Published online March 15, 2018

Agricultural & Environmental Letters

Research Letter

Organic Phosphorus Can Make an Important Contribution to Phosphorus Loss from Riparian Buffers

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Core Ideas

- Forested and vegetative buffers can retain P runoff from adjacent fields.
- High concentrations of molybdate unreactive P were detected in soil water extracts.
- With time, these buffer soils can be a source of soluble inorganic and organic P.
- High microbial activity in buffer soils suggests biologically mediated P release.

Abstract: Vegetative buffer strips (VBS) and managed or unmanaged riparian zones between the edge of field and receiving watercourse are widely adopted conservation practices aimed at reducing nonpoint nutrient pollution. However, their effectiveness at decreasing phosphorus (P) loss has been mixed. This study investigated the effectiveness of a VBS and a forested riparian zone (FRZ) in decreasing P loss from pasture soils receiving swine manure and aimed to determine the potential factors controlling P release, using water extractable P (WEP) as a proxy for P loss. The inorganic WEP concentrations were significantly greater in the fertilized pasture zone soils than the VBS or FRZ soils. However, there was no significant difference between the field and riparian soils for total WEP due to increased contribution from organic WEP in these soils. Degree of P saturation, which is a function of soil test P, was a good predictor of inorganic WEP, but not organic WEP, where the variation in concentrations was better explained by variables involved in biotic P release.

Forested riparian zones (FRZs) or vegetated buffer strips (VBS) are composed of a zone of managed or unmanaged vegetation between the edge of the field and the receiving watercourse. They are widely used to decrease nutrient and sediment runoff leaving agricultural fields and entering adjacent flowing waters. The main functions of these areas are to slow the flow of surface runoff, promoting sedimentation and infiltration, and to act as a filter to trap sediment and reduce dissolved nutrient concentrations through soil sorption and plant uptake (Hoffmann et al., 2009). Numerous studies have demonstrated the effectiveness of VBS at decreasing particulate P loss; however, their effect on dissolved P is less clear (Dodd and Sharpley, 2016). Detailed reviews of the literature have highlighted studies where such VBS have become sources rather than sinks of P where soil P concentrations are elevated (e.g., Hoffmann et al., 2009; Roberts et al., 2012; Sheppard et al., 2006).

Three possible mechanisms for the release of P from VBS have been suggested (Roberts et al., 2012): (i) decreased P sorption capacity due to saturation of P sorption sites, (ii) desorption of P from soil surfaces or dissolution of precipitated P, and (iii) biological cycling through the plant and microbial pools. Compared to much-studied geochemical processes, relatively little is known about processes involved in the microbial P cycle or the impact of differing land management strategies on these. Furthermore, the contribution of dissolved organic P forms to P loss from VBS is often overlooked (Dodd and Sharpley, 2015), and we suggest that organic forms could make up a substantial proportion of dissolved P in soils with active microbial P cycling. This study aims to address this research gap.

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Agric. Environ. Lett. 3:180002 (2018)
doi:10.2134/ael2018.01.0002

Received 17 Jan. 2018.
Accepted 19 Feb. 2018.
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Abbreviations: DPS, degree of soil phosphorus saturation; FPZ, fertilized pasture zone; FRZ, forested riparian zone; M3-P, Mehlich extractable P; MBC, microbial biomass C; MBN, microbial biomass N; MBP, microbial biomass P; TC, total C; TN, total N; TP, total P; TWEP, total water extractable phosphorus; VBS, vegetated buffer strips; WEP, water extractable phosphorus; WEPi, inorganic water extractable phosphorus; WEPo, organic water extractable phosphorus.

The Buffalo River is an important recreation area in northwest Arkansas. In 2013, a concentrated animal feeding operation (CAFO) was permitted to operate in this watershed (Arkansas Department of Environmental Quality, 2017), raising concerns of potential impairment of area waters for recreational use. In this operation, swine manure is land applied to pasture land, either grazed by cattle or hayed. Fields adjacent to a stream have a 30-m buffer, to which no manure or fertilizer can be applied, providing an ideal opportunity to investigate the fate and cycling of soil P along a gradient of a fertilized pasture zone (FPZ), grass VBS, and a forested riparian zone (FRZ). Three fields with different management histories, soil properties, and slope were selected to investigate the potential for dissolved P release, as measured by water extractable P, across these three zones. We addressed two main objectives:

1. To determine the effect of landscape position on the potential for P release as both dissolved inorganic and organic P.

2. To investigate the soil chemical and biological properties that control the release of dissolved P from these soils.

While it is acknowledged that vegetation can be an additional source of P loss, especially from forested riparian areas, where there may be accumulation of litter material, quantification of its contribution was beyond the scope of this study, which focuses on the release of soil P to water.

Materials and Methods

The study site is located in Mount Judea, AR (Fig. 1). Three fields were sampled (Fields 1, 5a, and 12; Fig. 2). Dominant soil types, along with management, for these are listed in Table 1. All three fields received poultry litter once every 2 yr in March from 2004 to 2012 (4.5 Mg ha^{-1} yr^{-1}; approximately 50 kg P and 120 kg N ha^{-1} yr^{-1}). Fields 1 and 12 currently receive only swine manure. In 2014, Field 1 received a total of 47 kg P ha^{-1} and 94 kg N ha^{-1} and Field 12 received 65 kg P ha^{-1} and 128 kg N ha^{-1}. In 2015, Field 1 received a total of 7.3 kg P ha^{-1} and 32 kg N ha^{-1} and Field 12 received 35 kg P ha^{-1} and 146 kg N ha^{-1}. While no swine manure has been applied to Field 5a, diammonium phosphate fertilizer was applied annually since 2012 at 11 kg P and 25 kg N ha^{-1}.

On Fields 1 and 12, receiving swine manure, a required application buffer of 30 m from the field edge is in place. Field 1 has a steep topography and drains into an ephemeral stream located within the riparian zone and connected to Big Creek. Fields 5a and 12 have slopes of <2%. These fields border Big Creek and are prone to flooding during large storm events. Field 1 is continuously grazed by cattle, whereas grass is cut for silage in Fields 5a and 12.

At each field, three transects were laid across the site running through the FPZ, VBS, and into the FRZ. For each transect, soil samples were taken at the 0- to 10-cm depth from three locations within the FPZ, one location within the manure application VBS, and one location in the FRZ, which borders the stream. Soil sampling at all fields was performed over the course of 1 d on four occasions, October 2014, January 2015, April 2015, and July 2015, corresponding to autumn, winter, spring, and summer to account for seasonal variability.

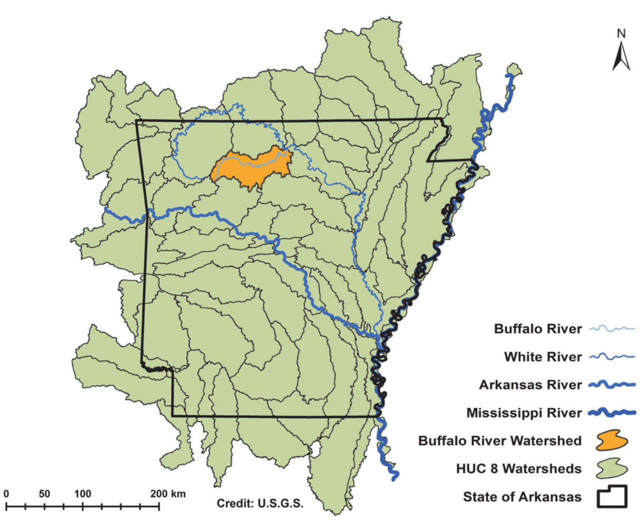

Fig. 1. Buffalo River watershed location in Arkansas, USA.

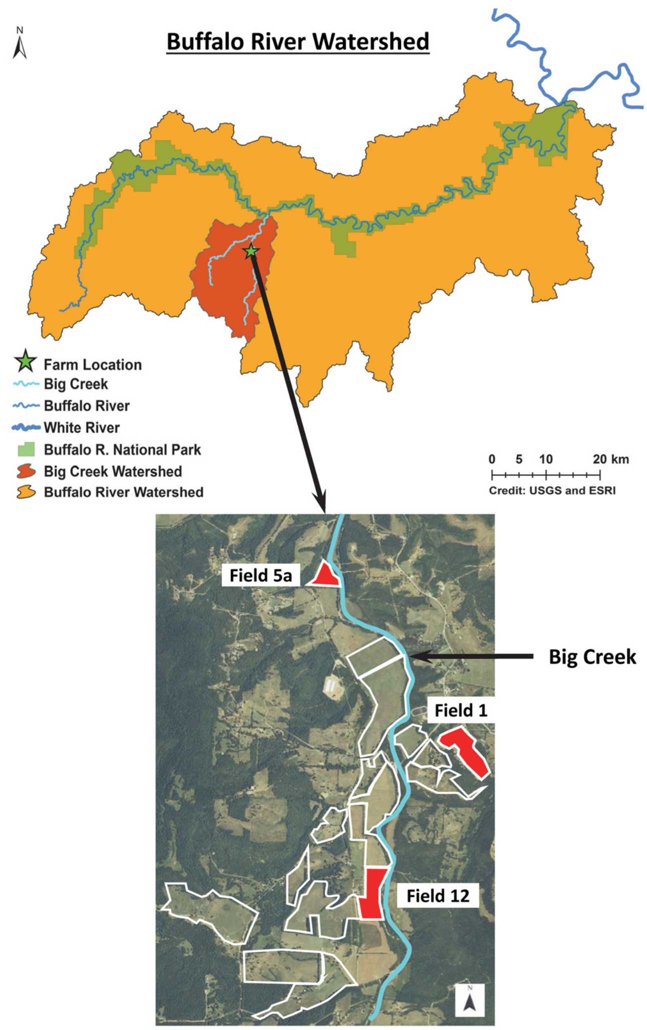

Fig. 2. Location of Big Creek watershed, farm, and fields studied.

Table 1. Field properties and management.

Site	Soil series	Area	Range in slope	Management
		ha	%	
Field 1	Noark very cherty silt loam	6.3	2.0–20.0	Grazed at 0.5 animal units ha^{-1}
Field 5a	Razort loam	10.8	0.2–1.0	Hayed and grazed at 0.3 animal units ha^{-1}
Field 12	Spadra loam	9.6	0.5–2.0	Hayed and grazed at 0.3 animal units ha^{-1}

As much of the vegetation mat as possible was removed in the field. Soil samples were separated into two subsamples for biotic and abiotic analysis. Samples for biotic analysis (microbial biomass and enzyme activity) were sieved <2 mm and stored at 4°C until analysis. Samples for abiotic analysis were air-dried, ground, and sieved <2 mm. Additional plant material, shoots, and roots were removed by hand before sieving.

Soil samples were analyzed for the following properties using the methods outlined in Table 2: total WEP (TWEP), inorganic WEP (WEPi), organic WEP (WEPo), Mehlich extractable P (M3-P), degree of soil P saturation (DPS), total P (TP), total C (TC), total N (TN), pH, microbial biomass P, C, and N (MBP, MBC, MBN), and phosphatase enzyme activities. Phosphorus concentration for all analyses except M3-P was determined using the molybdate blue method of Watanabe and Olsen (1965); M3-P concentrations were determined via inductively coupled plasma.

The P content determined colorimetrically directly following extraction with water is more accurately described as molybdate reactive P and consists mainly of orthophosphate ions and a small proportion of easily hydrolyzable inorganic and organic P. The difference between this value and that determined following digestion is more accurately described as molybdate unreactive P and consists mainly of organic P forms but also a smaller fraction of condensed inorganic P, such as polyphosphates (Haygarth and Sharpley 2000). Due to the dominance of inorganic P in molybdate reactive P and organic P in molybdate unreactive P, WEPi and WEPo have been used to distinguish between these two forms of P to avoid confusion and allow a clear message to be presented.

Before all statistical analysis, the data were examined for normality and the following parameters were log-transformed: TWEP, WEPi, and WEPo. To examine the differences in soil properties across the three landscape positions, the data from the three samples taken along each transect within the FPZ were averaged to provide one value for each zone (FPZ, VBS, and FRZ) for each transect. Data from each of the three fields and from each of the transects within the fields were treated as replicates, giving nine location replicates per zone. These data were subjected to a one-way ANOVA by zone blocked by season, providing four seasonal replicates for each location replicate and a total replication of 36 data points per zone. For all parameters, a Tukey test was used to determine significant differences between the zones at the $p < 0.05$ level of significance.

To determine which soil properties were contributing to the release of WEP and which soil parameters are important in regulating the release of P, a stepwise regression was undertaken using the following parameters: acid phosphomonoesterase, alkaline phosphomonoesterase, phosphodiesterase, total phosphatase, MBN, MBP, MBC, M3-P, DPS, pH,

Table 2. Summary of analytical methods used.

Parameter†	Analytical method	Reference
TWEP	1:20 soil-to-water extraction followed by centrifugation, filtration <0.45 μm, and acid persulfate digestion	Self-Davis et al. (2009) and Rowland and Haygarth (1997)
WEPi	1:20 soil-to-water extraction followed by centrifugation and filtration <0.45 μm	Self-Davis et al. (2009)
WEPo	Assumed to be the difference between TWEP and WEPi	—
M3-P	1:10 soil-to-Mehlich-3 extractant and centrifugation	Mehlich (1984)
DPS	Calculated from M3-P, Fe, and Al according to the equation DPS = M3-P/0.5 × (M3-Fe + M3-Al) × 100	Adapted from Schoumans (2009)
TP	Alkaline oxidation	Dick and Tabatabai (1977)
TC	Combustion on an Elementar VarioMax CN	Provin (2014)
TN	Combustion on an Elementar VarioMax CN	Provin (2014)
pH	1:2 soil-to-water extraction	—
MBP	Chloroform-fumigation extraction	Adapted from Brookes et al. (1985) and McLaughlin et al. (1986)
MBC	Chloroform-fumigation extraction	Vance et al. (1987)
MBN	Chloroform-fumigation extraction	Vance et al. (1987)
Acid P_{mono}	Enzyme assays using 5mM *para*-nitrophenyl phosphate as the substrate buffered at pH 6.5	Tabatabai (1994)
Alk P_{mono}	Enzyme assays using 5mM *para*-nitrophenyl phosphate as the substrate buffered at pH 11	Tabatabai (1994)
Pdi	Enzyme assays using 1 mM bis-*para*-nitrophenyl phosphate as the substrate buffered at pH 8	Tabatabai (1994)
Total phosphatase	Sum of acid P_{mono}, alk P_{mono}, and Pdi	—

† acid P_{mono}, acid phosphomonoesterase; alk P_{mono}, alkaline phosphomonoesterase; DPS, degree of soil phosphorus saturation; M3-P, Mehlich extractable P; MBC, microbial biomass C; MBN, microbial biomass N; MBP, microbial biomass P; Pdi, phosphodiesterase; TC, total C; TN, total N; TP, total P; TWEP, total water extractable phosphorus; WEPi, inorganic water extractable phosphorus; WEPo, organic water extractable phosphorus.

TP, TC, and TN. All analyses were performed using the SPSS statistical package version 22 (IBM, 2013).

Results and Discussion

Water extractable soil P concentration has been shown to be directly related to the potential for dissolved P release from soils to surface runoff (Pote et al., 1996; Sharpley, 1995). The total, inorganic, and organic WEP (TWEP, WEPi, WEPo) concentrations across the three fields was significantly lower in the VBS than the FPZ, reflecting the larger inputs of P to the FPZ (Fig. 3). However, there was no significant difference in TWEP between the pasture and FRZs despite a decrease in WEPi. This is a result of the significantly higher concentrations of WEPo present in the FRZ, where WEPo made up 57% of TWEP in these soils compared with just 24% in the pasture soils. This suggests that dissolved organic P can contribute to total P release in riparian soils.

The release of soil P to water can occur through abiotic and biotic processes. Desorption and dissolution reactions dominate the abiotic release mechanisms and are governed by soil chemical properties and number of available sorption sites (Arai and Sparks, 2007). Microbial soil biomass can contain a significant pool of P in temperate pastures (Oberson and Joner, 2005). This pool is in constant flux, immobilizing P from or replenishing P in the soil solution during microbial growth or cell death. Phosphorus release from this pool occurs through three main mechanisms: (i) mineralization (Oehl et al., 2001), (ii) cell lysis in response to environmental stress (e.g., dessication) (Turner and Haygarth, 2001), or (iii) predation by soil fauna (Bonkowski, 2004). Biotic processes can also control the form of dissolved P in solution through the exudation of phosphatase enzymes, which can catalyze the conversion of soluble organic P compounds to orthophosphate ions for plant uptake (Richardson et al., 2011).

Table 3 shows the abiotic and biotic soil properties of the soils across the three landscape zones. The FPZ soils had significantly higher concentrations of TP and M3-P, but lower concentrations of TC and TN, compared with the FRZ soils. Additionally, the DPS was significantly higher in the FPZ soils compared with the VBS and FRZ soils, indicating more of the P sorption sites had become saturated. Surprisingly, we saw no significant difference in microbial biomass P, C, or N concentrations among zones, despite expected increased leaf litter inputs in the FRZ. However, the total phosphatase activity was 17% higher in the FRZ soils than the field soils, suggesting increased microbial activity.

To determine which pools of P and which soil properties were key in controlling the release of P to water, we performed a stepwise regressions for TWEP, WEPi, and WEPo using data from all three sites and four sampling dates. The results from this analysis are shown in Table 4. Both TWEP and WEPi were well predicted by the model (adjusted r^2 =

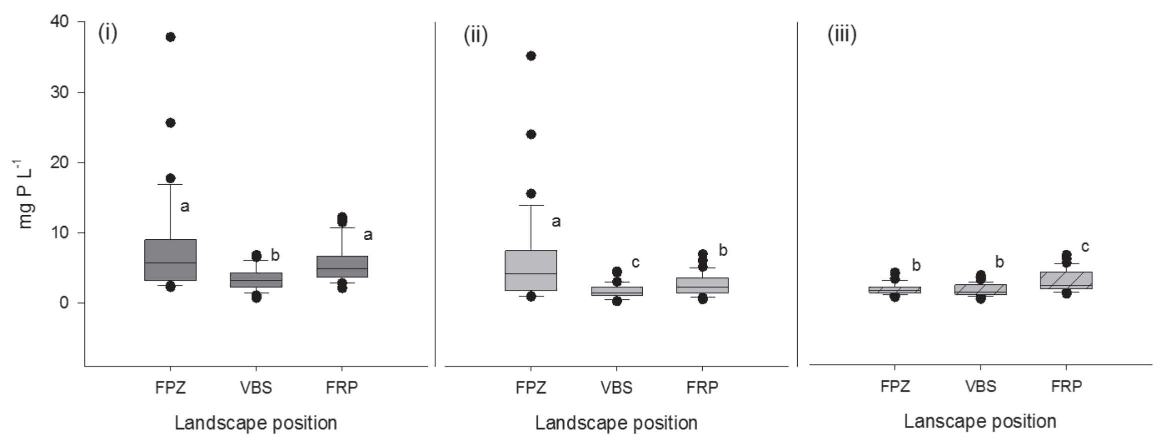

Fig. 3. Box plots showing the concentration of (i) total water extractable P, (ii) inorganic water extractable P, and (iii) organic water extractable P across the three zones (fertilized pasture zone [FPZ], vegetative buffer strip [VBS], and forested riparian zone [FRZ]). Letters denote significant differences between zones at $p < 0.05$ as determined by Tukey's test of multiple comparisons.

Table 3. Difference in mean soil properties across the different landscape zones, fertilized pasture zone (FPZ), vegetative buffer strip (VBS), forested riparian zone (FRZ): pH, total C (TC), total N (TN), total P (TP), Mehlich-3 P (M3-P), degree of P saturation (DPS), microbial biomass P (MBP), microbial biomass C (MBC), microbial biomass N (MBN), acid phosphomonoesterase (acid P_{mono}), alkaline phosphomonoesterase (alk P_{mono}), phosphodiesterase (Pdi), and total phosphatase activities.

Zone	Soil chemical properties						Soil biological properties						
	pH	TC	TN	TP	M3-P	DPS	MBP	MBC	MBN	Acid P_{mono}	Alk P_{mono}	Pdi	Total phosphatase
		——— % ———		— mg kg⁻¹ —		%	——— mg kg⁻¹ ———			———— µmol pNP† g⁻¹ h⁻¹ ————			
FPZ	5.87b‡	2.06b	0.23b	640a	67a	7.48a	26	371	85	3.00a	1.33b	1.20b	5.53b
VBS	5.71b	1.88b	0.21b	584ab	48b	4.89b	23	386	79	2.59ab	0.93b	0.96b	4.56b
FRZ	6.40a	3.21a	0.26a	521b	28c	4.57b	28	356	101	2.33b	2.05a	2.05a	6.66a
p value	<0.001	<0.001	<0.05	<0.01	<0.005	<0.001	NS	NS	NS	<0.005	<0.001	<0.001	<0.001

† pNP, *para*-nitrophenyl phosphate.

‡ Means followed by the same letter are not significantly different at the $p < 0.05$ level of significance according to Tukey's test for multiple comparisons.

Table 4. Model predictions of total water extractable P (TWEP), inorganic water extractable P (WEPi), and organic water extractable P (WEPo) from stepwise regression across all data. The *F* statistic for all three model predictions is <0.001.

TWEP			WEPi			WEPo		
$r^2_{adjusted}$	Predictor	Relative importance	$r^2_{adjusted}$	Predictor	Relative importance	$r^2_{adjusted}$	Predictor	Relative importance
0.66	Degree of soil P saturation	0.80	0.65	Degree of soil P saturation	0.93	0.37	Total phosphatase activity	0.78
	Total phosphatase activity	0.18		Total phosphatase activity	0.07		Microbial biomass N	0.17
	M3-P	0.02					pH	0.05

0.66 and 0.65, respectively), and variation in these concentrations was mostly explained by DPS, with a small contribution from total phosphatase activity, an indicator of biologically mediated P release.

In contrast to WEPi, variation in WEPo was less closely related to any of the measured parameters (adjusted $r^2 = 0.37$). Furthermore, DPS was not included in the selected model, and total phosphatase activity explained most of the variation in WEPo. While total phosphatase activity was greatest in FRZ soils, the activity of the different types of enzyme varied across the landscape positions (Table 3). Acid phosphomonoesterase activity was highest in the FPZ soils and of a similar magnitude to that found agricultural soils with a history of poultry manure application and high soil test P**???Spelled out STP; correct???** concentrations (Tomlinson et al., 2008). Acid phosphomonoesterase is thought to be mainly released by plant roots and some microbes, and there is evidence that high concentrations phosphatase enzymes can be present in manures (Nannipieri et al., 2011). Furthermore, these enzymes have been shown to sorb strongly onto soil particles (Burns, 1986; Nannipieri et al., 2011); hence, the large acid phosphomonoesterase activates found in the FPZ may be directly due to manure application. In contrast, alkaline phosphomonoesterase and phosphodiesterase activities were greatest in the FRZ, in keeping with the small increase in pH (Table 3). These enzymes are thought to be released by soil microorganisms rather than plant roots. The differences in phosphatase activities across the zones suggest that release of P from riparian soils is likely to be controlled in part by the biologically mediated release of organic P.

This study demonstrates that the significant decrease in soil test P concentrations in FRZ soils compared with regularly fertilized FPZ does not necessarily translate to a reduction in the total amount of P, which can be released to runoff due to the increase in WEPo. Furthermore, while DPS, of which soil test P is a component, was a good predictor of WEPi release, additional factors relating to biological cycling need to be considered when trying to account for the potential release of organic P.

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