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Anna L. Erickson

*University of Arkansas, Fayetteville*

Stephanie M. Williamson

*University of Arkansas, Fayetteville*

Brian E. Haggard

*University of Arkansas, Fayetteville*

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# Method analysis of laboratory measures of stream sediment and water phosphorus equilibrium

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*Anna L. Erickson<sup>\*</sup>, Stephanie M. Williamson<sup>†</sup>, and Brian E. Haggard<sup>§</sup>*

## **ABSTRACT**

Elevated phosphorus concentrations in aquatic ecosystems of northwest Arkansas prompted an investigation of the effects of sample preparation and extraction methods on laboratory measures of sediment-phosphorus interactions. Two streams of contrasting phosphorus (P) concentrations were selected to determine the effect of using a  $\text{CaCl}_2$  solution instead of filtered stream water, refrigerated or dried sediments instead of fresh wet sediments, and vortexing the suspensions instead of shaking them. Sediment equilibrium P concentration ( $\text{EPC}_0$ ) and P buffering capacity (K) were used to determine differences in extraction methods.  $\text{EPC}_0$  and K from extractions using fresh sediments and a  $\text{CaCl}_2$  solution matching the electrical conductivity of the stream water were not significantly different from extractions using fresh sediments and filtered stream water. However, using dried sediments instead of fresh, wet sediments in the extraction procedure affected  $\text{EPC}_0$  and K estimation. In the P-enriched system, sediment extractions using refrigerated sediments or vortex mixing of the sediment-slurry suspension produced  $\text{EPC}_0$  and K estimates that were significantly different than estimates from fresh, wet sediment and filtered stream-water extractions. Overall, method analysis of laboratory measures of stream sediment and water P equilibrium suggested that in low-P-concentration streams, estimates varied little whereas in high-P streams the method of extraction was more important.

<sup>\*</sup> Anna L. Erickson will graduate in May 2005 with a degree in biological engineering.

<sup>†</sup> Stephanie M. Williamson, faculty sponsor, is a program technician II in the Department of Biological Engineering.

<sup>§</sup> Brian E. Haggard, faculty sponsor, is an adjunct assistant professor in the Department of Biological Engineering.

## **MEET THE STUDENT-AUTHOR**

I graduated from the Arkansas School of Mathematics and Sciences in 2001 and am currently attending the University of Arkansas, majoring in biological engineering. I have been involved in the Biological Engineering Student Club, Phi Sigma Rho, Women In Engineering, and Campus Civitan. During my junior year, I was selected to be the Biological Engineering Department Mentor for Women in Engineering. I also have worked as a laboratory assistant for Dr. Brian Haggard, my faculty sponsor, for two years. While working on another project, several complications with the method analysis of the laboratory procedures were questioned. Dr. Haggard encouraged me to complete this project to settle those questions and to gain further research and writing experience.



*Anna L. Erickson*

## **INTRODUCTION**

Elevated phosphorous (P) concentrations in aquatic ecosystems have become one of the greatest water-quality concerns in northwest Arkansas. Phosphorus is essential for plant nutrition and is a crucial nutrient in aquatic ecosystems, often limiting algal growth. Phosphorus originates from a variety of sources, particularly municipal wastewater-treatment plants (WWTP) and runoff from urban and agricultural landscapes. An abundant amount of P acquired in a stream or lake can stimulate excess algal growth, accelerating the natural process of eutrophication. Accelerated eutrophication results in a decline in water quality, as well as economic losses such as limiting irrigation withdrawals, reducing aesthetic value and recreational activities, and increasing drinking water-treatment costs (USGS, 1999).

The effects of increasing P concentrations in aquatic ecosystems may occasionally be altered by the role of benthic sediments (Haggard et al., 1999). Streambed sediments can regulate P concentrations in the water column by adsorbing and desorbing soluble inorganic P (Meyer, 1979). Differences in experimental design and laboratory methods have significantly affected laboratory measures of sediment-P interactions (; Fox, et al., 1989; Klotz, 1988; Meyer, 1979; 1971Popova, 2000; Taylor and Kunishi). These cited studies have investigat-

ed a variety of different factors in the extraction process.

One of the more common laboratory experiments is a series of extractions to determine the sediment equilibrium-P concentration ( $EPC_0$ ). Sediment  $EPC_0$  is the dissolved inorganic P concentration in the water column when there is no net sediment adsorption or desorption of  $PO_4$  from the water column;  $EPC_0$  may also indicate if sediments act as a sink or source of P for the water column (Taylor and Kunishi, 1971). Differences in  $EPC_0$  are often related to particle size, surface-to-volume ratio of sediments, and sediment-to-solution ratio (Klotz, 1988; Meyer, 1979; Taylor and Kunishi, 1971). Although not affected by temperature changes,  $EPC_0$  may increase with a decrease in solution pH (Fox, et al., 1989; Klotz, 1988; Meyer, 1979). The effect of extraction time was minimal, and 1 hour equilibration period provided a useful approximation of  $EPC_0$  (Taylor and Kunishi, 1971). Air drying and the speed the sediments are shaken during the extractions likely affect laboratory measures of sediment-P interactions (Meyer, 1979; Srivastava, 1998).

The objectives of this study were to 1) investigate the effect of varying extraction methods as well as 2) sample handling, storage, and drying on sediment  $EPC_0$  estimation and P buffering capacity in two streams of contrasting dissolved-P concentrations.

## **MATERIALS AND METHODS**

### *Study Sites*

Two contrasting streams and catchments located in the Ozark Plateau of northwestern Arkansas—Columbia Hollow Watershed and Mud Creek Watershed—were selected for this study. The Mud Creek sampling site is a small urban tributary with relatively low soluble-P concentrations and external-P inputs from urban nonpoint sources. The Columbia Hollow sampling site is a slightly larger catchment with greater soluble-P concentrations and external-P inputs originating from urban and agricultural nonpoint sources and a WWTP approximately 3 km upstream in Decatur, Ark.

### *Stream Water and Sediment Collection*

Stream water and bottom sediments were collected from three lateral transects perpendicular to stream flow at the Columbia Hollow and Mud Creek sampling sites. Three water and sediment samples (A, B, C) were collected from each stream, with A representing the most upstream transect and C being the most downstream transect. Stream water was collected in 1 L acid-cleaned polyethylene bottles at each site. The stream water was refrigerated in the dark until return to the laboratory where the water samples were filtered through a 0.45  $\mu$ m nylon membrane into clean 1 L polyethylene bottles. Two 20 mL aliquots were also collected at each transect in a syringe and filtered through a 0.45  $\mu$ m nylon membrane. One of the filtered aliquots was acidified to pH <2 using concentrated HCl and used for measuring dissolved-P concentration. Sediments from the top 10 cm of the streambed were collected using a shovel at each site. Sediment samples were stored in plastic bags and refrigerated until return to the laboratory. The sediments were then sieved, and the fraction less than 4.76 mm was used in the proceeding extractions.

### *Extraction Procedures*

A series of five extraction methods were conducted on the sediments collected at the two streams to determine the effect of solution chemistry and sample handling, storage, and drying on sediment-P interactions.

Sediment-P interactions were evaluated by determining sediment  $EPC_0$  and P buffering capacity. The amount of P sorbed per gram of sediment was regressed against the initial P concentration where  $EPC_0$  was calculated as the x-intercept of this relation (Klotz, 1985; Taylor and Kunishi, 1971). The amount of P adsorbed is the difference between the initial soluble-P concentration in the solution mixed with sediments and the final soluble-P concentration after 1 h of shaking. The slope of this linear relationship between P sorbed and initial P concentration was also calculated to determine the

amount of P that may be desorbed or adsorbed per unit increase in initial P concentration. This slope (K) may be interpreted as a measure of the ability of stream sediments to buffer increasing P concentrations, with greater slopes suggesting greater P buffering capacity (Bache and Williams, 1971).

The prototypical extraction procedure consisted of weighing approximately 25 g of fresh wet sediment into 250 mL Erlenmeyer flasks. One-hundred mL of filtered stream water was then added to the Erlenmeyer flasks. Sediment slurries were spiked with a series of P additions resulting in the ambient concentration increasing by 0, 0.5, 1, 2, and 5 mg/L. The flasks were shaken for 1 h at 100 oscillations/minute. Subsequently, an aliquot from the sediment slurry was filtered through a 0.45  $\mu$ m nylon membrane and then acidified to pH <2 using concentrated HCl. The remaining sediment slurry was poured into pre-weighed aluminum pans and dried for 48 hours at 80°C in order to determine the amount of dry sediments. The acidified, filtered aliquot was used to determine the final soluble reactive P (SRP) in the sediment slurry. SRP was determined using the Skalar SanPlus continuous flow analyzer and the ascorbic acid reduction method in which ammonium molybdate and potassium (K) antimony tartrate react in an acidic medium with reactive  $PO_4$  molecules to form an antimony-phospho-molybdate complex, which is reduced to a blue-colored complex by ascorbic acid (APHA, 1992). The  $EPC_0$  and K estimates of the prototypical extractions were compared to the estimates from four other extractions that differed from the prototypical extractions by one variable.

The effect of solution chemistry was determined by comparing  $EPC_0$  and K from extractions using a solution of  $CaCl_2$  instead of filtered stream water. The  $CaCl_2$  solution was made by diluting 1 M  $CaCl_2$  with deionized distilled water so that its electrical conductivity was equivalent to that of the filtered stream water from each sampling site.

Sample handling effects were ascertained by vortexing the flasks for 3 sec every 10 min for 1 h instead of shaking the samples as described in the prototypical extraction.

Comparison of sample storage effects was completed by refrigerating the sediments for approximately 24 h and completing the prototypical extractions as defined above.

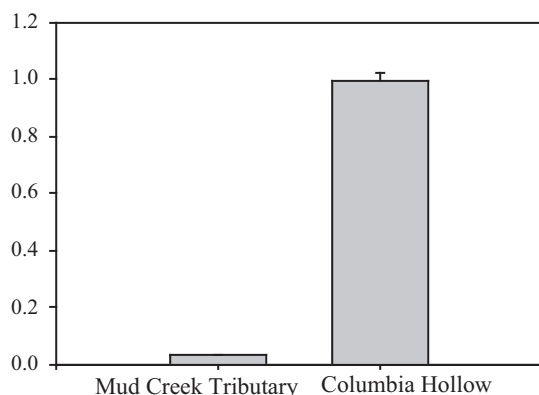
The effect of drying was determined on sediments by drying fresh, wet sediments for 48 hours at 80°C and then completing extractions. The amount of dried sediments added to the 250 mL Erlenmeyer flasks was equal to the dry-matter percentage (approximately 17 g). This

quantity kept the ratio of the amount of sediment-to-solution volume relatively similar.

Simple linear regressions were used to define the x-intercept ( $EPC_0$ ) and slope ( $K$ ) when the slope was significantly different than zero ( $P < 0.1$ ). Differences in  $EPC_0$  and  $K$  for each treatment were evaluated using a one-way analysis of variance (ANOVA) and means separation was determined using least significant difference (LSD) (Statistix 7.1 Analytical Software). The  $EPC_0$  and  $K$  means of the prototypical extraction were compared to the results of the other methods to observe any differences ( $P < 0.1$ ).

## RESULTS AND DISCUSSION

These two streams had drastically different concentrations of dissolved P (T-test,  $T = 2.92$ ,  $p < 0.001$ ); average SRP concentration in Mud Creek and Columbia Hollow was 0.03 mg/L and 1.00 mg/L, respectively (Fig. 1). The municipal WWTP discharging into Columbia Hollow increased SRP concentration 30-fold compared to a stream without wastewater treatment-plant effluent. This effect has been observed in many northwest Arkansas streams receiving effluent discharges from municipal WWTPs (Haggard et al., 2001).



**Fig. 1.** Mean ( $\pm$  standard deviation) SRP concentrations for Mud Creek and Columbia Hollow.

The amount of P adsorbed and the initial SRP concentration for the transects at the Mud Creek tributary displayed significant linear relationships for all  $EPC_0$  methods (simple linear regression,  $r^2 > 0.94$ ,  $p < 0.01$ ). The  $EPC_0$  estimation of the fresh sediments was only significantly different from extractions using dried sediments (ANOVA LSD,  $p = 0.01$ ) whereas it was similar to the extractions using refrigerated sediments and extrac-

tions using the vortex-mixing technique, as well as the extractions using a  $CaCl_2$  solution (Table 1). The increase in  $EPC_0$  of the dried sediments may be accounted for by the release of P from microbes destroyed by desiccation (Srivastava, 1998). Phosphorus sorption in sediments that contain inhibited microbial growth was less than P sorption in fresh sediments (Haggard, et al., 1999; Klotz, 1985; Meyer, 1979). The buffering capacity ( $K$ ), however, was only affected by the mixing technique where vortexing instead of shaking resulted in a greater  $K$  (ANOVA LSD,  $p = 0.01$ ).

At Columbia Hollow, extractions involving the dried sediments and the vortexing technique did not display a significant linear relationship ( $p > 0.1$ ) (Table 1). Estimated  $EPC_0$  from extractions using refrigerated sediments with filtered stream water and from extractions using fresh sediments and a  $CaCl_2$  solution was not significantly different from the prototypical extractions. When comparing  $K$ , only the extractions using fresh sediments and a  $CaCl_2$  solution were not significantly different from the extractions using fresh sediments and filtered stream water whereas the extractions with refrigerated sediments were significantly different (ANOVA LSD,  $p = 0.01$ ).

Some discrepancies were observed between  $EPC_0$  and  $K$  when sediments were vortexed, refrigerated, or dried, especially in the high-P concentration stream. Overall,  $EPC_0$  and  $K$  estimates were statistically similar between methods using fresh sediments and either filtered stream water or a  $CaCl_2$  solution with a conductivity similar to that of the stream. An increase in the concentration of a  $CaCl_2$  solution may decrease sediment  $EPC_0$  (Klotz, 1988), and a previous study at Columbia Hollow suggested that using a  $CaCl_2$  solution of similar conductivity to that in the stream produced significantly reduced sediment  $EPC_0$  estimates (Popova, 2000). Due to these effects of solution chemistry,  $EPC_0$  estimation using filtered stream water and fresh sediments would best measure the sediment-phosphorus interactions.

$EPC_0$  estimation of the extractions using fresh sediments and filtered stream water was compared to the SRP concentration in the water column at each stream to determine whether the sediments act as a sink or source of P or are in equilibrium with the water column. At the Mud Creek tributary, there was no significant difference in  $EPC_0$  and the SRP concentration of the water column so the sediments were most likely in equilibrium with the stream. However, at Columbia Hollow, sediments were probably acting as a source of P because sediment  $EPC_0$  was greater than the SRP concentration in the water column (ANOVA LSD,  $p = 0.01$ ). Sediment  $EPC_0$

at Mud Creek was much less than at Columbia Hollow (Fig. 2). Contrarily, K was much greater for Mud Creek compared to that observed from the Columbia Hollow sediments. Thus, the Mud Creek sediments have a greater ability to buffer increasing P concentrations in the water column, possibly because this stream does not receive any municipal WWTP discharge. Based on these results, it is suggested that fresh, wet sediments and filtered stream water should be used when evaluating sediment-P interactions, especially in phosphorous-enriched streams.

## **ACKNOWLEDGMENTS**

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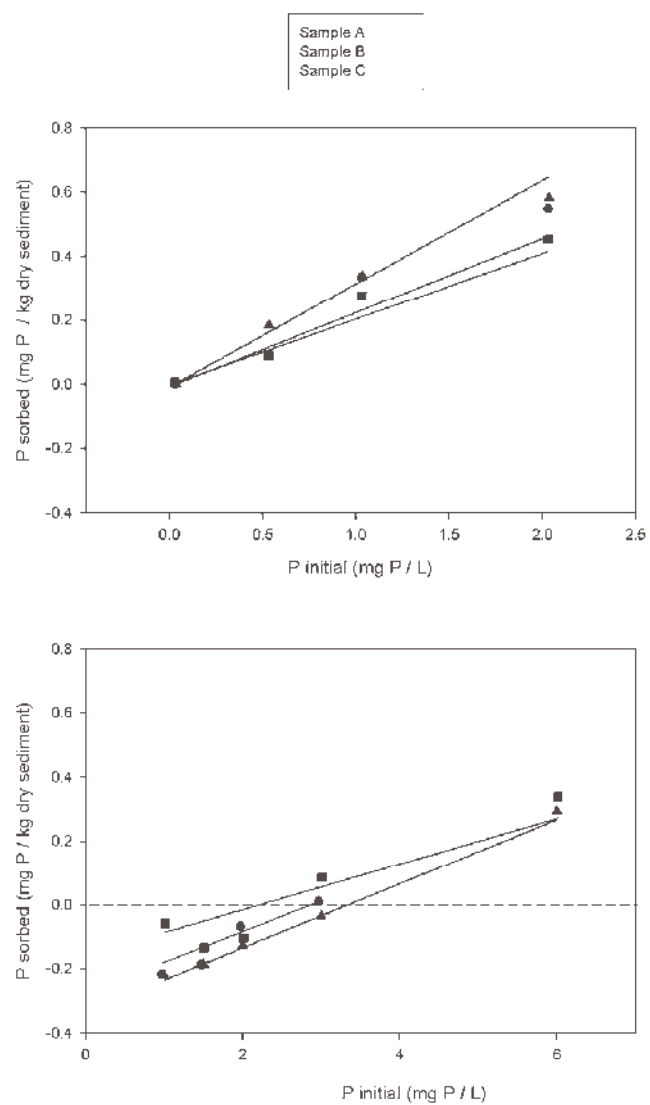
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**Table 1. EPC<sub>0</sub> and K means for the Mud Creek Tributary and Columbia Hollow**

Watershed	Treatment	EPC <sub>0</sub> mean	Heterogeneous groups based on EPC <sub>0</sub>	K mean	Heterogeneous groups based on K
Mud Creek Trib.	Dried sediments	0.117	1	0.298	2, 3
Mud Creek Trib.	Refrigerated sediments	0.086	1, 2	0.240	3
Mud Creek Trib.	Live sediments	0.007	2, 3	0.268	2, 3
Mud Creek Trib.	Vortexed sediments	0.004	3	0.378	1
Mud Creek Trib.	CaCl <sub>2</sub> solution	-0.046	3	0.328	1, 2
Columbia Hollow	Refrigerated sediments	2.864	1	0.224	1
Columbia Hollow	Live sediments	2.824	1	0.106	2
Columbia Hollow	CaCl <sub>2</sub> solution	3.656	1	0.088	2





**Fig. 2.**  $EPC_0$  and  $K$  from extractions using filtered stream water and fresh, wet sediments from Columbia Hollow (bottom) and Mud Creek (top) tributaries.