



## SPATIAL CONSIDERATIONS IN WET AND DRY PERIODS FOR PHOSPHORUS IN STREAMS OF THE FORT COBB WATERSHED, UNITED STATES<sup>1</sup>

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**ABSTRACT:** The Fort Cobb Watershed in Oklahoma has diverse biogeophysical settings and provides an opportunity to explore the association of water quality with a diverse set of landscapes during both wet (April 2007–December 2009) and dry (January 2005–March 2007) periods. The objective of this work was to identify spatial patterns in phosphorus (P) (soluble reactive P [SRP] and bioavailable P [BAP]) associated with landscape metrics for two distinct streamflow regimes. Spatial autocorrelation of P was evaluated using contiguous (side-by-side) and upstream (upstream:downstream) connectivity matrices. Biogeophysical metrics were compiled for each contributing area, and were partitioned based on association to P concentrations. Results for both SRP and BAP indicated that spatial autocorrelation was present ( $p < 0.05$ ). There was more spatial autocorrelation and stream P concentrations were three to five times higher in the Wet phase than in the Dry phase ( $p < 0.05$ ). Analysis with recursive partitioning resulted in higher  $R^2$  with spatial autocorrelation than without spatial autocorrelation and indicated that lateral metrics (topography, soil, geology, management) were better predictors for SRP than instream metrics. During Wet phase, lateral metrics indicative of rapid surface and subsurface water movement were associated with higher P stream concentrations. This research demonstrated that we can detect landscapes more vulnerable to P losses and/or contaminations in either drought or very wet periods.

(KEY TERMS: phosphorus; watershed; water quality; spatial autocorrelation; recursive partitioning.)

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### INTRODUCTION

Elevated phosphorus (P) concentrations in streams have been shown to be associated with eutrophication of lakes (Hilton *et al.*, 2006) and occasionally streams (Heathwaite *et al.*, 1996). While it is critical to include P as an essential element in management programs designed to decrease eutrophication of

freshwaters (Carpenter, 2008; Schindler *et al.*, 2008), it is still unclear to what extent the landscape (i.e., geology, topography, or fluvial morphology) influences the impact of management on nutrient concentrations in streams (Tong and Chen, 2002). Allan (2004) reported variable success in quantifying associations between land use and stream response to identify pathways of influence. While land use has been shown to influence stream-nutrient concentrations

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(Fisher *et al.*, 2000) the extent to which a given land use or management influences stream P concentrations varies both spatially and temporally. We still have much to learn as to how variables such as time or seasons (temporal), landscape metrics such as geology, geomorphology, soil metrics, or location (spatial) or channel metrics affect the influence of a particular land use. Researchers have shown that impacts of land uses on nutrients in streams vary spatially and temporally and that linking combinations of landscape characteristics and land use with temporal metrics will enable further understanding of simultaneous influences of several different processes (Palmer *et al.*, 2008). Dent and Grimm (1999) showed that nitrogen concentrations were spatially autocorrelated during floods, and that correlations lessened over time following the flood. In southern Sweden, spatial and temporal variables, including relief, basin area, erosion risk, soil category, stream length, precipitation, air temperature, and season, were analyzed using empirical time series and Kendall's  $\tau$  to detect and quantify correlations between stream-nutrient concentration and landscape metrics for 35 small streams (Arheimer and Liden, 2000). They found that median winter stream P concentrations were highly correlated with soil texture in each catchment.

Using both modeled and measured stream discharge to determine time series of water flow, Arheimer and Liden (2000) found that partitioning the data into high and low streamflow regimes improved the prediction of nutrient concentration dynamics. Additional partitioning of each of the flow regimes may have improved predictions further. Such partitioning could be accomplished with recursive partitioning (RP), which, like other classification and regression trees (CART), has been shown to be a robust and flexible analytical tool to discern relationships between complex ecological data (Bücker *et al.*, 2008). It has been used to identify *a priori* most important independent variables or predictive variables of the dependent variables (soluble reactive P [SRP] and bioavailable P [BAP] in this study). RP has been used in climate studies (Cannon and Whitfield, 2002), in the analysis of breakthrough curve data (Young, 1992), and in stream ecology studies (Qian and Anderson, 1999; Lamon and Stow, 2004). Because ecological data are often complex (composed of both continuous and categorical data that are unbalanced, missing data points and nonlinear relationships), CART analysis is ideally suited for exploring and modeling ecological data (De'ath and Fabricius, 2000; Hawkins, 2009). RP selects the most predictive feature and splits the data based on that feature. Splits (or partitions) are done recursively forming a tree-structured model until additional variables do not add appreciable predictive

power. While sensitive to outliers, this method often isolates them or quarantines them as a terminal node making it obvious that they are outliers.

In an earlier article, Poff *et al.* (1997) found that the influences of assumed static environmental features such as geology, topography, soil, and vegetation were dynamic and helped to determine the quantity of water, the pathway by which the water reaches the stream, and the quality of stream water. They also describe how the quantity, quality, and flow path of water vary under drought and flood flow regimes for a given stream. When considering potential adaptations of organisms living in running waters and how those organisms might adapt to different flow regimes, Lytle and Poff (2004) described the importance of natural flow regimes in sustaining ecosystem services provided by river networks. Because rivers worldwide have experienced dramatic changes in flow and are expected to experience additional changes (Palmer *et al.*, 2008), further discovery is needed into how flow variation interacts with variation in biogeochemical characteristics of water. This is especially needed when streams are affected by land management practices that may potentially alter the ability of a river network to sustain ecosystem services such as habitat provision and nutrient cycling (Fisher *et al.*, 1982; Nilsson and Renöfält, 2008; Palmer *et al.*, 2008). Partitioning of P stream concentrations referenced with landscape metrics for wet and for dry streamflow regimes may provide a better perspective of a watershed's vulnerabilities and potential for resiliency. In turn, a broader perspective of a watershed's water quality response will also improve our ability to design land management practices, water allocations, and to reduce ecological and health problems associated with extreme weather conditions (Young, 1992; De'ath and Fabricius, 2000; Bücker *et al.*, 2008).

An increasing number of studies are examining the existence of spatial dependencies and are accounting for spatial autocorrelation (SAC) in their analysis (Allan, 2004). Dent and Grimm (1999) stated measures of spatial dependence such as SAC and semi-variograms can test hypotheses about potential causes and consequences of spatial pattern. Nutrient retention, transformations, and dilutions can vary greatly depending on stream morphology (Gücker and Boëchat, 2004). In a regional scale study of the Mid-Atlantic area, Jones *et al.* (2001) determined that landscape metrics explained 73% of the variability in P stream concentrations. Of the landscape metrics examined, length of riparian forest was found to account for 63% variability of P. We theorize based on the findings of the authors and others (Franklin *et al.*, 2002; Terziotti *et al.*, 2010) that background influences such as a landscape metric varies between ecoregions and biogeophysical settings and that an

understanding of background variations in P concentrations is necessary to develop reliable predictive models. The Fort Cobb Watershed in Oklahoma has diverse biophysical settings (Steiner *et al.*, 2008) and provides an opportunity to explore the association of water quality with landscape metrics.

While stream order can affect water quality (Wiens, 2002), much of the land use effect on water quality is observed in the first- to fourth-order streams as defined by Strahler (1952). Meyer *et al.* (2007) showed that small streams are a vital part of the biological integrity of waterways and that entire river networks may be greatly dependent on the individual cumulative impacts occurring in small or headwater streams. Connectivity of a stream to its surroundings and the interactive pathways are described by freshwater ecologists as having one dimension in time and as three dimensions in space (Freeman *et al.*, 2007). The three spatial dimensions are longitudinal (i.e., instream processes, upstream nutrient concentrations influencing downstream concentration or bank erosion), lateral (i.e., drainage basin morphology, geology, soil, and management via runoff-shallow and subsurface flow), and vertical (atmosphere, rainfall, temperature). The objective of this work was to identify spatial and temporal patterns in P (SRP and BAP) associated with landscape metrics and climate for two distinct streamflow regimes.

## MATERIALS AND METHODS

The Fort Cobb Reservoir Watershed (FCRW) is a 786-km<sup>2</sup> watershed made up of first- through fourth-order tributaries in southwestern Oklahoma. Agriculture is the dominant land use (Steiner *et al.*, 2008) for each of the four main drainage basins: Cobb Creek (419 km<sup>2</sup>), Fivemile Creek (109 km<sup>2</sup>), Lake Creek (168 km<sup>2</sup>), and Willow Creek (73 km<sup>2</sup>). Cropland and Pasture are dominant land uses in the FCRW (Table 1). Generally, land use identified as Forest is located near streams. The watershed is made up of diverse geologic formations and hence has diverse biogeophysical settings (Steiner *et al.*, 2008) and hydrologic groups (Figure 1). The subhumid climate has a normal annual precipitation of about 750 mm (Garbrecht, 2008).

Water samples were collected biweekly from January 2005 through December 2009 from 15 sites distributed throughout the watershed (Figure 1). Grab samples were taken from mid-stream and transported to the laboratory in a dark, iced cooler and stored in a refrigerator until processed. Phosphorus analysis

TABLE 1. Percent Land Use Within the Fort Cobb Reservoir Watershed.

Subbasin	Cropland	Pasture	Forest	Urban	Water
Cobb (Co1)	44.6	47.2	4.2	3.1	0.9
Cobb (Co2)	43.1	48.2	4.1	4.6	0.0
Cobb (Co3)	63.4	29.8	2.3	4.0	0.5
Cobb (Co4)	66.3	27.0	2.1	3.8	0.8
Five Mile (FM1)	46.3	45.0	3.5	4.3	0.9
Five Mile (FM2)	62.3	30.7	2.6	4.3	0.1
Five Mile (FM3)	58.0	34.3	3.5	3.8	0.4
Lake (L1)	52.0	36.2	6.9	4.2	0.7
Lake (L2)	53.3	38.3	4.1	4.2	0.1
Lake (L3)	58.9	33.2	3.6	4.2	0.1
Lake (L4)	66.6	21.4	8.3	3.4	0.3
Willow (W1)	56.5	35.3	4.5	3.6	0.1
Cherry Dale (CD)	52.4	40.2	3.0	4.3	0.1
Willow (W2)	48.1	42.2	5.1	4.1	0.5
Willow (W3)	62.7	24.5	8.8	3.9	0.1

Note: Percent area in each subbasin within the Fort Cobb Reservoir Watershed for Cropland, Pasture, Forest, Urban, and Water.

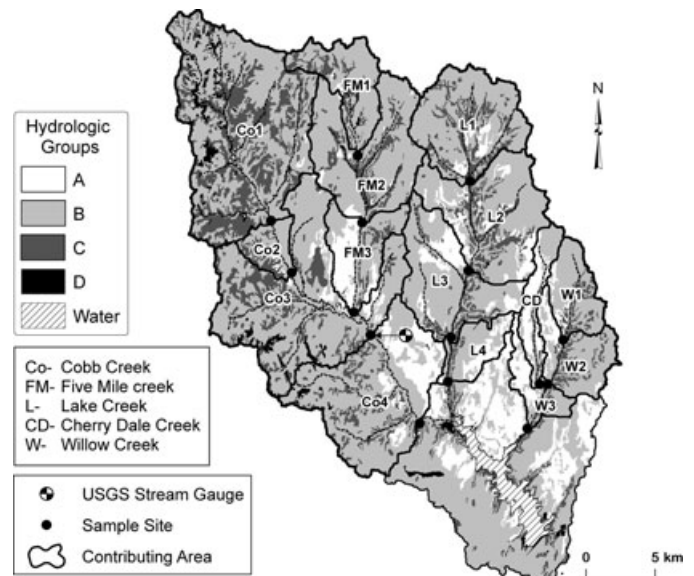


FIGURE 1. Fort Cobb Reservoir Watershed Located in Southwestern Oklahoma. Grayscale boxes A, B, C, and D identify corresponding hydrologic groups. The four main drainage basins Cobb Creek (CO), Fivemile (FM), Lake Creek (L), and Willow Creek (W) are identified along with sampling sites and streamflow-gauging site.

was completed within a week of collection. Unfiltered samples were analyzed for BAP using the sodium hydroxide method (Sharpley *et al.*, 1991). Samples were filtered (0.45  $\mu$ m) and filtrate analyzed for SRP by the molybdate blue method (Murphy and Riley, 1962).

SRP and BAP were analyzed for spatial dependence, temporal dependence, and modeled using RP (described below) to identify best predictive variables using the lateral, longitudinal, and vertical metrics according to Freeman *et al.* (2007) as described in the

Introduction. *Lateral metrics* were Topography, Soil metrics, Land use and Management, and Geology. *Longitudinal metrics* were Stream geomorphic stage and Water chemistry. *Vertical metrics* were Weather parameters (Quarter or year, based on Day of Year [DOY]; Prec\_max, maximum 30-min precipitation in contributing area in sampling interval; Prec\_tot, total precipitation in two-week sampling interval; and Prec\_cum3, cumulative precipitation over three sampling intervals [six weeks]). Further details on these metrics can be found in Table 2.

Watershed-wide spatial dependence (SAC) was examined in biweekly SRP and BAP stream concentrations using Moran's coefficient (Griffith, 1993;

Franklin *et al.*, 2002). Calculations of SAC as determined by Moran's coefficient were carried out using first-nearest neighbor methods in SAS (Griffith, 1993; SAS Institute, 2008). This requires the development of a binary connectivity matrix describing the nearest neighbor binary relationships. We used two connectivity matrices (each  $N_{15} \times N_{15}$ , 1 = adjacent and 0 = not adjacent) following procedures developed by Franklin *et al.* (2002) based on nearest neighbor relationships in FCRW: (1) the Contiguity matrix, a standard measure of lateral (areal or side-by-side; 1 = adjacent and 0 = not adjacent) spatial dependence (e.g., Basin of upper Fivemile [FM1] is adjacent to upper Cobb Creek [Co1], therefore 1), and (2) the Upstream matrix, a

TABLE 2. Lateral, Longitudinal, and Vertical Variables Considered for Best Predictable Variable for SRP or BAP Stream Concentrations in the Recursive Partitioning Analysis.

Characteristic	Units	Minimum	Maximum	Source
<i>Lateral</i>				
Topographic				10 m DEM (USGS, 2003)
Contributing area	ha	1,990	30,925	
Average slope	%	4.0	5.9	
Maximum slope	%	9.2	16.5	
Stream length	m	6,655	166,580	
Stream density	m/ha	2.3	6.9	
Soil				STATSGO (USDA-NRCS, 1994)
Soil Hydrologic Group A	% contributing area	0	41	
Soil Hydrologic Group B	% contributing area	54	85	
Soil Hydrologic Group C	% contributing area	5	32	
Sand, areal-weighted surface layer	% by weight	21.7	76.5	
Clay, areal-weighted surface layer	% by weight	10.1	18.1	
Organic carbon, areal-weighted surface layer	% by weight	0.59	0.97	
Geology				Cederstrand, 1996
Cloud Chief Formation	% contributing area	0	43	
Rush Springs Formation	% contributing area	34	100	
Weatherford Gypsum Bed	% contributing area	0	23	
Management and land use				USDA-NRCS, 2005 Steiner <i>et al.</i> 2008
Irrigable by center pivot	% contributing area	0	21	
Crop land	% contributing area	43	67	
Pasture	% contributing area	21	48	
Forest	% contributing area	2	9	
Water	% contributing area	0	1	
<i>Longitudinal</i>				
Stream geomorphic stage				Simon and Klimetz, 2008; Steiner <i>et al.</i> , (2008)
RGA Stage 3 (degrading, vertical)	% stream length	0	36	
RGA Stage 4 (degrading, horizontal)	% stream length	0	100	
RGA Stage 5 (aggrading)	% stream length	0	100	
Water chemistry				Measured, as described in text
ORP	mV	-40	187	
pH	log(l/mol)	6.9	10.0	
TDS	g/l	0.1	0.8	
Turbidity	ntu	0	6,160	
<i>Vertical</i>				
Weather				Based on DOY Derived from ARS Micronet stations
Quarter	unitless	1	4	
Prec_max	mm/30 min	0	60	
Prec_tot	mm	0	259	
Prec_cum3	mm	2	457	

Notes: RGA, rapid geomorphic assessment; ORP, oxidation reduction potential; TDS, total dissolved solids; DEM, digital elevation model; STATSGO, State Soil Geographic referencing database; DOY, day of year; ARS, USDA Agriculture Research Service.



measure of longitudinal spatial dependence (sampling Site FM1 is not upstream of Co1, therefore 0) which is based on unidirectional nature of lotic systems and in-stream processes. Values for SAC range from  $-1$  to  $+1$ . All negative SACs (SAC = Yes<sup>-</sup> had Moran's coefficients from  $-0.20$  to  $-1$ ) were found to be insignificant ( $p > 0.05$ ) for both SRP and BAP. No spatial dependence or SAC = No was defined as Moran's coefficient  $-0.19 < \text{SAC} < 0.19$ , and spatial dependence or SAC = Yes<sup>+</sup> was defined as  $\text{SAC} \geq 0.20$  and were all found to be significant ( $p < 0.05$ ).

Streamflow was measured by the U.S. Geological Survey (USGS). Details of measurement methodology are available at <http://waterdat.usgs.gov/nwis/sw>. Using continuous measurements from 1968 through 2009 at Cobb Creek, near Eakley, the median flow for each day of the year was calculated to show the seasonal hydrologic regime of this watershed. For each sample date, the median flow ratio was calculated for this downstream site [ $\ln(\text{day's mean flow}/\text{daily median flow for that day of year})$ ]. Daily median flow for a specific day was calculated using continuous measurements from 1968 through 2009 (same location). A distinct change in median streamflow ratio occurred in April 2007 and demarks the records into Dry and

Wet phases: "Dry phase" (January 1, 2005 to April 1, 2007) and "Wet phase" (April 1, 2007 to January 1, 2010). Time series plots of mean streamflow and precipitation (Figure 2) from a USGS-gauging site as well as mean SRP and BAP stream concentrations and variability were analyzed for each sampling date. Significant differences ( $p < 0.001$ ) between Phase 1 and Phase 2 for median and mean streamflow, SRP, and BAP were determined with nonparametric Wilcoxon/Kruskal-Wallis tests: rank sums (JMP (8.0) SAS Institute Inc., 2008) and Tukey-Kramer HSD (SAS Institute, 2008).

We used RP (JMP (8.0) SAS Institute Inc., 2008) to identify predictive variables that contribute significantly to the variability of either SRP or BAP stream concentrations. The method utilizes binary or continuous CART to develop structural-tree models (Qian and Anderson, 1999; Cannon and Whitfield, 2002; SAS Institute Inc., 2010). For each split, RP assigns a coefficient of determination ( $r^2$ ) as the predictive power of the  $x$  variable (predictor variables) in determining SRP and BAP stream concentrations. All the metrics listed above (landscape and weather) were input into the RP analysis as predictive variables for 12 separate datasets to determine the best predictive variables for SRP and BAP. Datasets were based on connectivity matrix (Contiguous or Upstream), phase (Dry or Wet), and by either spatially correlated (SAC - Yes<sup>-</sup> or Yes<sup>+</sup>) or not spatially autocorrelated (SAC - No). The 12 datasets were: Contiguous, Dry phase, SAC - No; Contiguous, Dry phase, SAC - Yes<sup>-</sup>; Contiguous, Dry phase, SAC - Yes<sup>+</sup>; Contiguous, Wet phase, SAC - No; Contiguous, Wet phase, SAC - Yes<sup>-</sup>; Contiguous, Wet phase, SAC - Yes<sup>+</sup>; Upstream, Dry phase, SAC - No; Upstream, Dry phase, SAC - Yes<sup>-</sup>; Upstream, Dry phase, SAC - Yes<sup>+</sup>; Upstream, Wet phase, SAC - No; Upstream, Wet phase, SAC - Yes<sup>-</sup>; and Upstream, Wet phase, SAC - Yes<sup>+</sup>. See Table 3 (top) for SRP and Table 3 (bottom) for BAP.

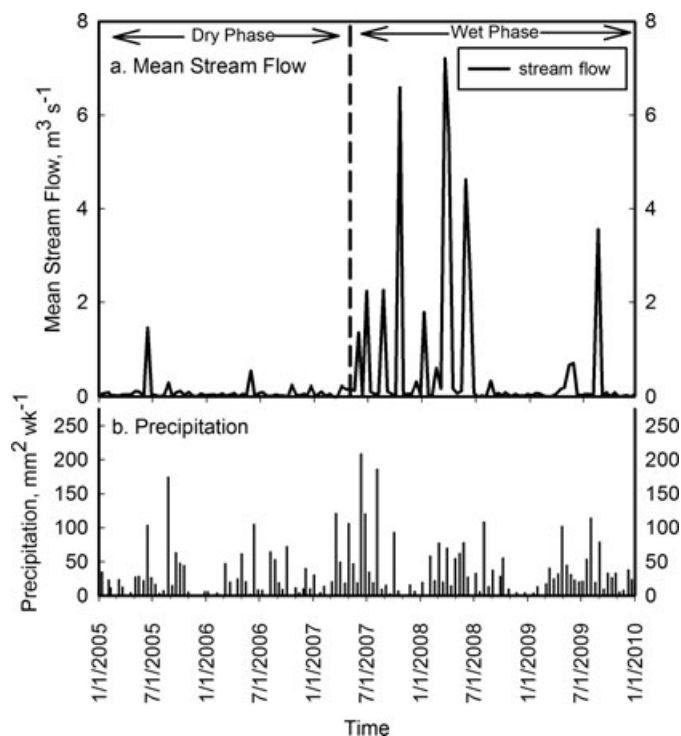


FIGURE 2. Time Series Graph of Precipitation for Each Two-Week Sampling Period and Streamflow on Sampling Date, Measured at the USGS Cobb Creek Gauging Station. Time series is from January 2005 through December 2009. Horizontal bars are the means for Dry phase (January 2005 through March 2007) and Wet phase (April 2007 through December 2009).

## RESULTS AND DISCUSSION

SRP ( $\text{PO}_4\text{-P}$ ) stream concentrations for the Fort Cobb Watershed ranged from the method detection limit ( $3 \mu\text{g P/l}$ ) to  $967 \mu\text{g P/l}$  over the five years (2005 through 2009) with a mean of  $181 \mu\text{g P/l}$  and a median value of  $143 \mu\text{g P/l}$ . Bioavailable P stream concentrations ranged from  $15$  to  $1,248 \mu\text{g P/l}$  with a mean of  $178 \mu\text{g P/l}$  and a median value of  $68 \mu\text{g P/l}$ . The Willow Creek basin had higher SRP and BAP stream concentrations ( $p < 0.05$ ; Figures 3a and 3b) than the other three main drainage basins (Cobb, Fivemile, and Lake). No statistical differences were noted for

TABLE 3. Summary Table for Soluble Reactive P and Bioavailable P Datasets.

Soluble Reactive P												
Matrix	Contiguous (N = 1,830)						Upstream (N = 1,830)					
Phase	Dry (780)			Wet (1,050)			Dry (825)			Wet (1,005)		
SAC	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>
n	555	75	150	630	45	375	675	75	75	795	45	165
Mean (µg P/l)	75.6	188	82.2	219.8	200.6	235.7	90.2	78.8	91.7	213.3	281.3	248.4
SD	78.6	46.5	61.9	148.7	101.8	96.9	85.6	34.9	66.9	128.0	176.3	101.6

Bioavailable P												
Matrix	Contiguous (N = 1,829)						Upstream (N = 1,829)					
Phase	Dry (794)			Wet (1,035)			Dry (794)			Wet (1,035)		
SAC	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>
n	555	30	209	585	30	420	643	15	135	675	30	330
Mean (µg P/l)	67.7	60	64.1	169.9	98.2	158.0	60.8	269.2	70.4	142.9	150.5	205.4
SD	89.2	39	68.1	197.1	116	163.7	75.5	191.5	66.9	182.0	129	180.7

Note: Datasets are in columns for connectivity matrix (Contiguous or Upstream), hydrologic phase (Dry or Wet), and spatial autocorrelation (SAC – No, Yes<sup>-</sup>, or Yes<sup>+</sup>).

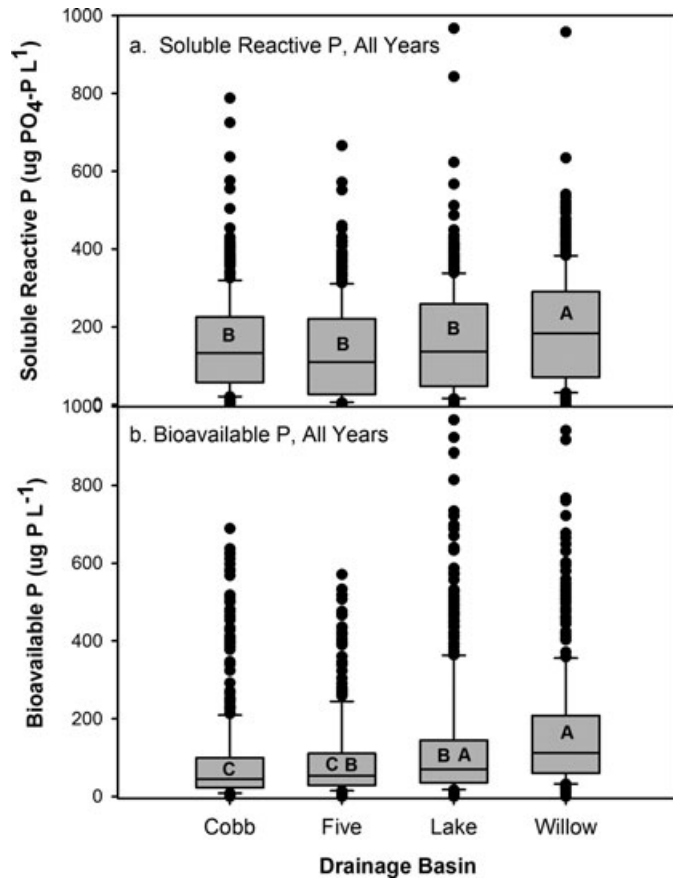


FIGURE 3. Boxplots Depicting Soluble Reactive P Creek (a) and Bioavailable P (b) by Drainage Basins: Cobb Creek, Fivemile Creek, Lake Creek, and Willow Creek for Years 2005 Through 2009. Within each P fraction, boxplots labeled with the same letter are not significantly different ( $p < 0.05$ ).

SRP between the other three main drainage basins, but there were differences in BAP (Figure 3b). Maynard *et al.* (2009) showed that SRP was the major source of BAP and that SRP and BAP are often well correlated (Allen *et al.*, 2006; Maynard *et al.*, 2009). In the FCRW, SRP and BAP were not well correlated for the combined dataset (0.35) or for Dry phase (0.27) or Wet phase 2 (0.25) datasets. This deviation from “normal behavior” suggests that biophysical parameters influenced SRP and BAP differently. Maynard *et al.* (2009) also showed that readily available BAP was largely associated with clay-size particles. In another study, Uusitalo *et al.* (2003) showed that relative contributions of particulate P and SRP were dependent on the characteristics of source water (surface runoff and drain flow). Source waters of the FCRW had diverse clay minerals that may explain why SRP and BAP were not well correlated.

*Spatial Dependence*

Results from the analysis for spatial dependence indicated that positive SAC (SAC > 0.20,  $p < 0.05 = \text{Yes}^+$ ) was present ( $p < 0.05$ ) for both SRP and BAP for both the Contiguous and the Upstream matrices (Table 3). Generally SAC for SRP was twice as common for Contiguous autocorrelation [29%; from Table 3, (150 + 375)/1,830] than Upstream autocorrelation (13%) of the sampling dates. While not as marked, SAC trends for BAP were similar, 34% for

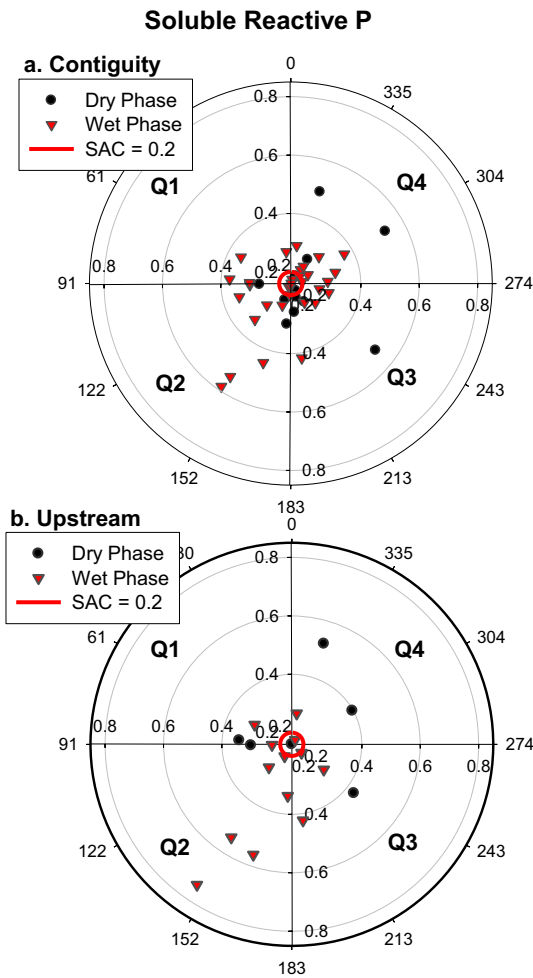


FIGURE 4. Soluble Reactive P Polar Plots Identify Dates with and Magnitude of Spatial Autocorrelation (SAC 0.20,  $p \leq 0.05$ ) Using the Contiguous Matrix (a) and the Upstream Matrix (b) for Dry (circle) and Wet (triangle) Phase Datasets. Degrees on the polar plot (north pole = 0 degrees) represent days of the year (DOY). Zero degrees to 91 represent January 1 to March 30 or the winter months and Quarter 1. Quarters 1, 2, 3, and 4 are depicted in the figure as DOY 0 to 91, DOY 91 to 183, DOY 183 to 274, and DOY 274 to 365, respectively.

Contiguous and 25% for Upstream (Table 3, Figures 4 and 5). Negative SAC was not found to be significant.

The proportion of dates with SAC varied depending on phase. For both SRP and BAP, there was more SAC for the Wet phase than for the Dry phase. Specifically, SAC for SRP, during the Dry phase, Contiguous and Upstream were 19 and 9%, respectively, and during the Wet phase, Contiguous and Upstream were 36 and 16%, respectively. For BAP SAC, during the Dry phase, Contiguous and Upstream were 26 and 17%, respectively, and during the Wet phase, Contiguous and Upstream were 41 and 32%, respectively (Table 3, Figures 4 and 5).

For SRP, more incidence of lateral spatial dependence (Contiguous connectivity matrix; landscape

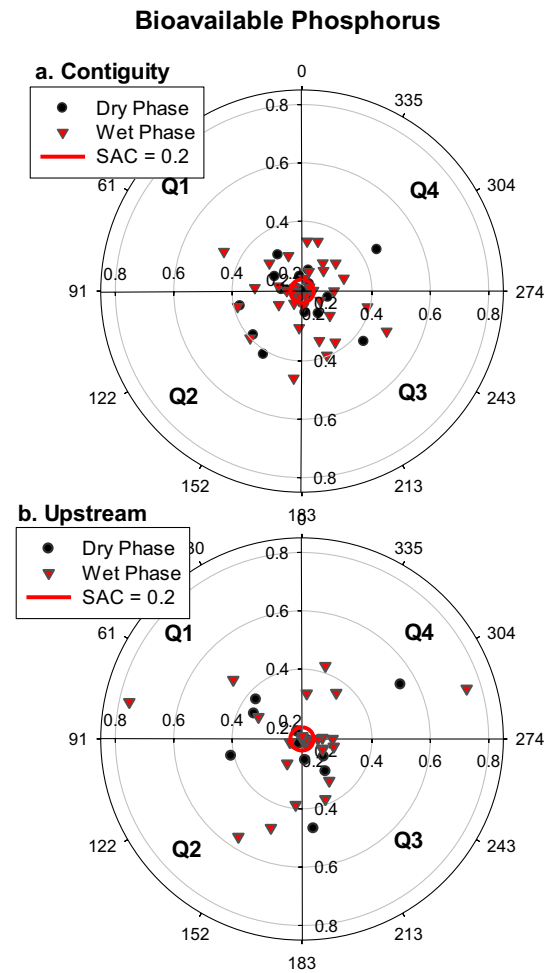


FIGURE 5. Bioavailable P Polar Plots Identify Dates with and Magnitude of Spatial Autocorrelation (SAC 0.20,  $p \leq 0.05$ ) Using the Contiguous Matrix (a) and the Upstream Matrix (b) for Dry (circle) and Wet (triangle) Phase Datasets. Degrees on the polar plot (north pole = 0 degrees) represent days of the year (DOY). Zero degrees to 91 represent Jan 1 to Mar 30 or the winter months and Quarter 1. Quarters 1, 2, 3, and 4 are depicted in the figure as DOY 0 to 91, DOY 91 to 183, DOY 183 to 274, and DOY 274 to 365, respectively.

influences) than longitudinal spatial dependence (Upstream matrix; within stream influences) was indicated. Lateral spatial dependence suggests that P stream concentrations were more influenced by lateral landscape metrics (hydrologic group, geology, or land use) than by the concentration of P in upstream reaches. In a study conducted in the Georgia Piedmont, longitudinal spatial dependence (influence from P concentrations upstream) was more common than lateral for SRP (Franklin *et al.*, 2002). In the current study, only during the Dry phase when there was Upstream spatial dependence were longitudinal predictive variables equally influential as the lateral variables on SRP stream concentrations. A discussion of what these predictor variables were follows in section titled “Potential Sources of Variability.”

### Temporal Variability

As indicated above, spatial dependence was not stable with time, nor were P concentrations. There was significantly more SAC in the Wet phase than in the Dry phase (Figures 4 and 5). Polar plots (Figures 4 and 5) also illustrate that there may be seasonal differences for both SRP and BAP and that seasonal differences appear more pronounced for SRP than for BAP. Vertical variables (predominantly precipitation) had most predictive power during the Wet phase.

Evaluation of temporal SRP patterns indicated that a shift in SRP stream concentrations occurred (Figure 6) and closely coincided with the shift noted above in SAC and in streamflow. Prior to splitting data based on SAC, comparisons of means between hydrologic phases for both SRP and BAP indicated a significant difference between Dry and Wet phases (not considering SAC; Figure 6). Wet phase means

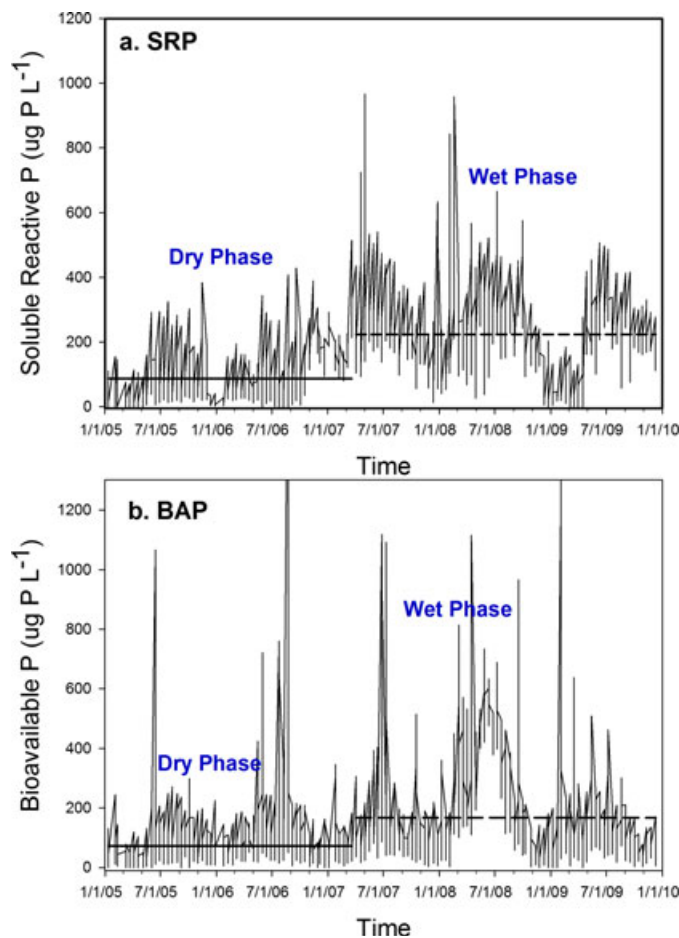


FIGURE 6. Time Series Graph of Soluble Reactive P from January 2005 Through December 2009. Horizontal bars are the means for Dry phase (January 2005 through March 2007) and the Wet phase (April 2007 through December 2009).

for both SRP and BAP streams concentrations were two to three times higher than Dry phase means. After splitting data based on SAC, SRP and BAP concentrations were also significantly higher in the Wet phase than in the Dry phase (Figures 7a and 7b). In this study, SRP and BAP concentrations increased with streamflow. In contrast, Arheimer and Liden (2000) reported that, in general, SRP concentrations in base flow decreased with increased streamflow (dilution effect).

### Potential Sources of Variability

Analysis and corresponding results will be presented for SRP and BAP throughout the rest of the article by connectivity matrix (Contiguous or Upstream), by phase (Dry or Wet), and by presence (SAC – Yes<sup>+</sup>) or absence (SAC – No) of autocorrelation. Variability for both SRP and BAP (standard deviations, Table 3 [top]) was always less when there was spatial dependence (SAC – Yes<sup>+</sup>) than when there was not spatial dependence (SAC – No). The same was also true for BAP (Table 3 [bottom]) but there was more variability in BAP concentrations than in SRP concentrations (Figure 6). Understanding the potential sources of this variability may enhance our ability to design management systems that are more resilient to extreme hydrologic conditions.

We present two structural-tree models (Figures 8 and 9; part of the output from RP) as illustrations of a simple partition and a complex partition, both for SRP. Following the presentation and explanation of RP tree-structure, we will discuss the tables of coefficients of determination ( $r^2$ ) for each P fraction (SRP, Table 4 and BAP, Table 5) separately. Each table is organized by variable type (lateral, longitudinal, and vertical). The variables presented are not all the variables examined (see Materials and Methods section for all the variables examined) but are those variables that RP indicated were likely important. If the variable was important for SRP it was left in the BAP table for consistency (and vice versa for SRP). RP splits a dataset based on the highest sum of squares. If sum of squares tie for a given parameter, the decision is next based on LogWorth [ $-\log_{10}(p\text{-value})$ ], where the  $p$ -value is associated with the sum of squares due to the difference in means between the potential splits (Sall, 2002). The output of the RP provides an  $r^2$  for the split, a value for the  $x$  variable, and the mean value for the  $y$  variable (SRP or BAP), where that variable splits. The value identified by the split may be useful if determining threshold values, especially when conditional threshold values are needed (Figures 8 and 9).



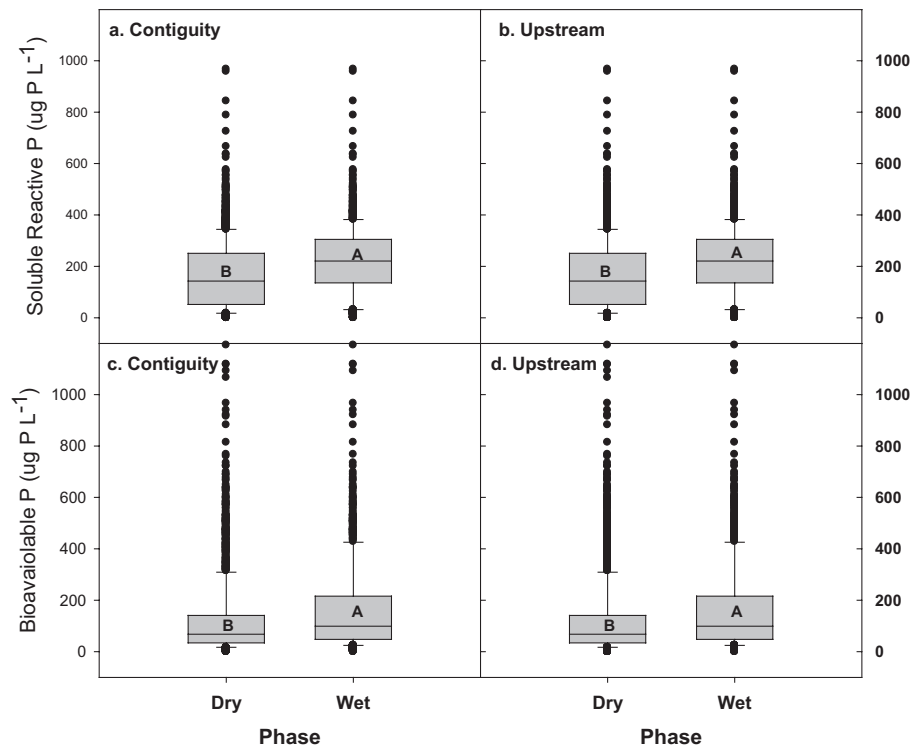


FIGURE 7. Boxplots Identify Range of Soluble Reactive P Stream Concentrations Between the Dry and Wet Phase for (a) Soluble Reactive P Using the Contiguous Matrix and (b) Soluble Reactive P Using the Upstream Matrix, (c) Bioavailable P Using the Contiguous Matrix, and (d) Bioavailable P Using the Upstream Matrix. For each P fraction and connectivity matrix, boxplots labeled with the same letter are not significantly different between flow phases Wet or Dry ( $p < 0.05$ ).

The first structural-tree model presented is for the Contiguous, Wet phase, SAC –Yes<sup>+</sup> dataset ( $n = 375$ ; Figure 8). The first split was on Hydrologic Group A. When a basin had more than 3% of the soils classified as Hydrologic Group A, the mean SRP stream concentration was  $257 \mu\text{g P/l}$ , and when  $\leq 3\%$  of the basin was classified as Hydrologic Group A, the mean SRP stream concentration was  $152 \mu\text{g P/l}$ . Subsplittings from Hydrologic Group A  $\leq 3\%$  was Pre\_cum3 (cumulative precipitation over three sampling intervals [six weeks]). Subsplittings from Hydrologic Group A  $>3\%$  dataset were on Pre\_cum3, Prec\_tot, stream density, maximum 30 min precipitation (in two-week period), and Quarter (Figure 8).

The second structural-tree model is for the Upstream, Dry phase, SAC – No dataset (Figure 9). The first split was on stream density. If stream density was  $>6.9 \text{ m/ha}$ , the mean SRP stream concentration was  $201 \mu\text{g P/l}$  compared with  $82 \mu\text{g P/l}$  when stream density was  $<6.9 \text{ m/ha}$ . Subsplittings from the stream density  $\leq 6.9 \text{ m/ha}$  sub-dataset were on oxidation reduction potential (ORP), Prec\_cum3, and pH. This illustration was chosen to draw attention to the unstable nature of RP when more than one factor has the same sum of squares and LogWorth. While it is considered unstable, it is also an unbiased tool for

identifying outliers and can be used as an artificial intelligence methodology to identify outliers and prevent any author bias. The first split of  $\text{SD} >6.9 \text{ m/ha}$  singled out a subbasin of the FCRW (CD, Figure 1) and is considered a terminal node. Multiple RP analyses were executed and the CD subbasin also split out on contributing area  $<2,006 \text{ ha}$ , Hydrologic Group A  $>51\%$ , and sand  $>76\%$ . A first split terminal node, which singles out an individual feature on multiple variables, may be considered an outlier. All four of these variables (small contributing area, high sand content in surface layer, Hydrologic Group A, and high stream density) suggest rapid movement of water across and through the surface and subsurface layers.

#### *Coefficients of Determination for Soluble Reactive P*

Coefficients of determination are presented in Table 4, organized by metric type (lateral, longitudinal, and vertical). The metrics presented are those that RP indicated were likely important for SRP, BAP, or both. Overall, metrics examined were better predictors for the Upstream matrix {sum of total  $R^2$ s = 1.99 excluding Yes<sup>-</sup>; [(Dry, SAC – No) + (Dry,

TABLE 4. Coefficients of Determination ( $r^2$  single variable;  $R^2$  column total) for Soluble Reactive P as Determined by Recursive Partitioning.

Connectivity	Contiguous Matrix						Upstream Matrix					
	Dry Phase			Wet Phase			Dry Phase			Wet Phase		
	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>
<i>Variable</i>												
Topography												
Contributing area			0.25 <sup>†</sup>									
Stream density		0.08				0.08	0.12*	0.15				
Soil												
Hydrologic Group A	0.17*					0.19						0.28
Hydrologic Group B		0.1										
SOC			0.11					0.35				
Geology												
Cloud Chief Formation			0.05						0.08			0.12
Rush Springs Formation												
Weatherford Gypsum												
Management												
Center pivot irrigation					0.03							
Cropland				0.04						0.04		
Forest					0.22							
Water									0.18			
Lateral total	0.17	0.18	0.41	0.04	0.25	0.27	0.12	0.50	0.26	0.04	0.0	0.40
Water chemistry												
ORP	0.03	0.48 <sup>2</sup>					0.10		0.14			
pH							0.05					
Turbidity	0.06			0.05					0.20			0.04
Stream Stage S3								0.04				
Stream Stage S5												
Longitudinal total	0.09	0.48	0.0	0.05	0.0	0.0	0.15	0.04	0.34	0.0	0.0	0.04
Weather												
Quarter			0.10	0.05 <sup>2</sup>		0.04				0.14 <sup>2</sup>	0.14 <sup>2</sup>	
Prec_max	0.01	0.06										0.04
Prec_tot			0.01	0.08		0.06						0.02
Prec_cum3	0.04		0.03	0.33 <sup>2</sup>		0.21 <sup>2</sup>	0.08			0.46 <sup>2</sup>		0.06
Vertical total	0.05	0.06	0.14	0.46	0.0	0.31	0.08	0.0	0.0	0.60	0.14	0.12
Total $R^2$	0.31	0.72	0.55	0.55	0.25	0.58	0.35	0.54	0.60	0.64	0.14	0.56

Notes: Number is  $r^2$  for a variable (row). Columns indicate connectivity matrix (Contiguous or Upstream), hydrologic phase (Dry or Wet), and spatial autocorrelation (SAC: No, Yes<sup>-</sup>, or Yes<sup>+</sup>). Superscript number indicates number of times variable is split by RP, symbol \* indicates variability is attributed to one subbasin, symbol † indicates two subbasins, when no superscript symbols are present variability can be attributed to more than two subbasins. ORP, oxidation reduction potential; Prec\_cum3, cumulative precipitation over three sampling intervals (six weeks); Prec\_max, maximum 30-min precipitation in two-week sampling interval; Prec\_tot, total precipitation in two-week sampling interval; SOC, soil organic carbon.

SAC – Yes<sup>+</sup>) + (Wet, SAC – No) + (Wet, SAC – Yes<sup>+</sup>)]}; than for the Contiguous matrix (sum of total  $R^2$ s = 2.15 excluding Yes<sup>-</sup>; Table 4). Similarly for all but the Upstream, Wet phase, SAC – Yes<sup>+</sup>,  $R^2$ s were larger when there was SAC. Lateral metrics (topography, soil, geology, management) were always better predictors for SRP concentrations for dates when there was SAC. Summing lateral metric  $r^2$  values [(Dry, SAC – No) + (Dry, SAC – Yes<sup>+</sup>) + (Wet, SAC – No) + (Wet, SAC – Yes<sup>+</sup>)] for the Contiguous matrix and for the Upstream matrix ( $r^2$  = 0.89 and 0.82, respectively; Table 4), we found that the lateral metrics were slightly better predictors for the Contiguous matrix than for the Upstream matrix. Theoretically, if lateral metrics are better predictors of SRP concen-

trations, then those best predictor variables can be the focus of management strategies for efficient use of fertilizer P. For example, these results indicate that implementation of land management practices rather than stream restoration would result in slightly more P reduction in streams.

For the Contiguous matrix, soil Hydrologic Group A and soil organic carbon were the two most important lateral predictor variables chosen by RP ( $r^2$  = 0.19 and 0.11, respectively; Table 4). For the Upstream matrix, soil Hydrologic Group A and the geologic Cloud Chief Formation were the two most important lateral predictor variables chosen by RP [ $r^2$  = 0.28 and (0.20 = 0.08 + 0.12), respectively]. An example from the Contiguous matrix RP results (Wet phase, SAC

TABLE 5. Coefficients of Determination ( $r^2$  single variable;  $R^2$  column total) for Bioavailable P as Determined by Recursive Partitioning.

Connectivity	Contiguous Matrix						Upstream Matrix						
	Dry Phase			Wet Phase			Dry Phase			Wet Phase			
	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	No	Yes <sup>-</sup>	Yes <sup>+</sup>	
<i>Variable</i>													
Topography													
Contributing area	0.02		0.03 <sup>†</sup>	0.02 <sup>†</sup>		0.03 <sup>†</sup>	.26*			0.04 <sup>†</sup>		0.03 <sup>†</sup>	
Stream density													
Soil													
Hydrologic Group A	0.19*												
Hydrologic Group B													
SOC													
Geology													
Cloud Chief Formation	0.16						0.05	0.22					
Rush Springs Formation													
Weatherford Gypsum	0.03												
Management													
Center pivot irrigation													
Cropland													
Forest													
Water	0.06						0.03						
Lateral total	0.24	0.0	0.25	0.02	0.0	0.03	0.31	0.0	0.25	0.04	0.0	0.03	
Water chemistry													
ORP	0.10												
pH				0.06	0.26								
Turbidity	0.02	0.13			0.05	0.31				0.10 <sup>2</sup>			
Stream Stage Cs3	0.42												
Stream Stage Cs5							0.74						
Longitudinal total	0.12	0.55	0.0	0.11	0.26	0.31	0.0	0.74	0.0	0.10	0.0	0.06	
Weather													
Quarter				0.10	0.02							0.02	0.32
Prec_max				0.12				0.12					
Prec_tot	0.03	0.10					0.06	0.04	0.02				
Prec_cum3	0.22 <sup>2</sup>					0.08	0.26			0.05	0.83	0.02	
Vertical total	0.03	0.0	0.32	0.22	0.02	0.14	0.04	0.0	0.40	0.07	0.83	0.48	
Total $R^2$	0.39	0.55	0.57	0.35	0.28	0.48	0.35	0.74	0.65	0.21	0.83	0.57	

Notes: Number is  $r^2$  for a variable (row). Columns indicate connectivity matrix (Contiguous or Upstream), hydrologic phase (Dry or Wet), and spatial autocorrelation (SAC: No, Yes<sup>-</sup>, or Yes<sup>+</sup>). Superscript number indicates number of times variable is split by RP, symbol \* indicates variability is attributed to one subbasin, symbol † indicates two subbasins, when no superscript symbols are present variability can be attributed to more than two subbasins. ORP, oxidation reduction potential; Prec\_cum3, cumulative precipitation over three sampling intervals (six weeks); Prec\_max, maximum 30-min precipitation in two-week sampling interval; Prec\_tot, total precipitation in two-week sampling interval; SOC, soil organic carbon.

Yes<sup>+</sup>): SRP stream concentrations were almost 1.5 times higher when Hydrologic Group A was >3% of the contributing area (Figures 1 and 8). In basins with landscape metrics that are indicative of rapid water and associated soluble nutrient movement (such as Hydrologic Group A), management strategies might include small pulse applications, precision application, or banding of nutrients when nutrients are most needed. In this example, it should also be noted that Hydrologic Group A was identified as a variable of importance during the Wet phase, which suggests that legacy P or banked SRP in the watershed was flushed from and through the landscape into the stream. In this system, the use of grasses or cover crops with

deep fibrous roots that recapture and retain excess nutrients and that can potentially slow water movement would be beneficial. For the Upstream matrix, soil Hydrologic Group A, the geologic Cloud Chief Formation, and percent basin area classified as Water were the three most important lateral predictor variables chosen by RP ( $r^2 = 0.28, 0.20,$  and  $0.18,$  respectively; Table 4). The Cloud Chief Formations influenced stream SRP regardless of connectivity matrix during the Wet Phase. The Cloud Chief formations are red-brown and greenish gray shale and siltstone, which can have dolomite and gypsum beds at their base (30 feet) and due to erosion can also have mappable escarpments. This decrease in SRP with an

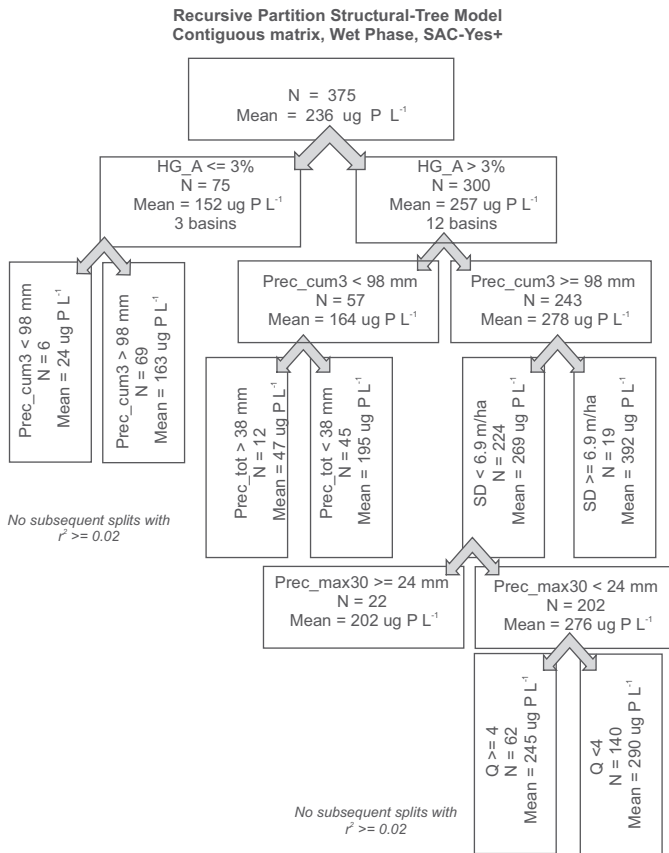


FIGURE 8. Structural-Tree Model Is Part of the Output from Recursive Partition Analysis. This model illustrates a simple partition for the Contiguous matrix, Dry phase, SAC – Yes<sup>+</sup> dataset.

increase in the percentage of the area with Cloud Chief Formation was likely due to the formation of calcium phosphates of low solubility as gypsum reacted with P. In a laboratory study using three soils (Watson silt loam, Klineville shaley silt loam, and Henlopen loamy sand), Stout *et al.* (2003) found that FGD (flue gas desulfurized) gypsum-amended soil decreased water-extractable soil P by 20.4, 9.0, and 11.4 mg P/kg depending on soil.

Of the longitudinal variables, ORP had the largest  $r^2$ : 0.10 and 0.14 for Upstream, Dry phase, SAC – No and SAC – Yes<sup>+</sup>, respectively. Of the Vertical variables, Prec\_cum3 and Quarter were the best predictors (Table 4) and Prec\_cum3 was always a better predictor during a Wet phase than a Dry phase. In fact, Prec\_cum3 had the largest single variable  $r^2$  (0.46) for stream SRP concentrations in a Wet phase with SAC – No. In the Wet phase, Prec\_cum3 was a better predictor for SAC – No than for SAC – Yes for both the Contiguous and the Upstream matrices. The RP analysis identified seasons (Quarter) to be a strong predictor for the Upstream matrix that coincides with polar plots for SRP concentrations (Figure 4).

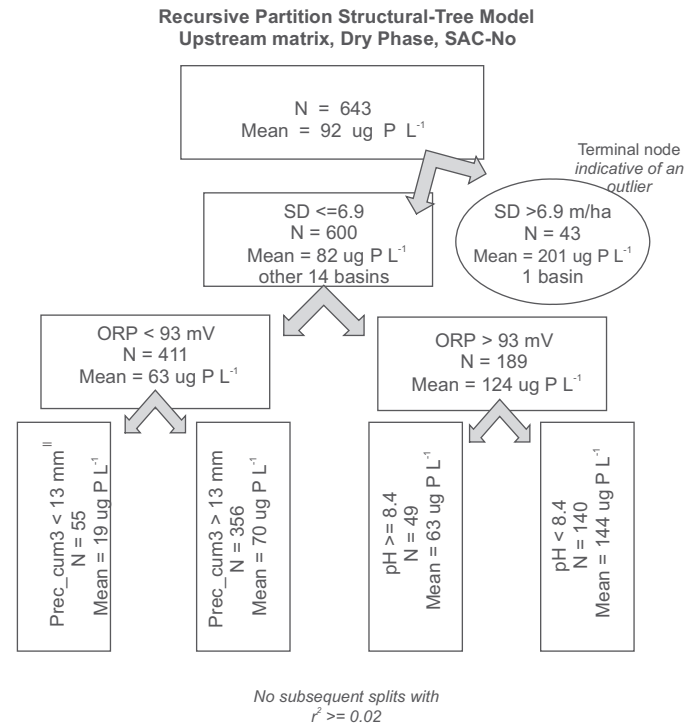


FIGURE 9. Structural-Tree Model Is Part of the Output from Recursive Partition Analysis. This model illustrates a complex partition for SRP using the Upstream matrix, Dry phase, SAC – No dataset, which identifies a terminal node or outlier within the dataset.

### Coefficients of Determination for Bioavailable P

Generally, predictor variables for the Upstream (sum of total  $R^2$ s = 1.78 excluding Yes<sup>-</sup>) matrix and the Contiguous matrix (sum of total  $R^2$ s = 1.79 excluding Yes<sup>-</sup>; Table 4) were similar for BAP stream concentrations (Table 5). Lateral metrics were better predictors during the Dry phases, longitudinal metrics were better predictors during the Wet phase, and the strength of predictors was mixed for Vertical metrics relative to Wet and Dry phases.

Of the lateral metrics, Cloud Chief Formation was again a strong predictor variable ( $r^2 = 0.16$  and 0.22) for BAP stream. Of the longitudinal metrics, turbidity and oxidation-reduction potential had the largest predictive values (Table 5). Of the vertical metrics, Quarter was the single strongest predictor variable ( $r^2 = 0.32$ ; Wet phase, Upstream matrix) as was indicated by the SAC polar plots.

The oxidation-reduction potential in streams is an example of a longitudinal predictor variable that though moderately important ( $r^2 = 0.10$ , 0.03, 0.10, and 0.14; Tables 4 and 5), RP repeatedly identified it in a split for BAP and for SRP under Dry phase conditions. Oxidation-reduction potentials are associated with predicting the stability of multiple compounds



that regulate nutrient availability in soil, sediments, and water (DeLaune and Reddy, 2005). The inorganic oxidants include multiple forms of oxygen, nitrogen, manganese, iron, sulfate, and CO<sub>2</sub>. All of these compounds can be associated with phosphorus (Perret *et al.*, 2000). From the RP analysis on BAP, when oxidation-reduction potential was >90 mV in one dataset and >166 mV in another dataset, BAP concentrations increased from 18 to 54 µg P/l and from 53 to 258 µg P/l, respectively. For SRP, oxidation-reduction potential values >72 and 93 mV were associated with increases in stream SRP concentrations from 43 to 115 µg P/l and from 63 to 124 µg P/l, respectively. Oxidation-reduction potentials up to 400 mV are considered to be reduced conditions in which bioreducible iron, manganese, and nitrogen (NO<sub>3</sub><sup>-</sup>) are in a reduced state. When oxidation-reduction potentials range from just below zero to 100 mV, reduction of ferric compounds are likely, and when oxidation-reduction potentials range from 100 to 400 mV, nitrate and manganese oxides are reduced (DeLaune and Reddy, 2005). Under normal flow conditions, the hyporheic zone has been shown to be a sink for P (Mulholland *et al.*, 1997). This reserve of P may also be a source for P release under extreme weather conditions (Turner and Haygarth, 2001). Under low-flow conditions (Dry phase), stream velocities are slower and less oxygen is dissolved into the shallow stream waters and into the hyporheic zones. This can result in perturbations of the hydrologic system, several of which have been shown to release P. Drying and rewetting has been shown to increase P concentrations in soils (Blackwell *et al.* (2010), and repeated drying and rewetting conditions also result in repeated oxidation-reduction cycles. The reduction of ferric phosphate [Fe<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> · 2H<sub>2</sub>O] to ferrous phosphate [Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] will occur under the ORP values identified by the RP analysis and can result in a release of PO<sub>4</sub><sup>-3</sup> (Kleeberg and Kozerski, 1997; Shenker *et al.*, 2005) and measured as BAP and/or SRP.

## SUMMARY AND CONCLUSIONS

Analysis of the FCRW indicated that the extent by which spatial (geophysical) and temporal (climate) features influenced P stream concentrations varied depending on absence or presence of SAC and hydrologic regime. Results for both SRP and BAP indicated that spatial dependence was present ( $p < 0.05$ ) within both the Contiguous and the Upstream matrices with significantly more SAC in the Wet Phase than in the Dry Phase. During the Wet Phase, P stream concen-

trations were 3 to 5 times larger than in the Dry Phase.

RP, by Dry and Wet phase and by presence or absence of SAC, resulted in higher  $R^2$  when SAC was present than when it was not, and indicated that lateral metrics (topography, soil, geology, management) were better predictors for SRP when there was SAC. During the Wet phase, lateral metrics that identified rapid water movement (sandy surface soils, Hydrologic Group A, and small highly dissected contributing areas) were associated with larger SRP concentrations. The analysis also showed that regardless of phase (Wet or Dry) when gypsum was predominant in the geology SRP stream P concentrations were low. For BAP, stream concentrations were only lower when gypsum was predominant in the geology during the Dry phase. Generally however, results were not as clear for BAP, where in most cases lateral metrics did result in higher  $r^2$  when there was SAC but more so in the Dry phase than in the Wet phase.

For both SRP and BAP, when lateral metrics (such as hydrologic group, geology, percent area of water in contributing area, stream density, and soil organic C) are identified as better predictors of P stream concentrations, then those best predictor variables can be focused on when developing management strategies for efficient use of fertilizer P, or can be included in predictive models when developing regional scale management plans. The strength of a predictive variable also depended on whether SAC was from a lateral influence (Contiguous connectivity matrix) or from within the stream (Upstream connectivity matrix) for both SRP and BAP. For instance, RP identified stronger associations for SRP stream concentrations from soil-related features for the Contiguous matrix. Results suggest that, in the FCRW, conservation measures focused on the landscape rather than within the stream would more effectively reduce P stream concentrations.

As expected, although influenced by landscape, weather features such as cumulative precipitation in three two-week periods or maximum precipitation in a two-week period were identified by RP as strong predictive variables. What was unexpected was that RP did not identify the same vertical predictive variables for both SRP and BAP (maximum precipitation in a two-week period had more influence on BAP than SRP) and that measured within stream metrics or influences seemed to affect BAP more than SRP. We have demonstrated how varied background P stream concentrations can be a result of both geophysical and climatic influences. In addition, we identified that subbasins with soils in Hydrologic Group A are more vulnerable to elevated stream P concentrations especially under prolonged wet weather condi-

tions, which suggests that at the landscape scale soluble P transport is both surface and subsurface.

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