Phosphorus Sorption by Sediments from Wetlands in the Cedar River Watershed

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ABSTRACT

Excess phosphorus can lead to eutrophication of aquatic ecosystems, which can indirectly cause many species to suffer due to lower oxygen levels. The intent of this project was to determine if wetlands draining agricultural soil in the Cedar River watershed are removing phosphorus prior to empting into a tributary of the Cedar River. To determine the fate and transport of phosphorus in the wetlands, the total phosphorus (TP) of both the water and sediments was measured, and the ability for sediments to remove phosphate was also determined. The TP in the water column in the wetlands varied temporally from 700 to 1700 µg/L. Dissolved inorganic phosphate (SRP) totals were usually less than 10% of the total P, with a modest spike observed after a rainfall event. The low levels of SRP in the water led to testing of the TP levels in sediments and TP sorption capabilities. The TP of the sediment varied spatially from 500-700 µg/gdw. Sediments from the tributary (Beaver Creek) had total phosphorus levels of about 500 µg/gdw and the inlet to the wetlands varied from 300-400 µg/gdw. Depending on sampling locations, maximum sorption for sediments from the main body of the wetland ranged from 2-9 mg/gdw. Sediments from both the tributary (Beaver Creek) and the inlet to the wetlands sorbed about 7 mg/gdw. The results suggest that sediments in the wetlands are not yet saturated with phosphorus and therefore, when aerobic, can prevent phosphorus transport to rivers and streams.

INTRODUCTION

Wetlands have an important ecological function in maintaining and/or enhancing the quality of water in streams and rivers by acting as a filter for dissolved and suspended sediments and nutrients, which enter wetlands through the watershed. Without wetlands, rivers and lakes would receive chemicals from rainwater runoff, fertilizers, roadside runoff, and farm chemicals more rapidly and in greater amounts [1].

In many freshwater systems phosphorus is the nutrient that limits the growth of algae. Eutrophication is the accelerated nutrient enrichment of water bodies caused by the accumulation of excess nutrients, specifically phosphorus. Eutrophication is a problem in many of Iowa's lakes and rivers. Eutrophication results in algal blooms of excessive biomass, which lead to low oxygen levels, which cause serious stress to aquatic organisms. Since phosphorus sorbs to sediment, phosphorus is often transported into wetland systems by agricultural runoff [2]. One of the functions that wetlands provide is to sequester phosphorus from agricultural runoff, preventing it from entering lakes and rivers, such as the Mississippi River, and thus circumventing such problems as the "dead zone" in the Gulf of Mexico.

Although wetlands sediment may sequester phosphorus from the water, it is not necessarily prevented from eventually being transported to a lake or stream. The phosphorus that is sequestered by wetland sediment can, depending on chemical and biological conditions, be released (desorb) from the soil and reenter the water [3].

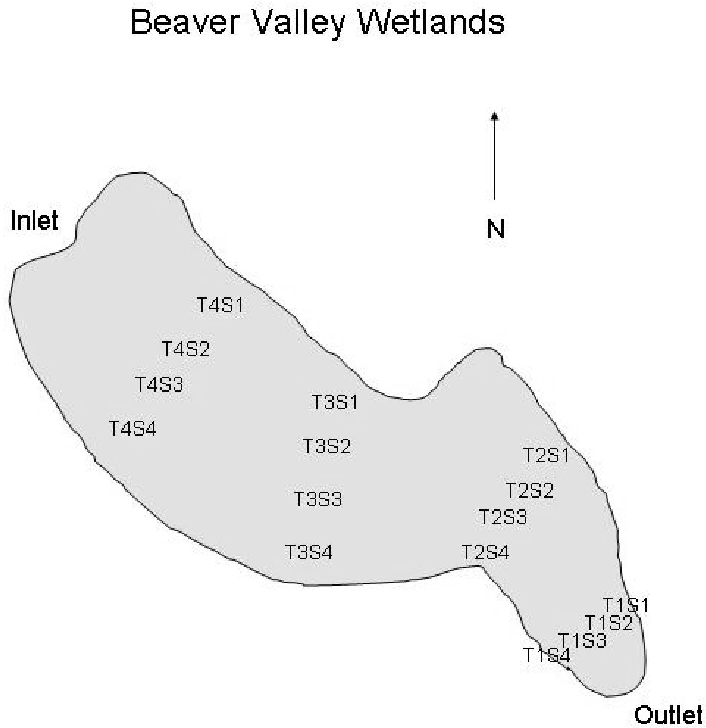

Figure 1. Map of Beaver Valley Wetlands sampling locations. The distance from the inlet to the outlet is approximately 500 m.

Therefore the levels of phosphorus in wetlands need to be monitored and controlled, because eventually wetland sediments saturated with phosphorus will become a source of, rather than a filter for, phosphorus in the watershed.

The goal of this project was to determine the fate and transport of phosphorus through the Beaver Valley Wetlands, Cedar Falls, Iowa. We measured different chemical forms of phosphorus, including water column and sediment total phosphorus, soluble reactive phosphate (SRP), and total particulate phosphate. Based on the results from these analyses we then examined the phosphorus (SRP) sorption capacities of wetlands sediments in order to determine if Beaver Valley Wetlands was a source or sink of phosphorus from agricultural runoff to the Cedar River in Iowa.

MATERIALS AND METHODS

Surface water samples were collected throughout the summer of 2003. Approximately two liters were collected by grab samples from collection sites and stored in coolers for transport back to the lab. Individual samples were collected from the lake at sixteen GPS (Global Positioning Systems) determined sites to get a representative sample of the wetlands (Figure 1). Samples for soluble reactive phosphorus (SRP) were filtered through type A/E glass fiber filters (Pall, Ann Arbor, MI) within one hour of collection and the filtrate was immediately analyzed by the Murphy–Riley ascorbic acid method. Unfiltered water samples were frozen and stored for total organic phosphorus (total P) by the persulfate digestion method [4].

Sediment samples were also collected from the wetlands by grab sample throughout the summer of 2003. Sediments were double bagged in Ziploc plastic bags, stored in coolers and then refrigerated (4^{o}C) upon return to the lab. The TP of each sediment sample was also determined by the persulfate digestion method modified for soils [5]. The water content of sediments was determined by weight difference before and after drying an aliquot to constant weight at 105^{o}C.

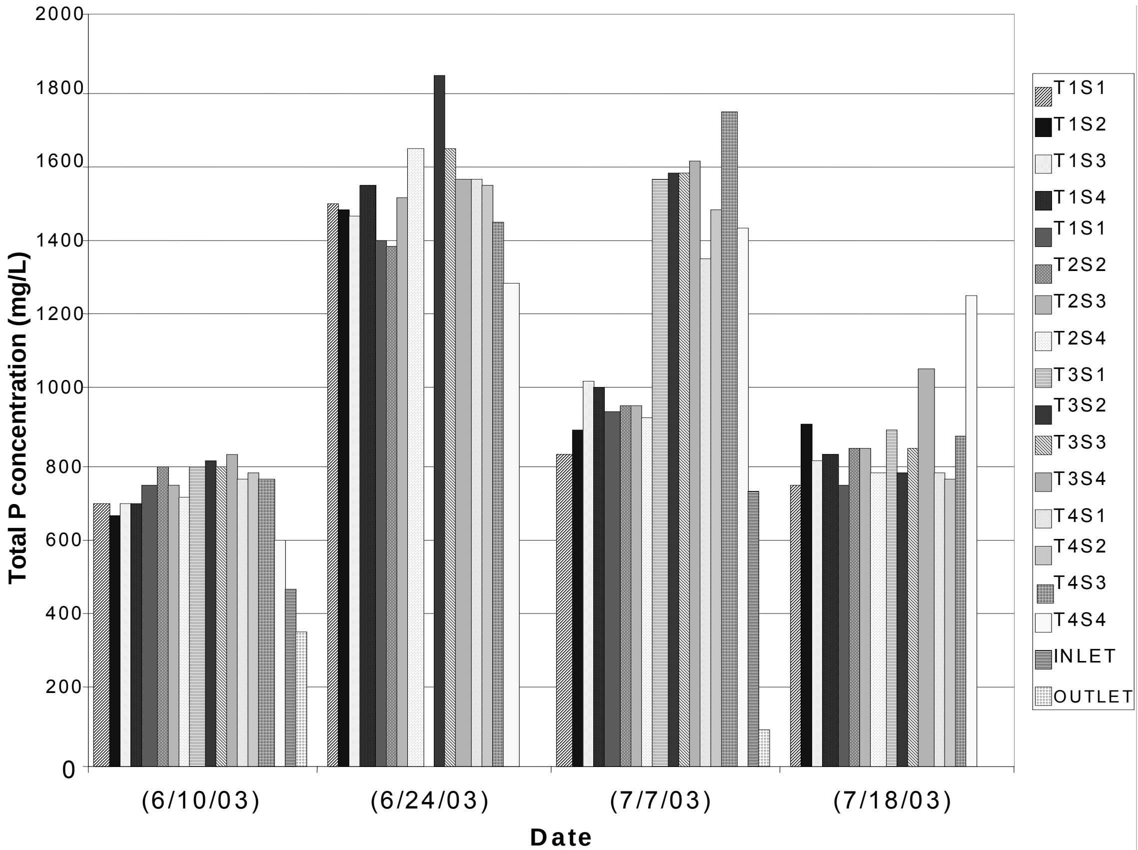

Figure 2. Total water column phosphorus in the Beaver Valley Wetlands from June 10th, 2003 to July 18th, 2003.

a. Phosphorus Sorption

The sorption capacity of sediment was determined by adding four grams of wet sediment to 100 mL of deionized water containing various amounts of KH_2PO_4 to give a range of added phosphate from 0.5 to 25 µg/mL (approximately 2.5 to 500 µg P/gdw sediment). The sediment-phosphate mixture was placed on a rotary shaker at 100 rpm for 24 hours, and then centrifuged to separate particulate P from SRP. The supernatant was further filtered through type A/E glass fibers filters before the SRP in the filtrate was measured to determine the amount of P released from the sediment.

RESULTS

Spatial and temporal variations of TP in water column samples taken from Beaver Valley Wetland transects were observed throughout the summer of 2003 (Figure 2). There was little spatial variation in SRP in water column samples (Figure 3), but a pronounced spike in SRP was observed throughout the wetlands following a rainfall event in July 2003. While the SRP values were quite high (often exceeding 50 µg/L), SRP generally made up less than 20% of the total P and is often less than 10% of the total P in water column samples (Figure 4).

Sediments throughout the wetland systems were capable of sequestering (through sorption) high amounts of dissolved P after only 24 hours in equilibrium (Figure 5). For example, 2 g of sediment collected from transect 2 on July 14 sequestered nearly 50% of 2.5 mg of dissolved inorganic phosphate contained in 100mL of deionized water (Figure 6). Plots of amount of phosphorus sequestered by sediment verses equilibrium SRP concentration (Figure 7) showed fairly typical saturation (Langmuir) sorption kinetics for several of the sediment samples. Linear conversion at these plots showed maximum sorption rang-

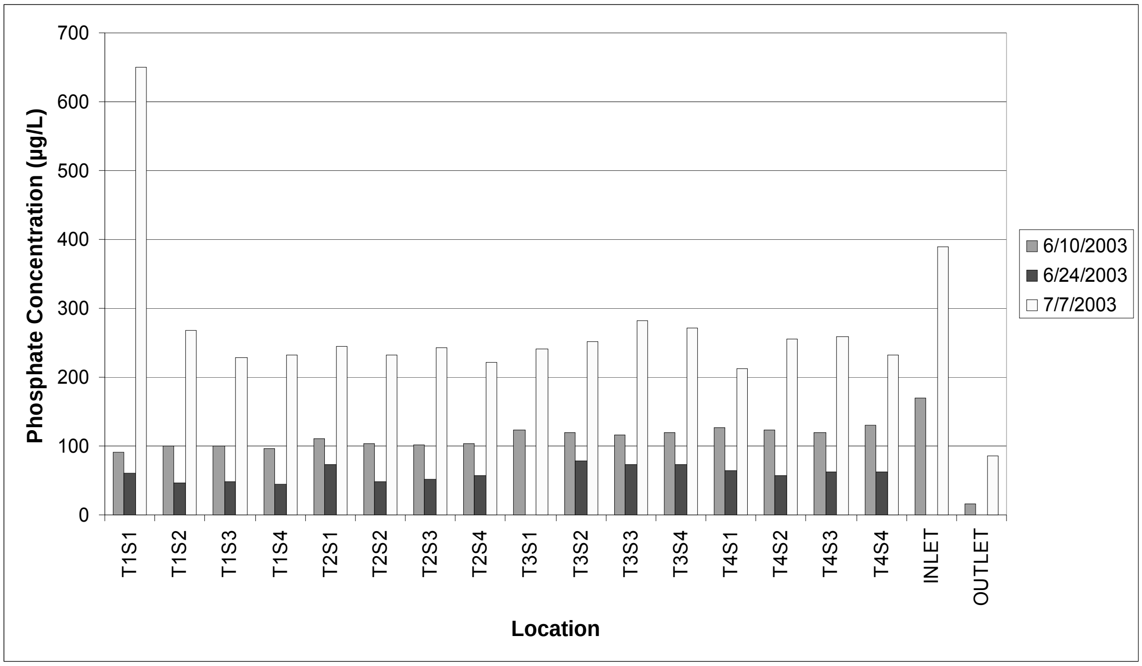

Figure 3. Dissolved inorganic phosphate (SRP) in the Beaver Valley Wetlands water column on June 10th, June 24th, and July 7th.

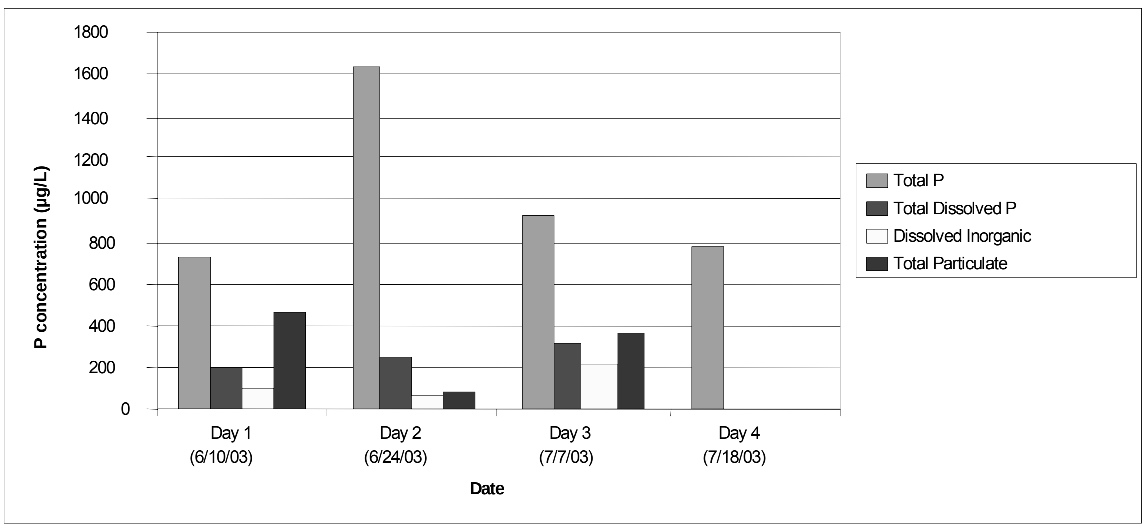

Figure 4. Fractionation of phosphorus in the water column for transect two sector four in June and July of 2003.

ing form approximately 2 to 10 mg P/gdw, with half saturation constants in the 1 to 5 mg/L range (Table 1). The quantity of SRP removed from the water as a function of sediment TP in experimental samples indicate that sediments in Beaver Valley Wetlands still have the ability to remove SRP from the water column (Figure 8).

DISCUSSION

Phosphorus is an essential element for all living organisms because it is a component of nucleic acids (e.g., DNA, RNA, ATP), the cell membrane (e.g., phospholipids), and the structural material of vertebrates. The only chemical form of P that can be directly assimilated by plants and algae is dissolved

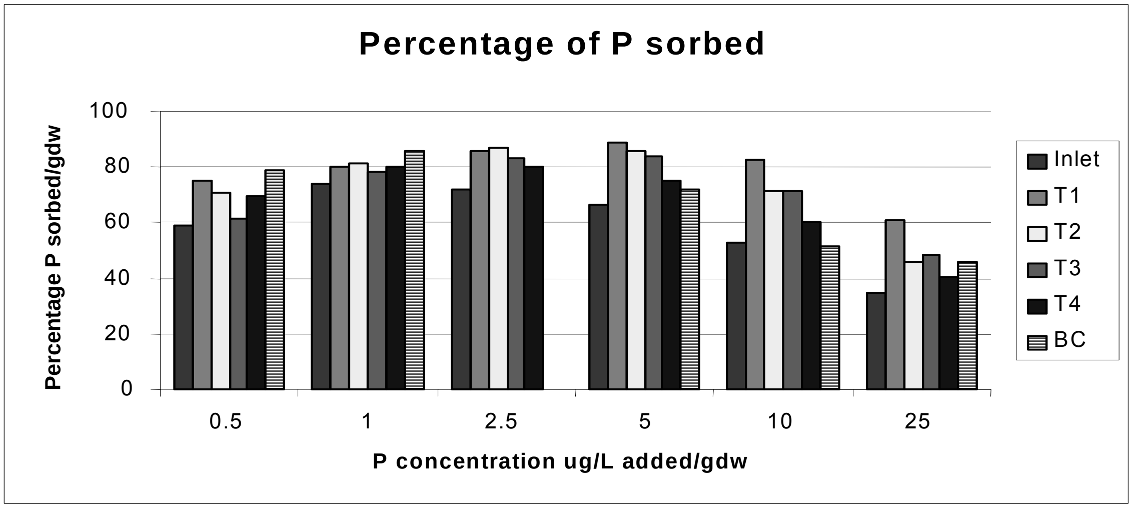

Figure 5. Amount of P sorbed as a function of added P for representative sediments collected in Beaver Valley Wetlands.

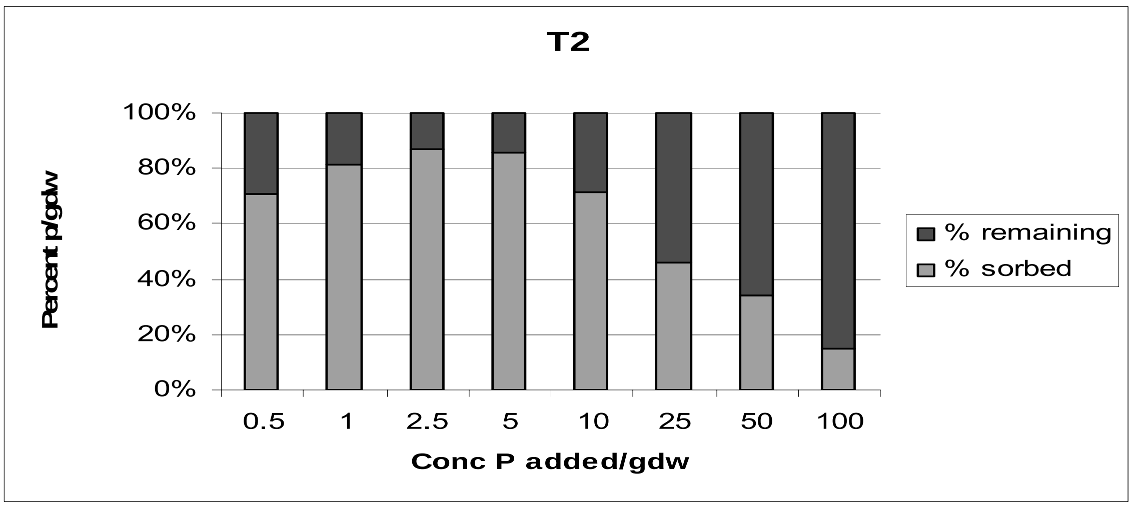

Figure 6. Amount of P sorbed as a function of added P for transect two collected on July 14, 2003.

inorganic phosphate, which analytically is represented by the soluble reactive phosphate (SRP) measurement. The partitioning of P between soil solution and the solid phase is considered to be controlled by sorption-desorption mechanisms [6]. Movement of sediment phase phosphate into solution (i.e., SRP) is influenced by the various other organic and inorganic forms of P present and by the rate and extent of the interaction of these forms with the surrounding aqueous phase [7]. For example, release of P from P bearing minerals is predicted on the basis of solubility products, which, for typical freshwater environments, are unlikely to maintain phosphate levels high enough to sustain large populations of algae (eutrophy). On the other hand, total organic P (TP), which includes algal biomass, correlates well with trophic status in most freshwater environments. There are many other forms of inorganic P that have been operationally defined based on chemical extraction procedures that can be converted to TP through the growth of algae. Chemically defined, occluded P is within soil/sediment mineral matrices and not in direct contact with solutions; thus, at least under aerobic conditions, its availability to algae is quite restricted. On the other hand, even though non-occluded (also called sorbed) soil/sediment P is not measured in the SRP fraction, it may have the ability to sustain dissolved phosphate in solution based on sorption/desorption reactions. Sorption/desorption reactions are influenced by cations in the solid phase, competing anionic species, pH, the surface area of the solid phase, contact time and oxidation-reduction conditions [5]. According to Pant and Reddy [8], P compounds in sediment maintain equilibrium with P in solution and can be described by Langmuir and Freundlich models. Soil tests in agriculture estimate plant available P by converting non-occluded P to SRP with mild acid extraction [5] or low replacement. Because

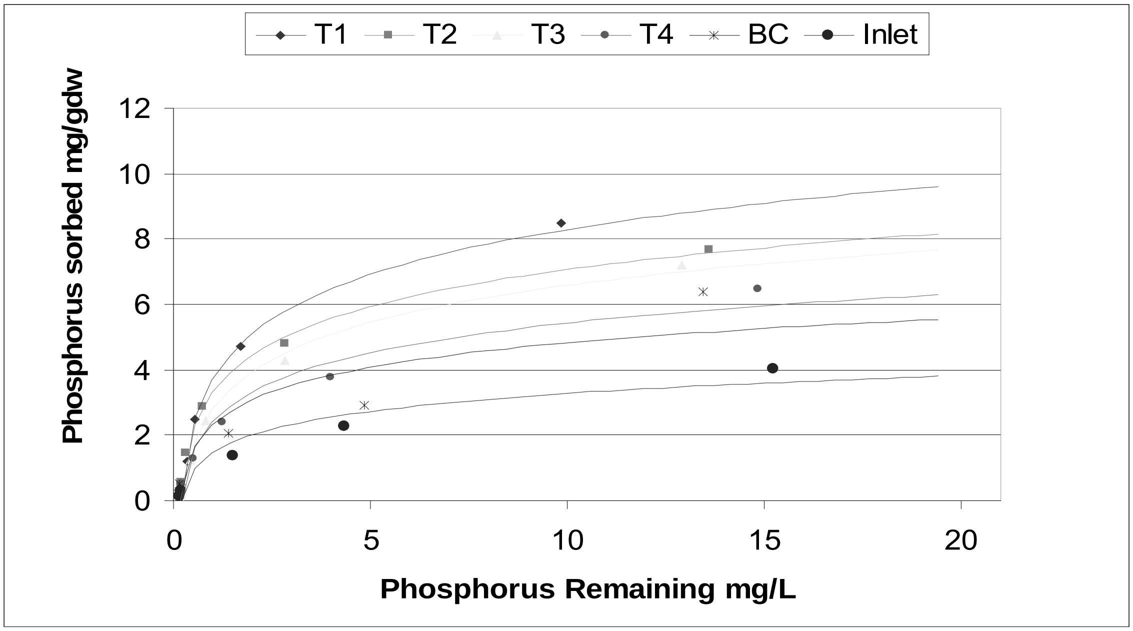

Figure 7. Sorption isotherms for typical sediments collected in the Beaver Valley Wetlands in the summer of 2003.

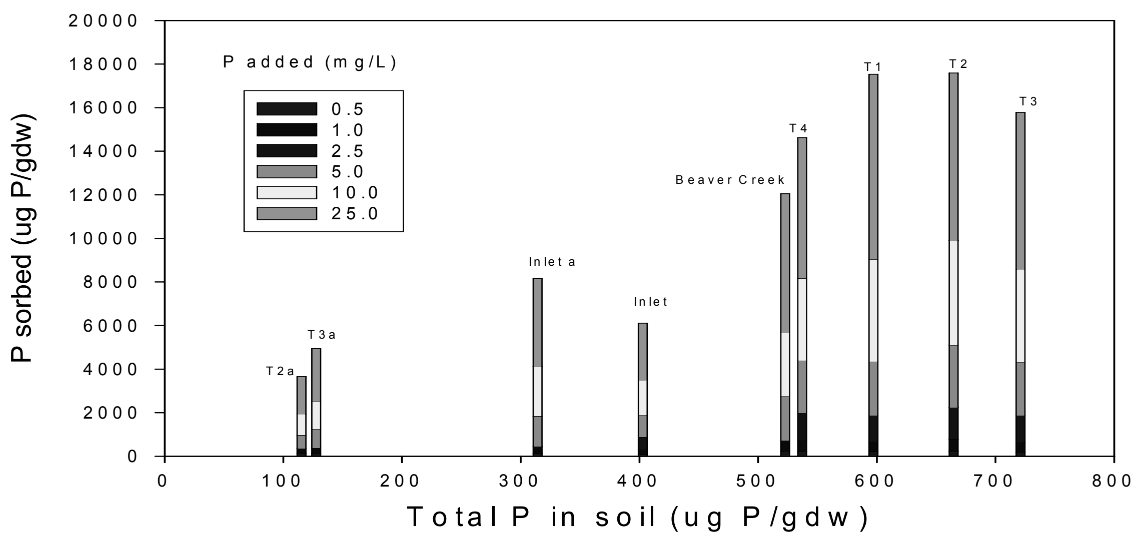

Figure 8. Amount of dissolved inorganic phosphate sorbed as a function of total P in the sediment.

much recent attention has been focused on wetlands restoration as a means of surface water quality protection, it has become necessary to evaluate the performance of specific wetlands systems with respect to phosphorus sorption and desorption (sequestration and release) reactions. Thus empirical measurements that characterize the ability of specific soils and sediments of specific wetlands to remove or supply P to its draining area are most informative.

Location	Maximum (mg P/g)	Langmuir Sm (mg/L)
Inlet	2.8	1.8
T1	9.7	1.4
T2	8.1	0.96
T3	7.8	1.4
T4	7.1	1.9
Beaver Creek	7.2	3.1
Inlet a	4.5	2.2
T2 a	2.1	4.4
T3 a	2.8	3.9

Table 1. Langmuir sorption constants for sediments from the Beaver Valley Wetlands watershed. Max is the maximum amount of SRP sorbed per gram sediment. Sm is the SRP concentration at half maximum.

In this study, we first evaluated SRP as an indication of P release. SRP concentrations were relatively low in all transects of the wetlands in comparison to the total P (Figure 2 and 3). These lower SRP values numbers led us to investigate sediment phosphorus levels, extractable by persulfate, which were also high compared to SRP levels. When we measured the sorption capacities we found that although Beaver Valley Wetlands sediments contain high levels of total P, they still have the capacity to remove large amounts of SRP, e.g., greater than 50% of SRP added, on average (Figures 5 and 6). The Langmuir sorption constants (MAX and Sm) provide an empirical measure of the capacity for sediments in Beaver Valley Wetlands to remove SRP from the water column. The measurements from the summer of 2003 can now be used as a benchmark for continued monitoring of Beaver Valley Wetlands and compared to other wetlands systems. Phosphorus-laden water from Beaver Valley Wetlands flows into the Cedar River. The undersaturation of the sediments can be due to different factors such as sediment composition and reducing anaerobic conditions.

Beaver Valley Wetlands drains agricultural land and hosts large numbers of migrating waterfowl. Input of P to the wetlands system has been significant, as reflected by TP concentrations in the water column approaching, at times, nearly 2000 µg/L (Figure 1). Such concentrations are typical throughout hypereutrophic systems. The range given by the OECD (Organization for Economic Co-operation and Development) for eutrophic lake water is from 16 to 390 µg PO_4^{3-}-P/L (based on scientists' opinions) and exceeds the standards of quality for waters for lakes and streams for states that have established those standards [9]. For example, Utah considers any surface water body that contains more than 25 µg PO_4^{3-}-P/L as total P (TP) to be eutrophic [10]. Such standards for wetlands are not yet published as the EPA has not yet published the Nutrient Technical Guidance for wetlands [11]. Are the wetlands serving as a sink for run off and waterfowl P or has it become a source of P to its tributary (Beaver Creek), the Cedar River? The sorption data (Figure 7) help to answer this question and show that the sediments are not saturated with P, and furthermore even those sediments with the highest P levels sorb more than sediments that have less P (Figure 8). Thus sorption, which is a function of P input, is also a function of sediment type. Since sediments are heterogeneous within and among wetland systems, empirical P sorption/desorption kinetics are necessary for predicting whether sediments are a source or sink for P.

CONCLUSIONS

The results indicate that while TP in the surface water in the Beaver Valley Wetlands is extremely high (characteristic of a hypereutrophic environment), the dissolved P remains relatively low. This can be explained by the fact that sediments have not reached maximum capability to sequester P. The data show that if sediments remain aerobic, and barring flooding events, the Beaver Valley Wetlands will continue to sequester P and prevent its rapid transport to the Cedar River watershed. Our results also show that empirical measurements of the sorption/desorption capacity of specific wetlands is a better predictor of P sequestration that TP or SRP analysis and is thus more useful to determine the effectiveness of removing (filtering out) P before the water reaches lakes and streams. Finally, since P sequestration is a function of sediment type as well as P input, wetlands, drainage ditches and catchment basins can enhance water quality if constructed with soils/minerals known to sequester large amounts of phosphorus such as the oxidized iron found with hematite [5].

REFERENCES

1. Lannoo, M. J. 1996. *Okiboji Wetlands: A Lesson in Natural History* (University of Iowa Press, Iowa City, Iowa USA, 1996) pp. 112-114.
2. Pant, H.K., and Reddy, K.H. “Potential internal loading of phosphorus in a wetland constructed in agricultural land,” *Water Research*, Vol. 37, pp. 965-972 (2003).
3. Hoeft, R.G. *Phosphorus: Agronomic, Economic and Environmental Considerations* (Department of Crop Science, University of Illinois, 2003).
4. Clesceri, L.S., Greenberg, A.E., and Eaton, A.D., (editors). *Standard Methods for the Examination of Water and Wastewater, 20th Edition*. (American Public Health Association, Washington D.C., 1998).
5. Clayton, M. E. Liegeois, S., and Brown, E. J. “Phosphorus sequestration in lake sediment with iron mine tailings” *Soil and Sediment Contamination*, Vol. 13, pp. 519-529 (2004).
6. Frossard, E., Brossard, M., Hedleym, M.J., and Metherell, A. “Reactions contolling the cycling of P in soils,” Chapter 7: Tiessen, H. (ed.). *SCOPE 54 Phosphorus in the Global Environment—Transfers, Cycles and Management* (Wiley & Sons, London, 1995).
7. Sagher, A. *Availability of soil runoff phosphorus to algae*. Ph.D. Thesis, University of Wisconsin. (University Microfilms, Ann Arbor Michigan, 1976).
8. Pant, H.K., and Reddy, K.H. “Phosphorus sorption characteristics of estuarine sediments under different redox conditions,” Journal of Environmental Quality, Vol. 30, pp. 1474-1480 (2001).
9. EPA (United States Evnironmental Protection Agency), *Nutrient Criteria Technical Guidance Manual Lakes and Reservoirs*. EPA-822-B00-001 (Office of Water, Washington D.C., 2000).
10. Utah Administrative Code. *Standards of quality for waters of the state* (Utah Administrative Code R317.2.14) (2005)
11. EPA (United States Environmental Protection Agency) *National nutrient guidance* (2003). http://www.epa.gov/owow/wetlands/what/definitions.html