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ABSTRACT

Internal phosphorus (P) loading may influence primary production in lakes, but the influence of sediment-derived P has not been well studied in Beaver Lake of Northwest Arkansas. Soluble reactive phosphorus (SRP), dissolved organic P (DOP), and total dissolved P (TDP) sediment-water fluxes were determined using intact sediment cores collected from deepwater environments in the riverine, transition zone, and lacustrine zones of Beaver Lake. The SRP, DOP, and TDP fluxes were also estimated from cores collected from shallow locations in the transition zone. There was a net positive SRP $(0.001 - 0.005\ \mu g\ P\ cm^{-2}\ h^{-1})$, DOP $(0.005 - 0.01\ \mu g\ P\ cm^{-2}\ h^{-1})$, and TDP $(0.005 - 0.01\ \mu g\ P\ cm^{-2}\ h^{-1})$ flux from deepwater sediments into the water column. However, DOP and TDP flux in shallow sediments were net negative $(-0.004$ and $-0.002\ \mu g\ P\ cm^{-2}\ h^{-1}$, respectively), suggesting that the majority of P was moving from water into sediment. The SRP flux from shallow sediments in the transition zone was similar to rates observed in deepwater sediments $(0.002\ \mu g\ P\ cm^{-2}\ h^{-1})$. However, the variability among flux rates, sites and depths was high, and therefore no statistical differences were found. Sediment oxygen demand was positively correlated with SRP and DOP flux rates from shallow transition zone sediments suggesting that microbial biomass and activity may have influenced sediment P flux. The P flux from shallow sediments supports approximately 1% to 5% of the daily P demand of phytoplankton. When compared to other lakes, sediment P flux in Beaver Lake appears minimal and is probably not an effective avenue to manage eutrophication in this system.

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MEET THE STUDENT-AUTHOR

I am an international student from Amman, Jordan. I graduated in 2010 with a Bachelor of Sciences in Agriculture with a major in Environmental, Soil and Water Sciences. I first came to the University of Arkansas while visiting Fayetteville, and I immediately decided that the U of A was the place for me to be. Being from the desert, I always had the affinity for water issues and quality.

With much help from Drs. Thad Scott, Duane Wolf and Brian Haggard, and the faculty and staff in the Crop, Soil, and Environmental Sciences Department I successfully defended my thesis and graduated with Honors. I am now a research intern in Columbia University Middle East Research Center in Amman, Jordan, and will be pursuing my masters degree next year.

Taraf Abu Hamdan

INTRODUCTION

Elevated nutrient levels in freshwaters are an ongoing water quality issue in Arkansas because of human activities. Increased phosphorus (P) in freshwater deteriorates water quality because P is the primary limiting factor in algal growth and P enrichment accelerates eutrophication (Sharpley et al., 2002). Eutrophication is the over enrichment of mineral nutrients that results in excessive autotrophic production, particularly, algae and cyanobacteria (Correll, 1998). The increased productivity and subsequent decomposition of dying algal blooms decreases dissolved oxygen (DO) creating water quality impairments. Phosphorus enrichment also increases the prevalence of harmful algae, such as *Microcystis*, a cyanobacterium that produces taste and odor compounds and even some toxic compounds as metabolic byproducts (Huisman et al., 2005). Moreover, the presence of algal blooms and the subsequent turbidity reduces the aesthetic value of the water body.

After input into lakes and reservoirs, soluble reactive P is generally assimilated biologically and deposited eventually in the bottom sediments (Correll, 1998). Additionally, P can enter lakes and reservoirs adsorbed to eroded soil material adding to the external P inputs to the water body, which is also deposited rapidly in bottom sediments. But P deposited in sediments can be released back to surface water in a process referred to as internal P flux. The entrapment and release of P by sediment is often linked to the interactions between iron (Fe), oxygen (O_2) and P (Mortimer,1941). This model has been used to explain P flux from sediments to overlying water; it is referred to in this paper as the 'ferrous-wheel-model' (Fig. 1). In the presence of O_2, SRP is bound by ferric iron (Fe III) in an oxidation-dependent reaction. When water overlying sediments become anoxic, Fe (III) is reduced to ferrous iron (Fe II), which causes P release. Therefore, P-driven eutrophication is a self-perpetuating process, where eutrophication increases bottom water anoxia, which in turn increases P release from bottom sediments (Fig. 1).

Some water quality problems in Beaver Lake of Northwest Arkansas have been attributed to increased P loads from the watershed (Sen et al., 2007). The Beaver Water District stated in their 2008 watershed report that the water quality concerns for Beaver Lake were algal blooms and turbidity caused by excess P in the water (Beaver Water District, 2008). Beaver Lake is an impoundment of the White River that provides drinking water to more than 250,000 people, making up 9% of Arkansas' population (Beaver Water District, 2008). Watershed management efforts have reduced P input into Beaver Lake. However, P concentrations in lake water have not declined (Sen et al., 2007). The internal P flux from sediments to overlying water may offset the decrease in external P loads (Mortimer, 1941; Böstrom et al., 1988). A study done on Lake Eucha Oklahoma, found that the internal P flux from bottom sediments accounted for 25% of the total P load (Haggard

et al., 2005). Several other studies have shown that P loading from sediments has an effect on the trophic state of reservoirs (Larson et al., 1979; Ryding, 1981).

Several approaches in laboratory studies and *in-situ* have been utilized to quantify P loads from sediments (Holdren and Armstrong, 1980), many using intact sediment cores (e.g., see Anderson, 1975; Haggard et al., 2005; Moore and Reddy, 1994; Moore et al., 1998). In a previous study on Beaver Lake (Sen et al., 2007), sediment cores were incubated under static conditions in the laboratory to estimate P flux from the sediments. They found that that the highest P flux occurred in cores bubbled with N_2 gas amended with 300 ppm CO_2, and P flux was lower in cores bubbled with air (Sen et al., 2007). Results of that study also showed that the highest P flux occurred in the river-reservoir transition zone, which is the location of Beaver Water District's water intake structures (Sen et al., 2007).

Although the sediment-P release rates reported by Sen et al. (2007) were a good initial estimate of the importance of sediment-P loading into Beaver Lake, the study focused on sediments from deep regions of the lake that were beneath anoxic waters. Phosphorus inputs from these deep sediments are cut off from the lake photic zone until lake turnover, which usually occurs in November or December each year. Therefore, P in deep waters is generally inaccessible by algae in the upper photic zone of the lake during the summer. Sediments in more shallow regions of the reservoir come into direct contact with the upper mixed layer where algae grow. But, P release from shallow sediments has not been well studied, and shallow-sediment P release has not been quantified for Beaver Lake. Some studies have indicated that P release from shallow sediments can influence lake water column P concentrations (Sondergaard et al., 1999). Therefore, more work is needed to quantify the role of shallow sediments as P sources influencing internal loading. Additionally, the previous sediment-P release studies on Beaver Lake have measured only SRP flux. No studies have attempted to quantify the total dissolved P (TDP) and dissolved organic P (DOP) in the lake, which may contribute a large portion of P flux and ultimately influence primary productivity.

The objectives of this study were to: (1) determine the differences in total, organic and inorganic dissolved P fluxes from Beaver Lake sediments, (2) determine the P flux from shallow transitional zones versus deep transitional zones in the lake, and (3) quantify the spatial variability of P flux between the three deep zones (riverine, transitional and lacustrine) in Beaver Lake. We expected to find SRP efflux from shallow transitional sediments, and that the rate of efflux could provide a substantial portion of phytoplankton P demand. I also expected to find that efflux of dissolved organic P from shallow sediments would be higher than SRP efflux, making shallow-sediment organic P another important form of P supply to phytoplankton. Finally, we expected to find a positive relationship between SRP efflux from sediments and the sediment oxygen demand (SOD), with higher rates of SOD being a proxy for microbial metabolism and P mineralization.

MATERIALS AND METHODS

Site Description. Beaver Lake is located in Northwest Arkansas and construction of the reservoir was completed in 1963. The Lake is an impoundment of the White River, managed by the U.S Army Corps of Engineers. Beaver Lake is a multipurpose reservoir used for flood control, hydroelectric power and most importantly water supply, along with recreational uses. Beaver lake is fed primarily by the White River, War Eagle Creek and Richland Creek. Beaver Lake, as expected from reservoirs (Kimmel et al., 1990), changes from more eutrophic conditions in regions close to the headwaters (riverine) and in the transitional zones to more pristine circumstances in the lacustrine zone (Haggard et al., 1999). These differences illustrate the importance in sampling all three zones within the lake.

Sediment Cores. Core collection sites were chosen following a previous coring study carried out on Beaver Lake (Sen et al., 2007). Eight cores were collected from the transitional zone (Fig. 2) at shallow depths between 0.5 and 2.0 m. Four cores were collected from each of the three zones (riverine, transitional and lacustrine) at depths of 12 m for the transitional and riverine, and 23 m for the lacustrine zones. Core collection occurred in September 2009 for the shallow zones and October 2009 for the deep zones. This time period was selected because it is the time of year when P release into anoxic hypolimnetic waters should be greatest, and it is also the time of the year when algal-derived taste and odor compounds are at their highest annual concentrations.

Shallow sediment cores were collected in 30-cm (7.5-cm diameter) clear polyvinyl tubes fitted with a one-way rubber valve on the upper end. Cores were pushed into the sediments using a 3-meter PVC pipe. The one-way valve ensured the integrity of sediment and the overlaying water during sample collection, which was confirmed through visual inspection of the turbidity of the overlying water. Cores from deepwater locations were collected directly into clear polyvinyl tubes by certified SCUBA divers.

Cores were sealed with rubber stoppers and insulation tape. Along with the cores, 60 L of lake water was collected from each coring zone. This was done in the deep zones using a pump lowered to the coring depth to pump out the anoxic water. After collection, the sealed cores were carefully transported to the lab.

Core Preparation and Incubation. In the lab, each core was fitted with a flow-through plunger sealed using an O-ring seal and Teflon tape. The flow-through plunger was fitted with Teflon inlet and outlet tubes (Fig. 3). The inlet and outlet tubes help maintain a continuous flow in the chamber. A water column of approximately 7.5 cm in height was maintained above the sediment surface in each core at all times. Lake water was pumped over the surface of the core at approximately 1 ml min^{-1}. Cores were incubated at ambient temperature. Inflow water for cores from shallow sites was continually aerated, whereas inflow water for cores from deepwater sites was not. Flow rates for each core were monitored daily over the entire experimental period of four days.

Sample Collection. The inflow and outflow water of each core was sampled daily for four days. Samples were collected in 40-ml beakers then filtered using a syringe filter (0.45-μm pore size) into a 20-ml scintillation vial. Filtered samples were then acidified with 2 drops of HCl for preservation. Samples designated for the measurement of TDP were digested using the acid-persulfate oxidation method. The digestion was carried out by mixing 15 ml of the filtered samples with 1.8 of the digestion solution (K_2SO_4) and autoclaved for one hour. Samples were analyzed for SRP and TDP spectrophotometrically using the ascorbic acid method (APHA, 1992). The dissolved organic P concentration of samples was calculated as the difference between SRP and TDP.

Phosphorus concentrations (SRP, TDP, DOP) from inflow and outflow measurements were converted into P flux estimates using the equation:

$$P_f = [(P_{out} - P_{in}) * Q]/ 45.4$$

Where P_f is the P flux (μg P cm^{-2} hour^{-1}); P_{out} and P_{in} are the P concentrations (μg ml^{-1}) in the outflow and inflow water, respectively, Q is the flow rate in ml h^{-1}, and 45.4 is the surface area of cores in cm^2.

Samples from shallow cores were also collected as described above for the first two days of each experiment to quantify sediment oxygen demand (SOD). Briefly, O_2/Ar ratios in inflow and outflow water were measured using a Membrane Inlet Mass Spectrometer (MIMS). Dissolved O_2 concentrations were determined from O_2/Ar ratios by assuming Ar was saturated in water at the ambient temperature of the incubation. The SOD was calculated similar to that for P flux (see equation above), with dissolved O_2 rather than P as the variable of interest.

The results were analyzed used a one-way analysis of variance to determine phosphorus flux, the same method was used for DO analysis. The P-value was set at 0.05, for both the phosphorus and DO readings.

RESULTS AND DISCUSSION

A net positive TDP and DOP flux occurred from deep sediments (0.0123 and 0.0098 μg P cm^{-2} h^{-1}, respectively), but a net negative TDP and DOP in shallow sediments from the transition zone (-0.0018 and -0.0034 μg P cm^{-2} h^{-1}, respectively) (Fig. 4). However, the SRP was always positive for all sites. This was because of relatively high variability observed in P flux rates among replicate cores at each site (reported as standard error of the mean in Fig. 4). The TDP flux appeared to be largely driven by the organic P fraction of TDP. Also noteworthy is that SRP efflux from shallow sediments was similar to the rate of SRP efflux from deepwater sediments. Sediment oxygen demand was positively correlated with SRP and DOP flux from the shallow transition zone sediments (Fig. 5).

There were no significant differences in SRP, DOP, or TDP sediment water flux between the reservoir zones or between water depths. These results did not support our hypotheses. The lack of statistical differences among sites was caused by large variability observed in P flux among cores from the same sites. A power analysis of the data (SAS 9.1) revealed that a minimum of 27 cores per site were needed to detect statistical differences ($\alpha = 0.05$) in the SRP flux data, and 17 cores per site were needed to detect statistical differences ($\alpha = 0.05$) in the DOP data. This level of sampling intensity was not feasible and likely will not be feasible in future studies. The high degree of error may have been caused by the short exposure time between water and sediments in the continuous flow core chambers. In this setup, water was exposed to sediments for a few hours as opposed to days worth of exposure time in static core incubations (e.g. Sen et al., 2007). Interestingly, power analysis confirmed that only 4 cores were needed per site to detect statistical differences in SOD. Therefore, continuous flow core chambers may be less appropriate for P flux studies even though they are widely used in nitrogen and O_2 flux studies (An et al., 2001, Gardner et al., 2006, Scott et al., 2008). Nevertheless, the P flux rates observed in this study were similar to those reported previously for deepwater areas in Beaver Lake using static cores (Sen et al., 2007), which were generally lower than sediment P flux compared to other lakes (Table 1).

Lake Eucha, Okla., had an anaerobic average SRP flux rate of 0.018 μg P cm^{-2} h^{-1} (Haggard et al., 2005). Other studies have reported P flux from anaerobic sediments to be as high as 0.11 μg P cm^{-2} h^{-1} (Freedman and Canale, 1977). The anaerobic P flux rates found in this study (~0.002 μg P cm^{-2} h^{-1} on average) were comparable to those of aerobic sediment P fluxes. For Example, Lake Eucha had an average aerobic SRP flux of 0.004 μg P cm^{-2} h^{-1} (Haggard et al., 2005), and deep Beaver Lake sediments that were oxidized

in the lab released P at a rate of 0.003 µg P cm^{-2} h^{-1} (Sen et al., 2007). This suggests that even though the Beaver Lake deep water becomes anoxic, P release from sediments is not nearly as high as it might be based on other studies.

Even though the P flux rates of this study were not consistent with the hypothesis or previous models, they still bear an importance in the process of understanding the dynamics of P in sediments and overlying water. For example, it is important to consider DOP as well as SRP sediment-water interactions. According to Böstrom et al. (1988), the magnitude of P release rates from sediments to oxic waters are frequently the same in magnitude to rates detected from hypolimnetic bottom areas to anoxic waters. This study confirmed that analysis for SRP, but DOP flux in Beaver Lake was much higher in deepwater sediments.

Results of this study also allow us to estimate the proportion of primary production in Beaver Lake that may be supported by internal P loading. If Beaver Lake is mesotrophic, then phytoplankton productivity should range from 500-1500 mg C m^{-2} day^{-1} (Wetzel, 2001). Assuming a stoichiometric growth rate near optimum, phytoplankton P demand in the upper mixed layer would be approximately 10-35 mg P m^{-2} day^{-1}. If we also assume that only 10% of sediments in Beaver Lake are exposed to the upper mixed layer when the lake is stratified, then P flux from shallow sediments would support from 1% to 5% of the daily phytoplankton P demand. This indicates the importance of P recycling in the upper mixed layer and external P sources as the probable controls on annual productivity in Beaver Lake.

ACKNOWLEDGEMENTS

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Table 1. A comparison between soluble reactive phosphorus flux rates under aerobic and anaerobic conditions from several studies.

| Location	P release rate ($\mu g\ P\ cm^{-2}\ h^{-2}$)		Source
	Aerobic	Anaerobic	
Beaver Lake			
Riverine Zone	nd*	0.001	This study
Transition Zone	0.002	0.002	This study
Lacustrine Zone	nd*	0.005	This study
Beaver Lake			
Riverine Zone	0.003	0.002	Sen et al., 2007
Transition Zone	0.004	0.006	Sen et al ,2007
Lacustrine Zone	< 0.001	0.002	Sen et al., 2007
Lake Eucha			
Riverine Zone	0.005	0.020	Haggard et al., 2005
Transition Zone	0.004	0.010	Haggard et al., 2005
Transition Zone	0.004	0.025	Haggard et al., 2005
Clear Lake	0.041	0.036	Porcella et al., 1970
Lake Mendota	0.204	0.221	Ahlgren, 1972
Lake Norriviken	0.021	0.042	Bjork 1972
Lake Trummen	nd*	0.063	Bjork ,1972
Lake Erie	0.003	0.032	Burns and Ross, 1972
Lake Ontario	0.002	nd*	Bannerman et al., 1974
Lake Warner	0.005	0.108	Fillos and Swanson, 1975

*nd = not defined
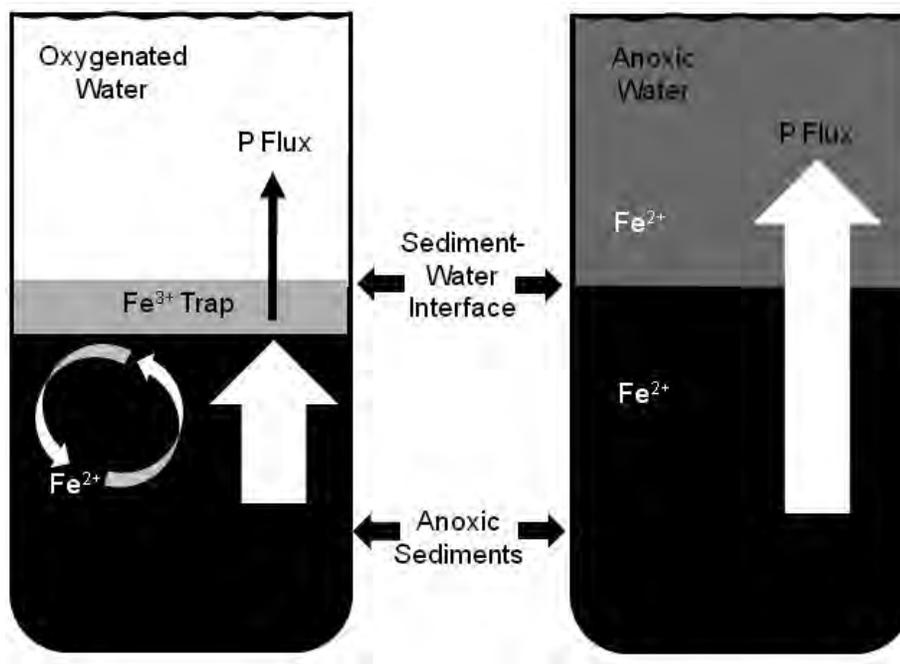
Fig 1. Ferrous wheel model in (left) oxic water, (right) anoxic water (Mortimer, 1941, Wetzel, 2001).

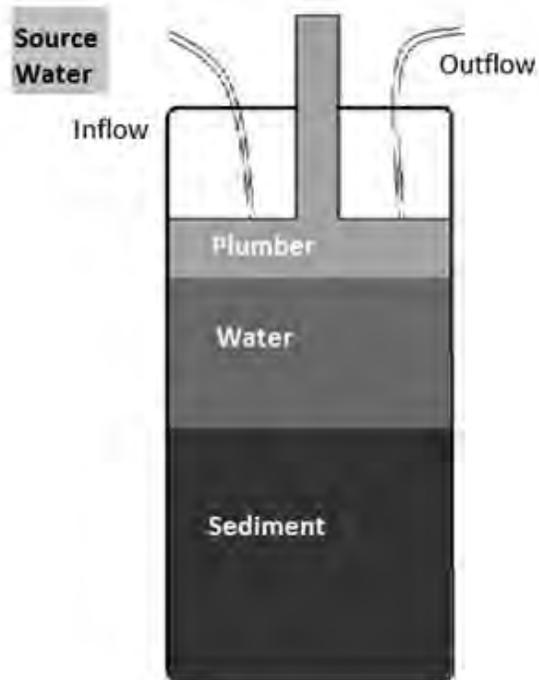**Fig 2.** A map of the three different coring zones within Beaver Lake.

Fig 3. An illustration of the continuous flow-through core setup used in the experiment.
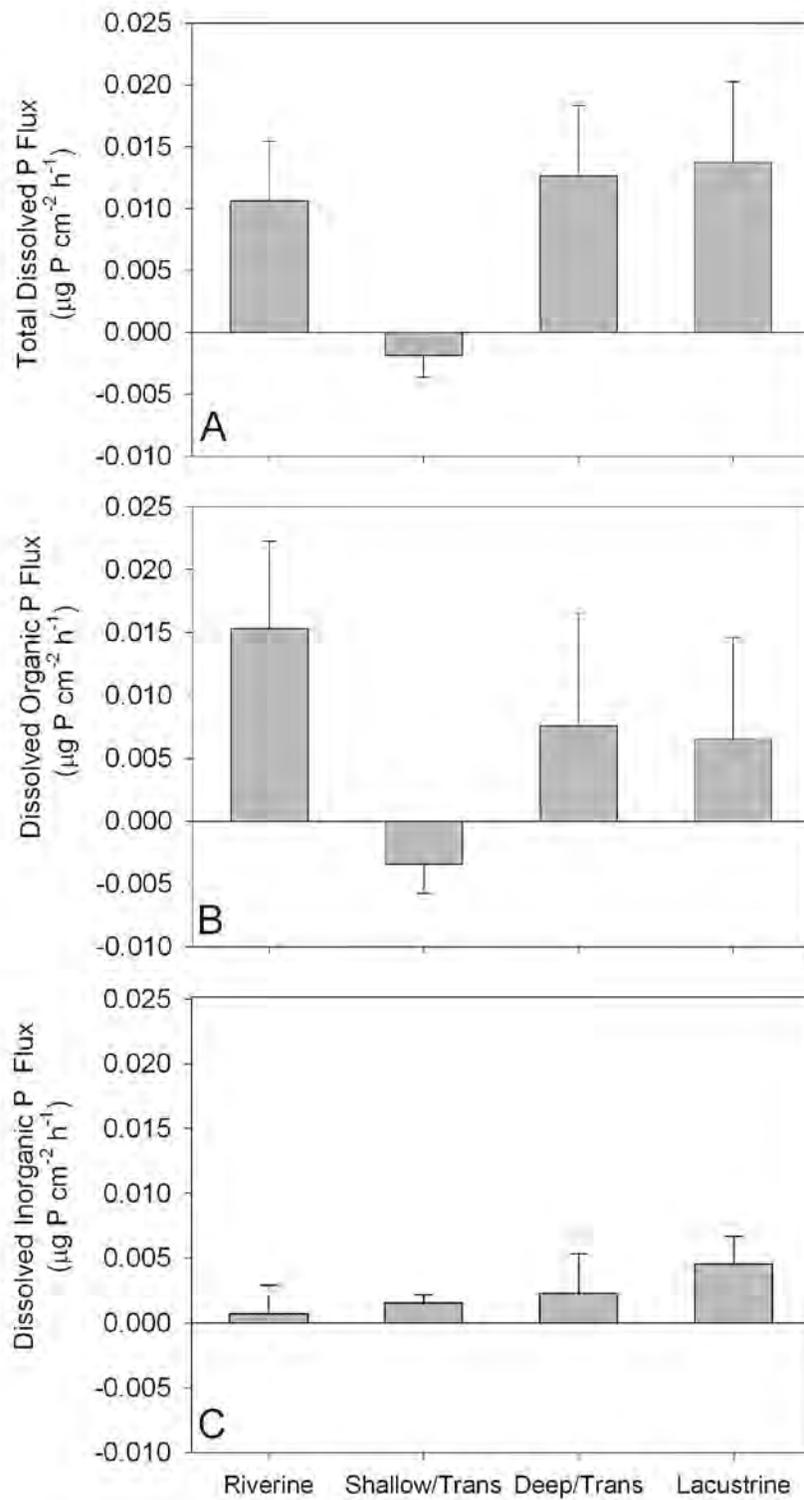
Fig 4. Total dissolved phosphorus flux (A), dissolved organic phosphorus (B), soluble reactive Phosphorus(C) . The standard error of the mean is indicated by bars.
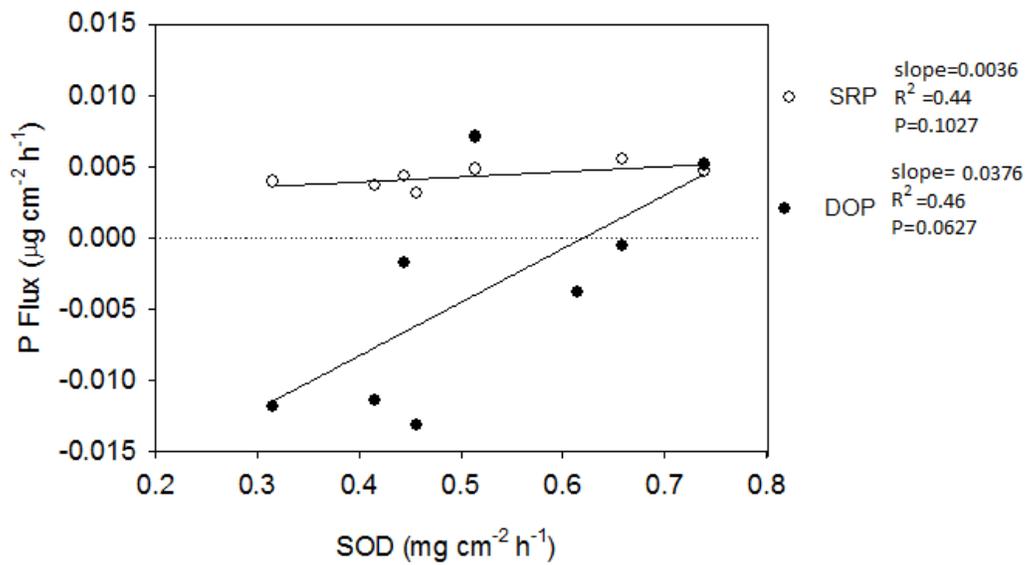
Fig 5. Relationship between sediment oxygen demand (SOD) and soluble reactive P (SRP) or dissolved organic P (DOP) flux in shallow sediment cores.