

Equilibrium Exchanges of Soluble Phosphorus by Resuspended Sediment in Goose Lake, MN



University of Wisconsin – Stout Sustainability Sciences Institute Center for Limnological Research and Rehabilitation Menomonie, Wisconsin 54751 715-338-4395 jamesw@uwstout.edu



Wenck Associates, Inc 1800 Pioneer Creek Center Maple Plain, MN 55359

763-749-4200 rkluckhohn@wenck.com

15 December, 2015

1.0 BACKGROUND.

Shallow Goose Lake currently exhibits excessive summer cyanobacterial blooms and poor water quality (WQ) conditions (high phosphorus and chlorophyll concentrations and low water clarity) that may be linked to internal phosphorus (P) recycling from sediments in the lake. While chlorophyll concentrations are excessive, empirical steady-state modeling and P mass balance approaches have suggested that currently quantified watershed loading and internal diffusive P fluxes do not entirely account for the high P concentrations in the water column. Internally-derived phosphorus contributions from bottom sediment can occur via diffusion under both aerobic and anaerobic conditions. In shallow systems like Goose Lake, P exchanges between resuspended sediment and the surrounding water column can occur via equilibrium reactions, resulting in either net removal (i.e., adsorption) or net addition (i.e., desorption) of soluble P depending on equilibrium conditions. Since sediment resuspension can be frequent in shallow systems due motor boat activity and wind-induced turbulence, equilibrium exchanges between sediment and the water column could represent a significant source of soluble P for algal uptake and growth.

Others have found that motor boat activity can cause sediment resuspension that contributes both particulate and soluble P to the water column (Asplund 2000, James et al. 2002). Resuspended P may or may not be directly available for assimilation by cyanobacteria, depending on equilibrium relationships between particulate and soluble P phases during resuspension. Thus, a portion of the water column P concentration may be composed of inorganic particulate P originating from resuspended fine silts and clays versus P incorporated as algal biomass (i.e., organic P). This source of total P would need to be accounted for in a total P budget for the lake. However, since this P fraction is not incorporated into algal biomass, predicted chlorophyll that is based on total P concentration would be much higher than the observed mean concentration.

2

In order to develop sound and effective management strategies to improve WQ in Goose Lake, there is a need to understand the role that sediment resuspension and equilibrium flux plays in the P economy and cyanobacterial blooms.

2.0 PURPOSE.

The objectives of this research were to examine the equilibrium P concentration and net soluble P flux for resuspended bottom sediments of Goose Lake. These results will be important in evaluating the P budget of the lake and potential P contributions to the water column by resuspended sediment that may drive cyanobacterial blooms.

3.0 METHODS.

Field sediment collection

Duplicate sediment cores were collected at two stations in Goose Lake for determination of P equilibrium characteristics and net soluble P flux from resuspended sediment (Figure 1). Station 1 was located near the north shore (6.3-ft deep; 45.0715, -93.0168) while station 2 (6.6-ft deep; 45.0683, -93.0197) was located within the designated water skiing area. The upper 1-cm of each three inch diameter core was sectioned for determination of P equilibrium characteristics. Six inch diameter intact cores (two from each station) were collected with a box corer for determination of net soluble P flux from resuspended sediment (Figure 1).

Table 1. Sediment physical-texctural characteristics.									
Lat	Long	Depth	Moisture content	Wet density	Dry density	Organic matter	Porosity		
		(m)	(%)	(g/cm ³)	(g/cm ³)	(%)	(%)		
-93.01683	45.07149	1.92	95.8	1.014	0.043	46.3	98.0		
-93.01973	45.06830	2.01	96.3	1.013	0.038	45.2	98.2		
	iment physical Lat -93.01683 -93.01973	iment physical-texctural cha Lat Long -93.01683 45.07149 -93.01973 45.06830	iment physical-texctural characteristic Lat Long Depth (m) -93.01683 45.07149 1.92 -93.01973 45.06830 2.01	iment physical-texctural characteristics. Lat Long Depth Moisture content (m) (%) -93.01683 45.07149 1.92 95.8 -93.01973 45.06830 2.01 96.3	Lat Long Depth Moisture vet density content (m) (%) (g/cm ³) -93.01683 45.07149 1.92 95.8 1.014 -93.01973 45.06830 2.01 96.3 1.013	Lat Long Depth Moisture content Wet density Dry density content (m) (%) (g/cm ³) (g/cm ³) -93.01683 45.07149 1.92 95.8 1.014 0.043 -93.01973 45.06830 2.01 96.3 1.013 0.038	Lat Long Depth Moisture content Wet density Dry density Organic matter (m) (%) (g/cm ³) (g/cm ³) (%) -93.01683 45.07149 1.92 95.8 1.014 0.043 46.3 -93.01973 45.06830 2.01 96.3 1.013 0.038 45.2		

Equilibrium phosphorus characteristics

Sediment slurries containing filtered lake water and sediment from the 1-cm section were preconditioned by gentle shaking in a darkened environment at ~ 20 °C for 24 hours to equilibrate sediment exchangeable P pools with soluble P. The sediment was concentrated via centrifugation and subsamples (500 mg/L dry weight equivalent) were subjected to soluble phosphorus (as KH₂PO₄) standards ranging from 0 to 1.0 mg/L for examination of P adsorption and desorption after 24 hours. Filtered water with similar ionic characteristics but low in phosphate collected in adjacent White Bear Lake was used as the aqueous medium for the assays. Tubes containing sediment, amended water, and known concentrations of phosphate were shaken uniformly in a darkened environment at a pH of ~ 8.0 to 8.3 and a temperature of ~ 20 °C , then filtered and analyzed for soluble reactive P (SRP; APHA 2005).



Figure 1. Sediment sampling station locations in Goose Lake.

The change in SRP mass (i.e., initial SRP - final SRP; mg) was divided by the dry mass equivalent of sediment to determine the mass of P desorbed or adsorbed (S; mg P/ g sediment). These data were plotted as a function of the final equilibrium SRP to determine the linear adsorption coefficient (k_d; L/g) and the equilibrium P concentration (EPC; mg P/L; the point where net sorption is zero; Froelich 1988). The k_d and EPC were calculated via regression analysis from linear relationships between final SRP concentration and the quantity of P adsorbed or desorbed at low equilibrium concentrations.

The EPC and k_d estimated from these assays were used to determine if resuspended sediment was a net source or sink for soluble P. If the EPC was high relative to ambient soluble P concentrations in the water, resuspended sediment would represent a net source of soluble P for algal assimilation and growth. If it was low, then resuspended sediment would act as a sink for soluble P.

Since municipal waste water from a nearby treatment facility was historically discharged into Goose Lake, there was concern that sediments might be saturated with P, leading to potential desorption during sediment resuspension. The extent of P saturation of sediment binding sites was estimated using the Langmuir equation,

$$\frac{EPC}{S'} = \frac{1}{S'_{max} \cdot K}$$

Where EPC = equilibrium SRP concentration (mg/L), S' = native S + the sorbed exchangeable P (mg/kg), S'_{max} = exchangeable P sorption maximum capacity (mg/kg), and K = binding partition coefficient (L/kg, different from k_d above). S_{max} was estimated as the inverse of the slope of the regression relationship between EPC/S (y-axis) versus EPC (x-axis). I assumed that the iron-bound P concentration of the sediment represented the native exchangeable P pool (native S) for determination of P saturation and binding capacity. Thus, S' = native S + sorbed S.

Equilibrium P fluxes during sediment resuspension

A vertically oscillating particle entrainment simulator (PES) developed by Tsai and Lick (1986) was used to subject intact cores to various shear stresses (Figure 2). The PES was programmed to oscillate above the sediment interface in a stepwise manner from 0 to ~ 4 dynes/cm at 10-min intervals. At 8 min into each cycle, a 50 mL sample was collected 2.54 cm (1 inch) below the water surface using a peristaltic pump. Water removed as a result of sampling was simultaneously replaced with filtered lake water (collected from White Bear Lake) using a peristaltic pump. Samples were analyzed for total suspended sediment (TSS), turbidity, and SRP using standard analytical procedures (APHA 2005).



Figure 2. Simulation of sediment resuspension using a particle entrainment simulator (PES).

4.0 RESULTS AND DISCUSSION.

Sediment phosphorus equilibrium conditions

Relationships between the final equilibrium P concentration and the change in the sediment exchangeable P concentration are shown in Figure 3. For sediments collected from both stations, the final equilibrium SRP concentration was near zero (i.e., below analytical detection limits) after subjecting sediment to phosphate-free White Bear Lake water for 24 hours. Thus, Goose Lake suspended sediment did not desorb or release SRP at low ambient SRP in this experimental assay. The estimated EPC was also near zero for station 1 and 2 sediments (Table 2). This pattern suggested that suspended sediments in the water column of Goose Lake probably contribute minor to negligible soluble P to the water column for potential cyanobacterial assimilation.

Table 2. The equilibrium phosphorus concentration (EPC), linear partition coefficient (K), and phosphorus sorption capacity results for sediments collected in Goose Lake. N.D. = below analytical detection limits.									
Station	EPC	К	Sorption capacity						
	(mg/L)	(L/g)	(mg/g)	(%)					
1	N.D.	26	0.833	19					
2	0.003	12	0.714	22					

In contrast, sediments adsorbed (i.e., sequestered and bound) aqueous P after 24 hours of exposure when subjected to White Bear Lake water containing higher initial SRP concentrations (Figure 3). Soluble P binding reached an asymptote as initial SRP concentration exceeded ~ 0.02 mg/L, suggesting that sediment binding sites were becoming increasingly saturated (i.e., filled) as the ambient SRP concentration increased. The P sorption capacity of station 1 and 2 sediments was similar at ~ 0.77 – 0.91 mg/g. The iron-bound P concentration of these sediments was ~ 0.24 mg/g, indicating that binding sites were only ~ 26% to 31% saturated. Low P saturation was probably related to the high linear adsorption coefficient k_d (i.e., buffering strength for P adsorption), indicating that Goose Lake sediments can strongly adsorb and sequester soluble P when resuspended.



Figure 3. The change in the sediment exchangeable phosphorus (S) concentration as a function of the final (i.e., after 24-h of exposure) equilibrium soluble P concentration.

Mean turbidity and TSS concentrations in the overlying water column increased linearly as a function of increasing simulated shear stress (Figure 4). The critical shear stress required for initiation of sediment resuspension was relatively low at 1.09 dynes/cm² for station 2 sediments and 1.27 dynes/cm² for station 1 sediments. In particular, station 2, located within the waterskiing zone of the lake, exhibited the lowest critical shear stress, indicating a high potential for sediment resuspension. Earlier research on Goose Lake found that sediments were very flocculent and exhibited a very high moisture content and low bulk density, characteristics that are conducive to resuspension at relatively low shear stress. Physical-textural characteristics for sediments collected at station 1 and 2 are shown in Table 1. Indeed, moisture content was very high at ~ 96%, while wet bulk density approached that of water (i.e., 1.00 g/cm³). Organic matter content was also high at ~ 45 to 46%. These attributes largely agree with the low critical shear stress and high susceptibility of sediments in Goose Lake to resuspension.



Figure 4. Changes in turbidity (NTU = Nepholometric Turbidity Units) total suspended sediment (TSS) concentration in the overlying water column as a function of shear stress. The inflection point approximates the critical shear stress or the shear stress required to initiate resuspension.

Variations in water column SRP concentration as a function of increasing simulated shear stress are shown in Figure 5. At low shear stress, below the critical value required to induce sediment resuspension, mean SRP increased in the overlying water column. The mean maximum concentration increase was 0.009 mg/L and 0.023 mg/L for station 1



Figure 5. Variations in soluble reactive phosphorus (P) concentration as a function of applied shear stress. Horizontal blue bar represents the equilibrium phosphorus (P) concentration with the applied shears exceeds the critical shear stress.

and 2 systems, respectively. These are moderately high concentrations that could be assimilated by cyanobacteria for growth. As shear stress increased, overlying water

column SRP concentration declined to an equilibrium value of ~ 0.003 mg/L (i.e., near analytical detection) and 0.009 mg/L in station 1 and 2 systems, respectively. These patterns suggested that mild disturbance might cause the entrainment of anaerobic porewater into the overlying water column, causing an increase in SRP concentration. Moderate shear stress resuspends fine sediment clays and silts which then bind the entrained SRP. Higher shear stresses further resuspends sediments resulting in an equilibrium between the particulate exchangeable sediment P pool and aqueous soluble P. These latter equilibrium concentrations were low and reflected the findings of the equilibrium P experiments.

Caution needs to be used in interpretation of these results because a portion of the "SRP" may actually represent phosphate adsorbed to low molecular-weight colloidal iron oxyhydroxides that are particulate in nature but pass through a 0.45 μ poresize filter and can be detected as SRP using conventional colorimetric methods (Nürnberg 1984). This precipitated and adsorbed PO₄³⁻ may not be directly available for algal assimilation (Baken et al. 2014).

Overall, the findings of this study suggest that flux of SRP to the water column by resuspended sediment is low and probably plays a minor role in driving cyanobacterial blooms. However, the low critical shear stress and flocculent nature of the surface sediments in Goose Lake do suggest a high potential for frequent resuspension of sediment P into the water column by motor boat activity and wind-induced mixing. Under this scenario, a significant portion of the total P in the water column may be as suspended sediment versus incorporated into algal biomass. Thus, total P concentrations may be high relative to chlorophyll due to suspended sediment P. Accounting for apparent P resuspension in the steady-state empirical model could improve total P prediction but overestimate chlorophyll. Since a goal in steady-state empirical modelling is to predict P incorporated as algal biomass (chlorophyll) in order to develop management scenarios, adjustments may be needed to predict only the total P that represents algal biomass. Alternatively, include a P resuspension input to predict total P but adjust the chlorophyll calibration to account for sediment P in the water column.

11

5.0 ACKNOWLEDGMENTS.

We gratefully acknowledge and thank members of the Vadnais Lake Area Water Management Organization and Brian Beck, Wenck Associates, Inc., for sediment sampling and Rachel Fleck and Miranda Vandenberg, University of Wisconsin – Stout, for laboratory analyses and particle entrainment simulation studies.

5.0 REFERENCES.

APHA (American Public Health Association). 2005. Standard Methods for the Examination of Water and Wastewater. 21th ed. American Public Health Association, American Water Works Association, Water Environment Federation.

Asplund T. 2000. The effects of motorized watercraft on aquatic ecosystems. University of Wisconsin – Madison and Wisconsin Department of Natural Resources.

Baken S, Nawara S, Van Moorleghem C, Smolders E. 2014. Iron colloids reduce the bioavailability of phosphorus to the green alga *Raphidocelis subcapitata*. Wat Res 59:198-206.

Froelich PN. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnol Oceanogr 33:49-668.

James WF, Barko JW, Eakin HL, Sorge PW. 2002. Phosphorus budget and management strategies for an urban Wisconsin Lake. Lake Reserv Manage 18:149-163.

Nürnberg GK. 1984. Iron and hydrogen sulfide interference in the analysis of soluble reactive phosphorus in anoxic waters. Wat Res 18:369-377.

Tsai CH, Lick W. 1986. A portable device for measuring sediment resuspension. J. Great Lakes Res. 12:314-321.