

Reducing Dissolved Phosphorus in Stream Water May Not Influence Estimation of Sediment Equilibrium Phosphorus Concentrations

Eleanor Henson,* Abbie Lasater, and Brian E. Haggard

Core Ideas

- The potential for stream sediments to adsorb or release P depends on the sediment equilibrium phosphorus concentration (EPC).
- Accurate estimations of sediment EPC are important for watershed modeling and total maximum daily load development.
- Existing methods for estimating sediment EPC often require extrapolating past a known dataset.
- This study used alum to promote desorption from sediments during EPC estimations.
- Results suggested current methods of EPC estimation are acceptable.

E. Henson and A. Lasater, Dep. of Biological and Agricultural Engineering, Univ. of Arkansas, Fayetteville, AR 72701; B.E. Haggard, Arkansas Water Resource Center, Univ. of Arkansas, Fayetteville, AR 72701 and Dep. of Biological and Agricultural Engineering, Univ. of Arkansas, Fayetteville, AR 72701.

Received 15 May 2019.

Accepted 24 Aug. 2019.

*Corresponding author (egh001@uark.edu).

Agrosyst. Geosci. Environ. 2:190037 (2019)
doi:10.2134/age2019.05.0037

ABSTRACT

The potential for stream sediments to adsorb or release phosphorus (P) depends on the equilibrium P concentration (EPC), which is the water column P concentration where P is neither (net) adsorbed nor released from the sediments. Current methods of measuring EPC in streams include adding known P concentrations to stream water, mixing with fresh sediments, and allowing the mixture to reach equilibrium through P sorption. Sediment EPC is usually calculated as the *x*-intercept of the linear relationship between initial P concentrations and P adsorbed by the sediments. However, the *x*-intercept is often an extrapolation past the known data set (i.e., no desorption of P from the sediments is simulated). The purpose of this study was to use aluminum sulfate (alum) to decrease ambient P concentrations and encourage P desorption from the sediments and to compare EPC estimations with and without the use of alum treatments. The results from this study found optimal alum dosages to be between 5 and 25 mg-Al₂(SO₄)₃ L⁻¹ to provide a range of P removal for the EPC experiments. Above 25 mg-Al₂(SO₄)₃ L⁻¹, stream water pH began to decrease. The other notable changes to water chemistry after alum treatments were increases in sulfate and residual concentrations of aluminum. However, EPC estimations were not significantly different between traditional calculation methods and the use of P desorption data points. These results suggest current methods for EPC estimations are acceptable, and spending time and money to promote desorption of P from the sediments is not necessary to estimate EPC.

Abbreviations: EPC, equilibrium phosphorus concentration; SRP, soluble reactive phosphorus; WWTTP, wastewater treatment plant.

Phosphorus enrichment in streams and rivers often leads to excessive algal growth and accelerated eutrophication. In addition to P inputs from the landscape, in-stream P behavior must be considered to apply effective management strategies (McDowell and Sharpley, 2003). Benthic sediments can adsorb or release P through physiochemical processes (e.g., sorption and desorption with Al and Fe hydroxides or coprecipitation with Ca) and biological processes (e.g., assimilation by bacteria, aquatic plants, and benthic algae) (Withers and Jarvie, 2008). These in-stream processes can modify edge-of-field P losses and P loads and forms transported downstream (Mulholland and Webster, 2010).

In theory, the potential for sediments to adsorb or release P depends on the equilibrium P concentration (EPC), which is the water column P concentration where P is neither sorbed nor released from the sediments (Froelich, 1988). This potential for sediments to either buffer or increase external P loads is increasingly important for watershed modeling and total maximum daily load development (Mittelstet et al., 2017; White et al., 2014). For the Soil and Water Assessment Tool, a widely used model for predicting hydrology, water quality, and management impacts (Gassman et al., 2007), an in-stream P cycling model has been developed and tested to include the EPC concept (White et al., 2014). However, to calibrate and validate EPC model estimates, EPC must be experimentally measured using stream sediment and water samples.

Current methods of measuring EPC in streams include adding known P concentrations to stream water (or other aqueous solutions), mixing with fresh sediments, and allowing the sediments and water to reach equilibrium through P sorption (Klotz, 1985; Taylor and Kunishi, 1971). Sediment EPC is determined by relating initial P concentration in

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Table 1. Ambient nutrient concentrations and sediment properties of the five equilibrium P concentration experiment sites.

| Site | Collection date | Ambient stream conditions | | | | | Sediment properties | | | | |
|---------------------------------|-----------------|---------------------------|-------|------|-----------------|-------|---------------------|------|------|------|------------------|
| | | SRP | TP | TN | NO ₃ | N+N | Conductivity | Sand | Silt | Clay | Loss on ignition |
| | | mg L ⁻¹ | | | | | μS cm ⁻¹ | % | | | |
| Spring Creek upstream | 5 July 2018 | 0.003 | 0.015 | 1.69 | 1.40 | 1.44 | 412.0 | 86.2 | 2.5 | 11.3 | 2.4 |
| Spring Creek 1 km downstream | 5 July 2018 | 0.088 | 0.105 | 2.78 | 1.974 | 2.067 | 644.3 | 88.6 | 4.6 | 6.7 | 2.5 |
| Spring Creek 8.75 km downstream | 13 June 2018 | 0.110 | 0.121 | 3.77 | 3.108 | 3.551 | 599.3 | 76.5 | 12.9 | 10.6 | 1.1 |
| Poteau River | 21 June 2018 | 0.224 | 0.283 | 5.97 | 4.990 | 5.502 | 849.3 | 29.8 | 41.8 | 28.4 | 2.6 |
| Prairie Creek | 21 June 2018 | 0.038 | 0.073 | 1.16 | 0.565 | 0.642 | 148.5 | 39.1 | 24.2 | 36.7 | 2.9 |

aqueous solution to that adsorbed by the sediments (Haggard et al., 2007). Through linear regression, the EPC is estimated as the *x*-intercept. However, if stream water is the aqueous solution, then often the ambient P concentration in the stream water limits desorption, and no data points are available below the *x* axis (i.e., desorption). Therefore, the *x*-intercept is an extrapolation past the known dataset. The ambient P concentration in stream water needs to be decreased to allow for P desorption from the sediments.

A common technique for removing P from the water involves the use of binding metal oxides, a widely used practice in reservoirs for nearly half a century (Landner, 1970). Aluminum sulfate (alum) is an option for controlling sediment P release (Erickson et al., 2004) because Al is not redox sensitive, unlike Fe (Huser et al., 2011). However, variability in the dosing rates and longevity of alum treatments has led to more research on the effects of water chemistry (Huser et al., 2011). The purpose of this study is to evaluate the use of alum to reduce ambient P concentrations in stream water and encourage sediment desorption in EPC experiments to (i) determine optimal alum dosage rates for P removal, (ii) evaluate the influence of alum treatments on the water chemistry, and (iii) compare EPC estimations using traditional methods with the inclusion of alum treatments of four streams in Arkansas.

METHODS

Study Site Description

Water samples were collected from four streams in Arkansas (Spring Creek, Cherokee Creek, Prairie Creek, and Poteau River) for use in determining appropriate alum dosages and the impacts of alum on water chemistry (further referred to as the alum treatment experiment). The four sites were selected to cover a range of ambient P concentrations (0.004–0.2 mg L⁻¹), land use, and sediment characteristics.

Spring Creek lies within the 1953-km² Illinois River Watershed in northwestern Arkansas (US Geological Survey, 2011). This watershed is part of the Ozark highland ecoregion, which is largely underlain with limestone, and streams typically have gavel-like substrate. Land use within the Spring Creek watershed is 44% urban, 43% pasture, and 12% forest (US Geological Survey, 2011), and the stream receives effluent from the wastewater treatment plant (WWTP) in Springdale, AR.

Cherokee Creek, Prairie Creek, and the Poteau River fall within the 4892-km² Upper Poteau River Watershed, which is one of the top 10 priority watersheds in Arkansas due to excess loading of P (ANRC, 2018). The sampling location on the Poteau River is ~12 km downstream of the Waldron WWTP. The Poteau River drainage area is predominantly forest (~68%) and partly pasture (~17%) and lies within the Ouachita Mountain ecoregion, which is predominantly underlain by shale and sandstone, and stream sub-

strates are often comprised of gravel, cobbles, or bedrock (Woods et al., 2004). The Cherokee Creek drainage area has approximately even amounts of forest and pasture land cover (~40% each) and lies within the Arkansas Valley (the alluvial valley between the Ouachitas and Ozarks) ecoregion, which is mostly underlain by sandstone, shale, and siltstone. Prairie Creek is also within the Arkansas Valley and has a drainage area that is mostly pasture (61%) and partly forest (~23%). All three sites in the Poteau River Watershed had small fractions of urban land use (~5%).

For EPC calculations, sediment and water samples were collected from the Poteau River, Prairie Creek, and three different locations on Spring Creek: one upstream, one ~1.00 km downstream, and one ~8.75 km downstream from the Springdale WWTP. These sites were selected to maintain a range in ambient P concentrations while taking into account the accessibility of collecting sediment samples (Table 1).

Alum Treatment Experiment

Water was collected in 10-L carboys on 29 May 2018 from the thalweg of each of the four streams and placed on ice until returning to the laboratory. Within 24 h, ~50 mL of water was filtered through 0.45-μm membrane filters, and the filtrate was analyzed for pH and soluble reactive P (SRP) using the automated ascorbic acid method (APHA, 1998) on a Skalar San Plus Wet Chemistry Autoanalyzer (Skalar).

Filtered stream water (50 mL) was dosed with alum (obtained at the Arkansas Water Resources Center, sources from Fisher Scientific) at treatment rates of 0, 0.1, 0.25, 0.5, 1, 5, 10, 25, 50, 100, and 150 mg-Al₂(SO₄)₃ L⁻¹. Samples were shaken for 1 h and centrifuged at ~3500 rpm for ~20 min, and the supernatant was separated into 20-mL vials to be analyzed for pH, SRP, NO₃-N, NH₄-N, trace metals (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Ti, V, and Zn), and anions (SO₄, Cl) at a water quality laboratory certified by the Arkansas Department of Environmental Quality (<https://arkansas-water-center.uark.edu/water-quality-lab/PDFs/Statement-of-Qualifications-2019-April-3-min.pdf>). Results from this experiment were used to determine optimal alum dosages for SRP removal and to analyze the impacts of alum on water chemistry. We used ANOVA with means separation (LSD) to determine whether water chemistry was different between treatments.

Equilibrium Phosphorus Concentration

Water and composite sediment samples were collected at three transects perpendicular to flow at each site of interest. Approximately 500 g of sediment was collected across each transect from the top 5 to 10 cm and sieved at 3.75 mm on-site. Upon returning to the laboratory, 25 g of fresh wet sediment were placed in Erlenmeyer flasks. Stream water (100 mL) was filtered (0.45 μm) and spiked with P at rates of 0.00, 0.10, 0.25, 0.50, 1.00, and 2.50 mg L⁻¹. Additional

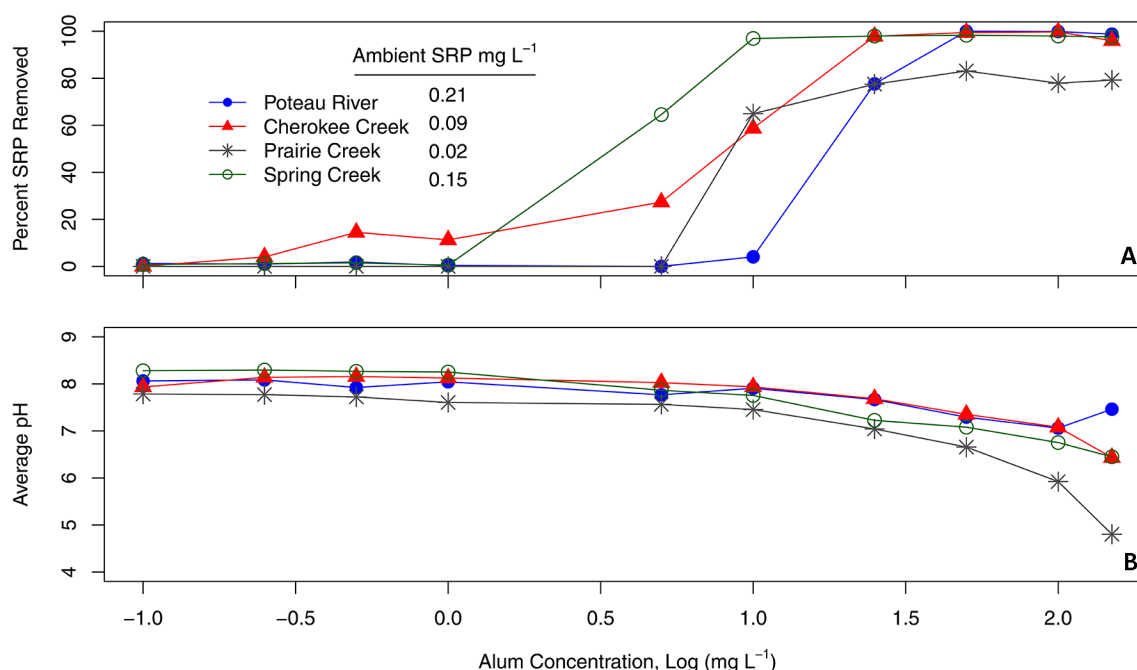


Fig. 1. (A) Percentage soluble reactive P (SRP) removed relative to \log_{10} alum treatment concentrations (mg L^{-1}) and ambient SRP concentrations for Poteau River, Cherokee Creek, Prairie Creek, and Spring Creek in Arkansas. (B) Decrease in average pH relative to alum treatment concentrations (mg L^{-1}) for Poteau River, Cherokee Creek, Prairie Creek, and Spring Creek in Arkansas.

stream water was treated with alum to remove ~25, 50, and 100% of initial P concentrations. For example, if the stream water had an ambient P concentration of 0.1 mg L^{-1} , then the initial P concentrations of the treatments were 0.10, 0.20, 0.35, 0.60, 1.10, 2.60 mg L^{-1} with spiked P and ~0.00, 0.50, and 0.75 mg L^{-1} SRP with alum reduced P (i.e., six treatments with P spikes and three treatments with alum-reduced P). This range of treatments allowed for P adsorption and desorption processes between the water and sediments.

The sediment and stream water slurry was shaken for 1 h and allowed to settle for ~30 min (e.g., see Haggard et al. [2004] and Taylor and Kunishi [1971]). The supernatant was collected, filtered, and analyzed for SRP. The remaining sediment slurry was placed in an oven at 80°C for 48 h to determine dry mass. The amount of P sorbed or released per dry weight sediment (mg P kg^{-1} dry sediment) was regressed against initial P concentration of the treatment solutions. Equilibrium P concentration was estimated as the x -intercept of the linear portion of the adsorption and desorption values. Paired t tests were used to determine if the inclusion of the alum treatments to reduce ambient P influenced EPC estimation.

RESULTS

Alum Treatment Experiment

An alum treatment concentration of $10 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ removed ~60 to 70% SRP in the stream water from Prairie Creek, Cherokee Creek, and Spring Creek, with ambient SRP concentrations of 0.02, 0.09, and 0.15 mg L^{-1} , respectively (Fig. 1). An alum treatment concentration of $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ removed almost 100% SRP from the stream water from these sites. For samples from the Poteau River, an alum treatment concentration of $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ removed ~77% of SRP from the stream water (ambient concentration of 0.21 mg L^{-1}), and an alum concentration between 25 and $50 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ removed 100% SRP.

Average pH decreased with increasing alum dosage across each site, especially when concentrations were

$>25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ (Fig. 1). Alum dosage concentrations of 0, 5, 10, and $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ caused very little deviation from neutral pH conditions. The largest change occurred in stream water from Prairie Creek, where ambient pH (7.8) decreased to 7.0 with a $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ (Fig. 1), possibly due to low ambient SRP (0.02 mg L^{-1}).

Most trace metals were unaffected by alum treatments across sites, except Al, Fe, and Zn. Aluminum concentrations peaked around alum dosages of 5 to $10 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ across each site. The Poteau River had the highest peak in Al (0.80 mg L^{-1}) with an alum dosage of $10 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$, which decreased back to 0.53 mg L^{-1} with an alum dosage of $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$. The remaining sites showed very low Al concentrations with an alum treatment concentration of $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$. Concentrations of Fe were significantly different between alum treatments at Bull Creek, Cherokee Creek, and Prairie Creek ($p < 0.05$), and, generally, concentrations decreased with increasing alum concentration. Concentrations of Zn were significantly different between alum treatments at Cherokee Creek and Prairie Creek ($p < 0.05$), and, similar to Fe, concentrations of Zn generally decreased with increasing alum concentration. Anion (F, Cl, and $\text{NO}_3\text{-N}$) concentrations were not different across alum treatments ($p > 0.05$). As expected, sulfate (SO_4) concentrations increased with increasing alum treatment concentrations [$\sim 10\text{--}15 \text{ mg L}^{-1}$ increase in SO_4 when increasing alum from 0 to $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$]. To obtain an optimal range of P removal that did not affect stream water chemistry, alum dosages were determined to be 5, 10, and $25 \text{ mg-Al}_2(\text{SO}_4)_3 \text{ L}^{-1}$ for use in EPC estimations.

Equilibrium Phosphorus Concentration Estimations

For all five sites, the amount of P sorbed regressed against initial P concentrations was significantly linear with and without the inclusion of alum treatments ($R^2 > 0.85$; $p < 0.05$) (Table 2). The three sites on Spring Creek showed slightly higher linear correlations ($R^2 = 0.98$; $p < 0.01$) compared with the Poteau River and Prairie Creek. No significant difference was found between the two

Table 2. Regression analysis for all sites between the two equilibrium P concentration calculation methods with and without alum treatment.

| Site | With alum | | | | Without alum | | | |
|---------------------------------|-----------|-----------------------|-----------|----------------|--------------|-----------------------|-----------|----------------|
| | <i>n</i> | <i>R</i> ² | Slope | <i>p</i> value | <i>n</i> | <i>R</i> ² | Slope | <i>p</i> value |
| Spring Creek upstream | 5 | 0.99–0.99 | 3.50–4.57 | <0.01 | 4 | 0.98–0.99 | 2.70–4.49 | ≤0.01 |
| Spring Creek 1 km downstream | 7 | 0.99–0.99 | 2.73–2.81 | <0.01 | 4 | 0.99–0.99 | 2.74–2.88 | ≤0.01 |
| Spring Creek 8.75 km downstream | 7 | 0.99–0.99 | 3.65–4.90 | <0.01 | 4 | 0.99–0.99 | 3.66–4.95 | ≤0.01 |
| Poteau River | 7–8 | 0.85–0.88 | 3.43–5.72 | <0.01 | 4–5 | 0.87–0.99 | 3.16–5.13 | ≤0.02 |
| Prairie Creek | 7 | 0.85–0.99 | 2.15–2.54 | <0.01 | 5 | 0.86–0.99 | 2.10–2.78 | ≤0.02 |

EPC estimation methods (i.e., with or without the use of alum treatments) for any site ($p > 0.05$) (Fig. 2). Prairie Creek had the greatest EPC estimations with and without alum treatments (0.204 and 0.210 mg L⁻¹, respectively) but had the lowest ambient P concentration (0.02 mg L⁻¹). The Poteau River had the largest difference in EPC estimations (from 0.195 mg L⁻¹ with alum treatments and 0.104 mg L⁻¹ without), but the difference was not significant ($p = 0.12$). Ambient P concentrations and standard errors were the greatest at this site as well. Upstream Spring Creek had the lowest EPC estimations with and without alum treatment (both ~0.016 mg L⁻¹).

DISCUSSION

Optimal alum treatment concentrations for P removal were determined to be 5, 10, and 25 mg-Al₂(SO₄)₃ L⁻¹, predominantly based on the removal of ambient SRP (mg L⁻¹) and the average pH for each treatment because most impacts on water chemistry were not significant ($p > 0.05$). The objective was to achieve a range of SRP concentrations below ambient for each stream, which was achieved using these alum concentrations. If alum treatments are to be used in EPC experiments, these results (Fig. 1) would allow for a user to determine optional alum dosages based on ambient P concentrations in streams of interest. However, as shown in the alum treatment experiment, alum concentrations >25 mg-Al₂(SO₄)₃ L⁻¹ began to lower the pH, which could alter the sorption properties of P and cause inaccurate estimations of EPC. Similar decreases in pH with alum treatments have been observed in lake and reservoir management (Berkowitz et al., 2005; Kennedy et al., 1987), where pH decreases quickly after alum application but returns to initial conditions after a couple of weeks. Often for lakes and reservoirs, the maxi-

mum allowable dose of alum is that which does not decrease the pH <6.0 and can often be applied with a pH buffer (i.e., sodium aluminate) to increase dissolved Al and to protect other biogeochemical processes (Kennedy and Cook, 1982).

Residual Al concentrations were observed after adding alum, which often occurs after alum treatments in lakes and reservoirs (Kennedy et al., 1987). Concentrations of Al peaked at alum treatment concentrations of 5 or 10 mg-Al₂(SO₄)₃ L⁻¹ across each site. At the lower alum treatment concentrations, the aluminum hydroxide floc may not be fully formed. Visually, flocs were easily noticed at the alum treatment concentration of 25 mg-Al₂(SO₄)₃ L⁻¹, slightly at the 10 mg-Al₂(SO₄)₃ L⁻¹ concentration, and not at all at the 5 mg-Al₂(SO₄)₃ L⁻¹ concentration. This suggests the Al was still dissolved in solution at lower alum dosages (instead of forming a floc), which could have led to measurable Al concentrations in the overlying water.

Concentrations of SO₄ increased with increasing alum treatments, as expected. Aluminum hydroxides form as alum is added to water, and P coprecipitates and/or adsorbs to the aluminum hydroxides, leaving sulfate suspended in solution. The decreases in Zn and Fe could be attributed to the diffuse double layer theory because the phosphates bound to the aluminum hydroxide flocs create a negative charge, attracting positively charged ions such as Zn and Fe (Breeuwsma and Lyklema, 1973; Trefalt et al., 2016). All other trace metal concentrations did not show a significant difference between alum treatments ($p > 0.05$), suggesting the impacts on water chemistry were minimal.

It would be expected for sediments to desorb more P as the initial P in the water decreases (with increasing alum treatment). However, at the Poteau River, sediment desorption did

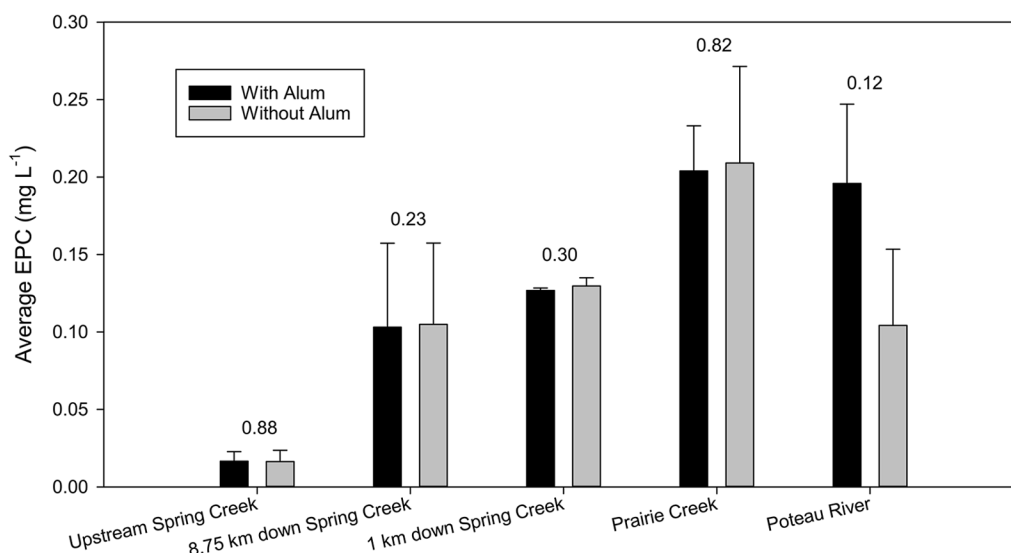


Fig. 2. Average (±SD) equilibrium P concentration (EPC) estimates across each site with and without reduced ambient P concentrations (i.e., with and without alum treatment); *p* values of the paired *t* test between estimation methods are shown above each site.

not follow this pattern. The greatest desorption occurred at the lowest alum treatment, which had initial P concentrations of 0.11 to 0.12 mg L⁻¹ at each transect (compared with the greatest alum treatment, which resulted in initial P concentrations of 0.02 mg L⁻¹). Therefore, the alum treatments removed P concentrations as expected, but desorption occurred oppositely to what was expected. This could be due to sediments inadequately being filtered from the supernatant after the EPC experiment. If sediment-bound P was not adequately filtered, greater P concentrations could be measured, resulting in higher desorption values. If the lowest alum treatments are removed, differences in estimated EPC values with and without alum decrease from 61 to 28%. However, whether these points are included or not, EPC is not significantly different with and without alum treatments ($p > 0.05$).

Including desorption of P from the sediments did not significantly alter the estimation of EPC across all sites (Fig. 2). Traditional methods of calculating EPC values by extrapolating past the known data set of P sorption from sediments are acceptable, and both time and money can be saved from not including alum treatments in EPC calculations. However, the inclusion of the x axis in the data range (i.e., desorption to adsorption) likely reduces the uncertainty in EPC estimation based on the linear regressions (Simpson et al., 2019). With the increasing interest in EPC values being included in watershed models such as the Soil and Water Assessment Tool, it is vital to have accurate estimations and to conserve time and funds (Mittelstet et al., 2017).

CONCLUSIONS

This study evaluated the influence that reducing dissolved P concentrations with the inclusion of alum treatments has on current EPC estimation methods and made the following observations: (i) Optimal alum dosages should be between 5 and 25 mg-Al₂(SO₄)₃ L⁻¹ to provide a range of P removal for the EPC experiments; (ii) Above 25 mg-Al₂(SO₄)₃ L⁻¹, stream water pH began to decrease. The only other notable changes to water chemistry after alum treatments were increases in sulfate (as expected) and residual Al concentrations in some treatments; (iii) Estimations of EPC were not significantly different between traditional calculation methods and the inclusion of P desorption data points.

These results indicate that the current methods for EPC estimations are acceptable and that spending extra time and money in simulating desorption of P from the sediments is not necessary. However, it may be necessary to test different stream systems to apply this conclusion universally.

ACKNOWLEDGMENTS

The authors thank Dr. Brad Austin, Brina Smith, Jennifer Purtle, Keith Trost, and all the REU program staff and lecturers. This work was supported in part by the Arkansas Water Resources Center through the USGS Water Resources Research Institute Program, the NSF Ecosystems REU Project (NSF DBI 165987), the USDA National Institute of Food and Agriculture, Hatch Project 2260, and the University of Arkansas Division of Agriculture.

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