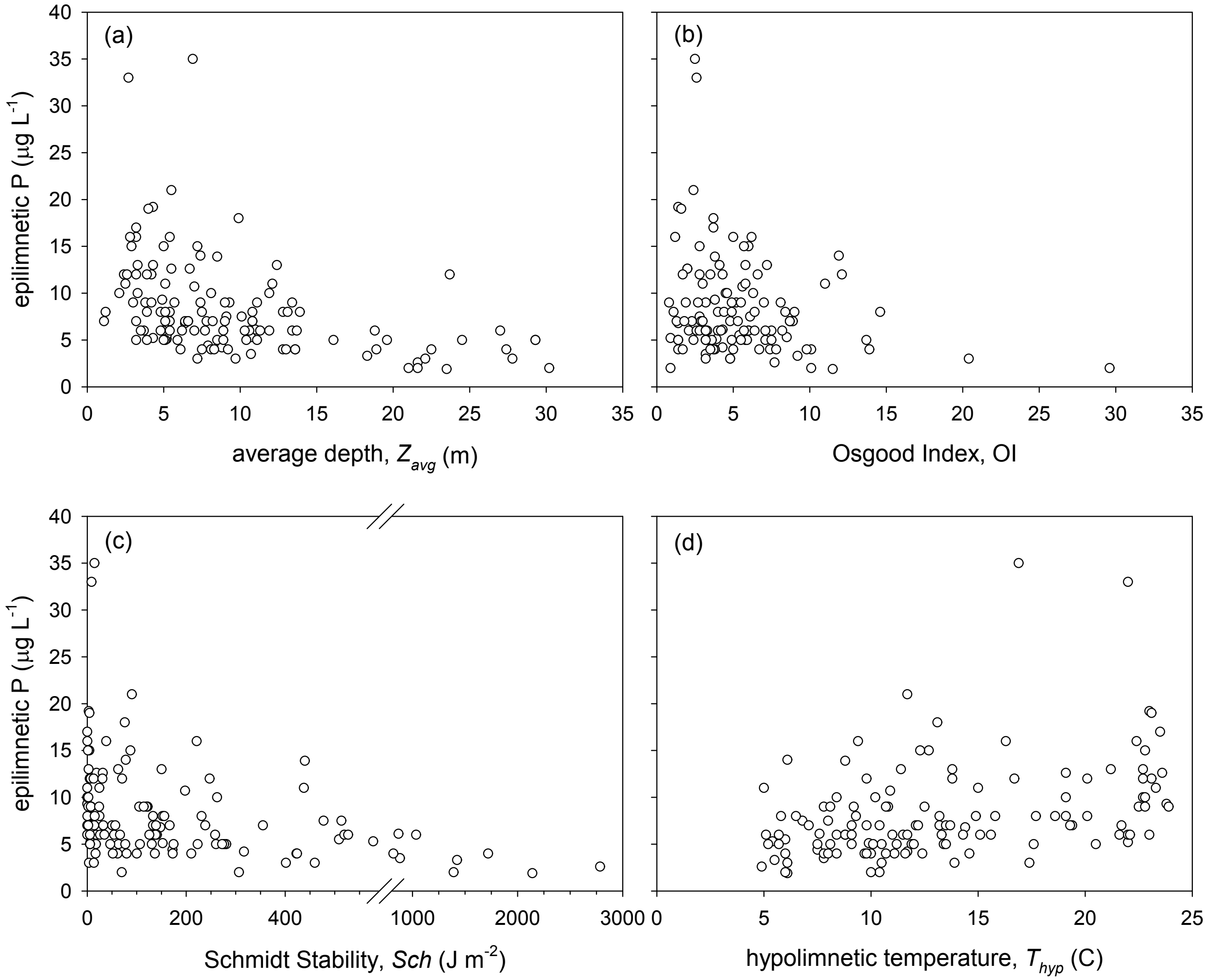
Figure captions

Figure 1: Epilimnetic P ($\mu g\ L^{-1}$) versus (a) area-averaged depth (Z_{avg}), r = -0.418; (b) Osgood Index (OI), r = -0.233; (c) Schmidt Stability (Sch), r = -0.303; and (d) hypolimnetic temperature (T_{hyp}), r = 0.399.

Figure 2. (a) Sediment $Al_{BD+NaOH}:Fe_{BD}$ molar ratio versus epilimnetic P ($\mu g\ L^{-1}$), r = -0.162. The dashed line shows $Al_{BD+NaOH}:Fe_{BD}$ ratio = 3; (b) sediment $Al_{BD+NaOH}:P_{BD}$ molar ratio versus epilimnetic P, r = -0.234. The dashed line shows $Al_{BD+NaOH}:P_{BD}$ ratio = 25.

Figure 3: (a) %Ag:WA for the lower 75th percentile $Al_{BD+NaOH}:P_{BD}$ versus log epilimnetic P ($\mu g\ L^{-1}$); and (b) the lower 50th percentile $Al_{BD+NaOH}:P_{BD}$ versus log epilimnetic P ($\mu g\ L^{-1}$). The 90th quantile QR models (solid line) for log epilimnetic P as a function of %Ag:WA for ranked $Al_{BD+NaOH}:P_{BD}$ values (75th and 50th, filled circles). The thresholds for the epilimnetic P concentrations for limiting a specific %Ag:WA target (log epilimnetic P = 1.18 corresponds to 15 $\mu g\ L^{-1}$, dashed line). The open circles indicate values above the percentile of interest. The crossing of the 90th quantile model and the threshold P concentration denotes the predicted %Ag:WA that should not be exceeded to maintain an epilimnetic P concentration of 15 $\mu g\ L^{-1}$ as an upper limit.

Figure 4: (a) %Ag:WA for the lower 75th percentile Z_{avg} versus log epilimnetic P ($\mu g\ L^{-1}$); and (b) the lower 50th percentile Z_{avg} versus log epilimnetic P ($\mu g\ L^{-1}$). The 90th quantile QR models (solid line) for log epilimnetic P as a function of %Ag:WA for ranked Z_{avg} values (75th and 50th, filled circles). The thresholds for the epilimnetic P concentrations for limiting a specific %Ag:WA target (log epilimnetic P = 1.18 corresponds to 15 $\mu g\ L^{-1}$, dashed line). The open circles indicate values above the percentile of interest. The crossing of the 90th quantile model and the threshold P concentration denotes the predicted %Ag:WA that should not be exceeded to maintain an epilimnetic P concentration of 15 $\mu g\ L^{-1}$ as an upper limit.



(a)
(b)
(c)
(d)
epilimnetic P (µg L-1)
average depth, Zavg (m)
Osgood Index, OI
Schmidt Stability, Sch (J m-2)
hypolimnetic temperature, Thyp (C)
0
5
10
15
20
25
30
35
40
200
400
1000
2000
3000

Figure 1

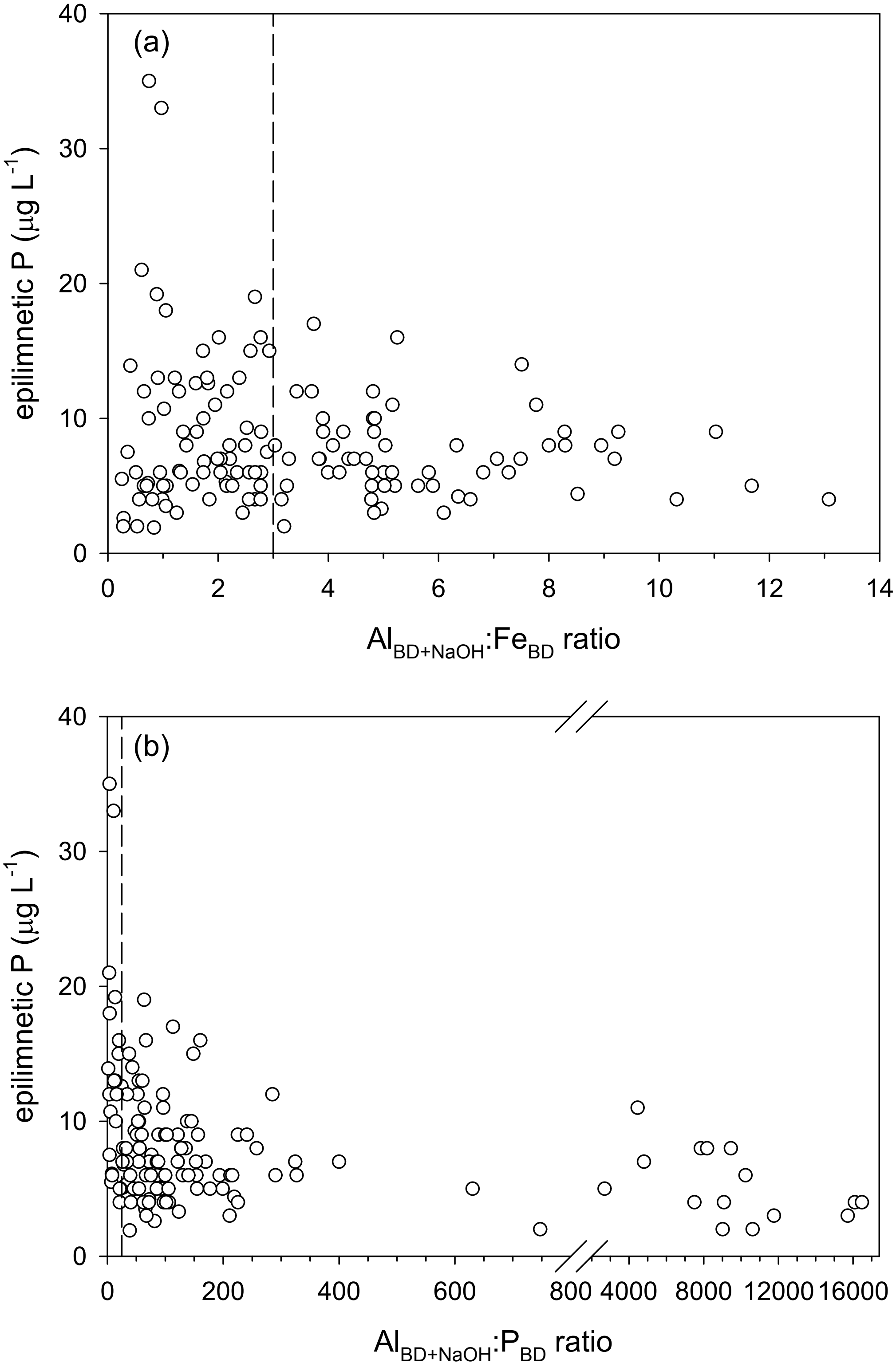

(a)
epilimnetic P (μg L-1)
Al BD+NaOH:Fe BD ratio
0
10
20
30
40
0
2
4
6
8
10
12
14
(b)
epilimnetic P (μg L-1)
Al BD+NaOH:P BD ratio
0
200
400
600
800
4000
8000
12000
16000

Figure 2

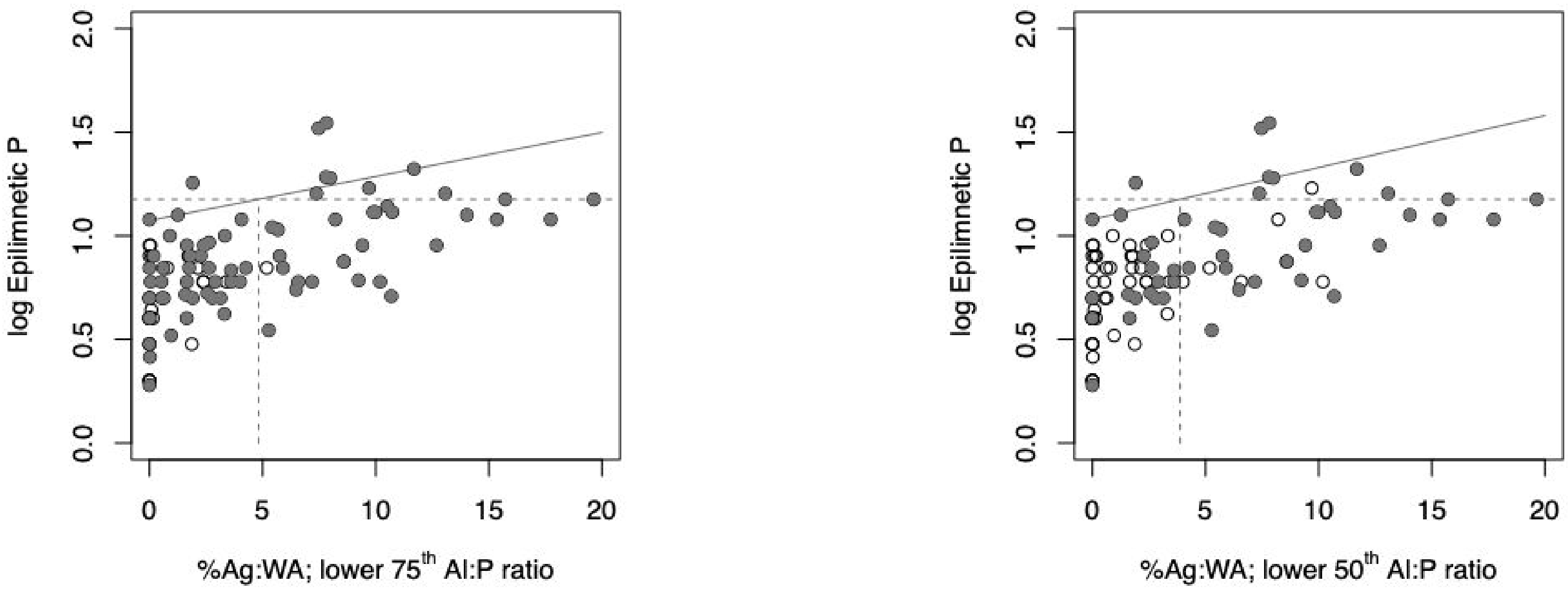

log Epilimnetic P
0.0
0.5
1.0
1.5
2.0
0
5
10
15
20
%Ag:WA; lower 75th Al:P ratio
log Epilimnetic P
0.0
0.5
1.0
1.5
2.0
0
5
10
15
20
%Ag:WA; lower 50th Al:P ratio

Figure 3

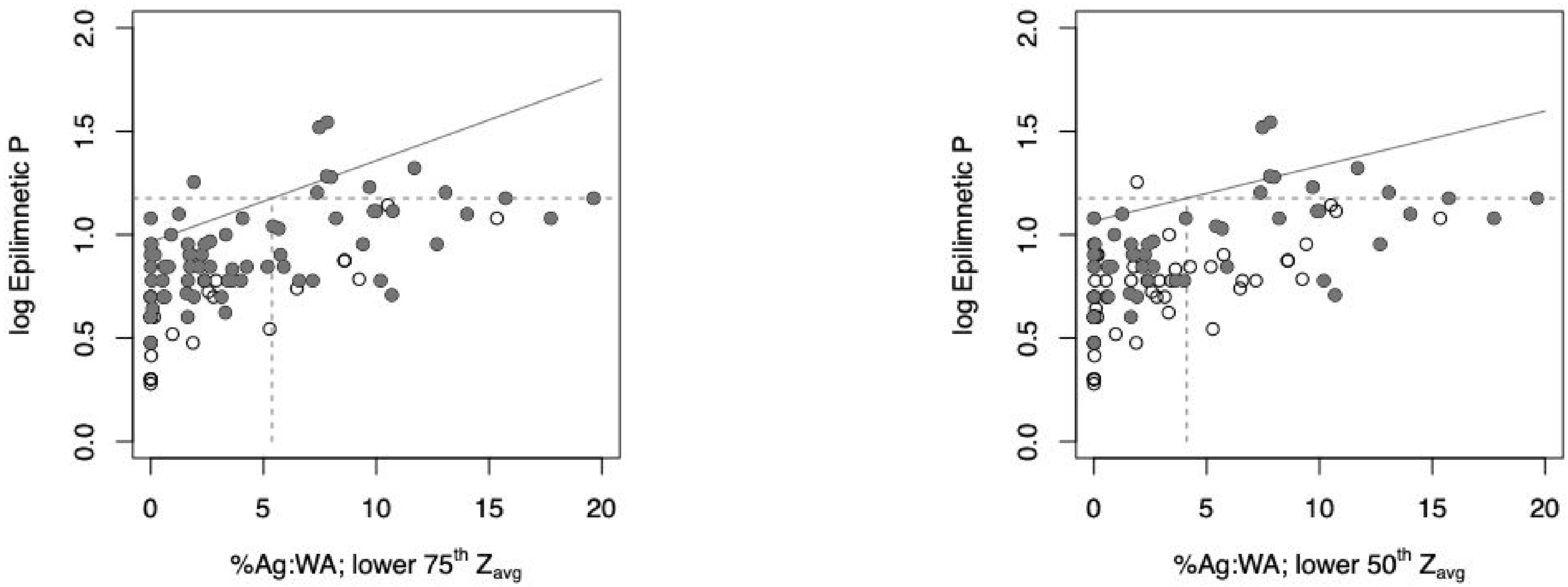

log Epilimnetic P
0.0
0.5
1.0
1.5
2.0
0
5
10
15
20
%Ag:WA; lower 75th Zavg
log Epilimnetic P
0.0
0.5
1.0
1.5
2.0
0
5
10
15
20
%Ag:WA; lower 50th Zavg

Figure 4